ARTICLE

Electrical properties of an individual ZnO micro/nanorod

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Abstract—Free standing, highly crystalline ZnO micro/nanorods have been successfully fabricated using low temperature hydrothermal synthesis. Current-voltage characteristic curves show that ZnO micro/nanorods' resistances are proportional to their geometrical ratios, satisfying classical Ohm's law. Temperature-dependent resistance measurements reveal exponential decay of current with temperature, implying good semiconducting properties. Finally, three different thermally-activated impurity levels were identified from the measurements, and these are attributed to Zn interstitials in the bulk. The results are important in supplementing research in nanoelectronics and nanocircuitries.

Keywords—Nanotechnology, Nanoelectronics, Hydrothermal synthesis, Micro/nanorod, Semiconductor

INTRODUCTION

Nanotechnology has influenced the way humans live, ranging from biology, chemistry, physics, and medicine. In addition, nanotechnology also paved the way for the miniaturization of materials and complex electronic devices that are found to be useful in many practical and scientific applications. In this respect, extensive researches are being conducted to improve these technologies, especially in the semiconductor field where nanotechnology is said to have the most varied applicability. These materials have electrical properties that are in between of a conductor and an insulator. Commonly utilized semiconductors include the elemental ones (Si, Ge) and the compound ones (GaAs, GaN, InP).

Another group known as wide gap semiconductors consists of materials that have energy band gap of more than ~ 2 eV, which include ZnO. It is a II-VI semiconductor having a hexagonal wurtzite crystal structure (lattice parameters of a = 0.325 nm and c = 0.521 nm). Due to its unique properties such as its wide gap of 3.34 eV and high excitonic binding energy of 60 meV, it is being utilized in different applications as sensors, UV emitters, LEDs and piezoelectric devices (Bill et al. 2005, Choi et al. 2010, Kim et al. 2008, Liu et al. 2008, Mahmoodi et al. 2009, Wu et al. 2009). These make ZnO a prospect material in nanotechnology applications, especially the micro/nanorod structures. This entails that these structures must possess good electrical properties, and that techniques of measuring and analyzing these must be studied thoroughly as well. Several studies have been done (Sakurai et al. 2009, Schlenker et al. 2007, Yoon et al. 2009) on the assessment of ZnO micro and nanostructures' electrical properties grown using different fabrication techniques. In this work, ZnO micro and nanostructures grown via hydrothermal growth method are characterized with focus on their electrical properties. A single ZnO micro/nanorod is mounted on patterned substrate through an Ohmic contact connection, and subsequently its I-V curve characteristics and RT measurements are obtained and analyzed.

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METHODOLOGY

The synthesis of ZnO structures was done using the hydrothermal method, with zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$) and hexamethylenetetramine (HMTA : $C_6H_{12}N_4$) as primary precursors. Equimolar amounts of these precursors were used in the synthesis, ranging from 0.008 M, 0.009 M and 0.010 M. The chemicals were diluted in fixed amount of water and were sonicated for 20 minutes, and subsequently were mixed and sonicated further for another 20 minutes. The proposed reaction for ZnO growth is

$$Zn(CH_3COO)_2 \cdot 2H_2O \leftrightarrow Zn^{2+} + 2CH_3COO^- + 2H_2O$$
$$C_6H_{12}N_4 + 6H_2O \leftrightarrow 4NH_3 + 6HCHOO$$
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
$$Zn^{2+} + 4OH^- \leftrightarrow Zn(OH)_4^{2-}$$
$$Zn(OH)_4^{2-} + heat \leftrightarrow ZnO + H_2O + 2OH^-$$

Silicon substrate was used to collect the synthesized ZnO structures, which was then brought into heat treatment at 95° C for 120 minutes using a hot plate. The system consisting of collected ZnO structures on Si substrate was washed with water to remove residual salts, air dried and annealed at 500° C for 20 minutes. It is worthwhile to note that our hydrothermal growth method did not make use of any seeding mechanism or template, showing the robustness and practicality of our technique.

With regards to the electrical characterization of the ZnO samples, we first implemented isolation strategies in order to measure the intended electrical properties of a single ZnO micro/nanorod. First, ZnO structures were sonicated in ethanol and dispersed using a micropipette on prefabricated chips with electrodes. Platinum was then deposited using Focused Ion Beam (FEI NOVA 600) to establish contacts between ZnO and the electrodes. The electrical characterization measurements for the single ZnO micro/nanorod-electrode system were divided into two parts: the current-voltage measurements (I-V measurement) and the resistivity versus temperature (RT) measurements. Preliminary sample preparation was done prior to these electrical measurements. The I-V characteristic curves were measured using four-point probe, while RT measurements were done using the two-point probe method. A 10 nA current source was used to supply current and the voltage output is measured afterwards for the RT measurements.

RESULTS AND DISCUSSION

The hydrothermally grown ZnO structures were determined using X-ray diffraction, and shown in Figure 1 are the X-ray diffractograms of the samples in different molarity concentrations. All the samples showed a prominent peak at 31.70° which corresponds to $(10\bar{1}0)$ growth direction. It can be noted that the reaction indeed produced ZnO in different growth directions, as other peaks show. Furthermore, it is noteworthy to mention that no significant and additional peaks other than ZnO peaks were observed. Thus, ZnO has been synthesized from the reaction and the peaks are in agreement with the JCPDS database with card no. 36-1451 for hexagonal wurtzite ZnO.

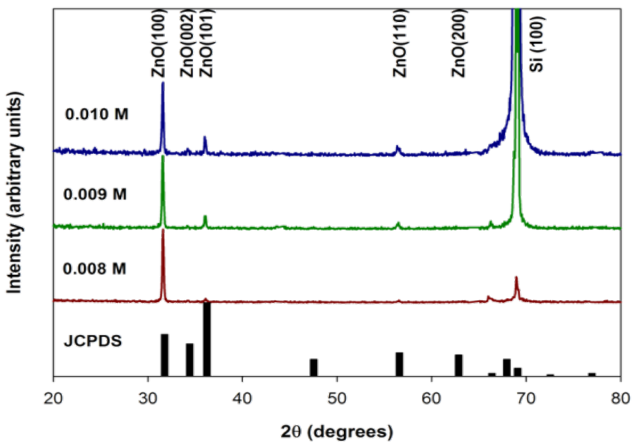

Figure 1. XRD spectra of ZnO grown hydrothermally using different equimolar concentrations of $Zn(CH_3COO)_2 \cdot 2H_2O$ and HMTA.

For the electrical characterization of a single ZnO micro/nanorod, the samples grown using 0.009 M growth parameter were used. Figure 2 shows the SEM micrographs of the individual ZnO micro/nanorod with their corresponding I-V characteristic curves. The plots show perfect linear trend indicating that the samples have Ohmic electrical properties, and that the contacts between the micro/nanorods are Ohmic in nature, as oppose to Schottky type that results to potential drops and thus deteriorates the electrical properties. The slope of each I-V curve denotes the resistance of a single ZnO micro/nanorod, and the resistances measured from the samples are of the order of 10^3 Ohms, which implies that the samples are highly resistive.

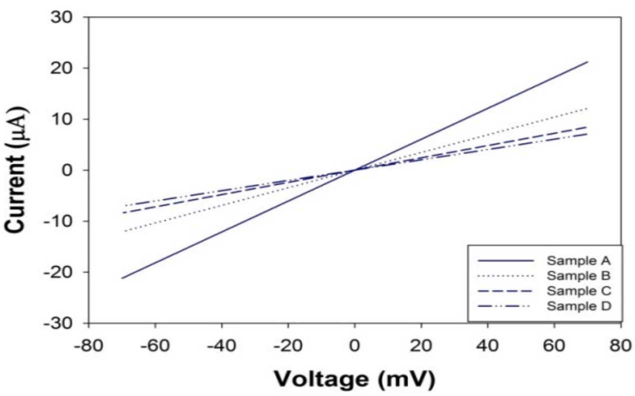

Figure 2. I-V characteristics curves of the individual ZnO micro/nanorods showing Ohmic property.

The geometrical ratio of each sample were obtained and summarized in Table 1. For sample A, the geometrical ratio is 3.35 ± 0.78 μm^{-1}, and the calculated resistance is 3.3 kΩ. On the other hand, for sample B having geometrical ratio of 7.98 ± 0.45 μm^{-1}, a higher value for the resistance was obtained, which is 5.8 kΩ. Furthermore, for the remaining samples C and D with geometrical ratios of 10.72 ± 0.85 μm^{-1} and 17.23 ± 4.78 μm^{-1}, the computed resistances are 8.3 kΩ and 9.9 kΩ, respectively. Thus, it was illustrated that higher geometrical ratio amounts to higher resistance, which is a signature property of classical Ohmic device.

TABLE 1. Summary of the dimensions, geometrical ratio and resistance obtained for each ZnO micro/nanorod.

Sample	Length (μm)	Area (μm²)	Ratio (L/A) (μm⁻¹)	Resistance (kΩ)
A	2.194 ± 0.032	0.502 ± 0.019	3.35 ± 0.78	3.3
B	3.59 ± 0.016	0.502 ± 0.0037	7.98 ± 0.45	5.8
C	5.04 ± 0.014	0.426 ± 0.0058	10.72 ± 0.85	8.3
D	2.46 ± 0.084	0.235 ± 0.00969	17.23 ± 4.78	9.9

The resistivity of the samples, ρ, is obtained statistically following Ohm's law behaviour relating the resistance R to its aspect ratio, given by

$$R = \rho \frac{L}{A} \qquad \text{Equation 1}$$

From the samples considered above, the resistivity of the ZnO micro/nanorods is calculated to be equal to 4.83 x 10^{-2} Ω•m.

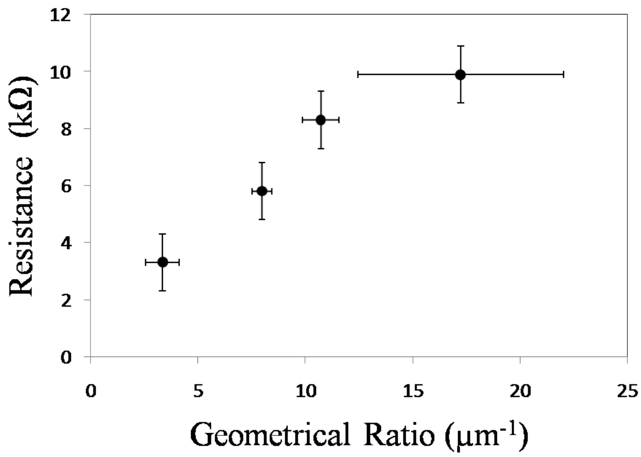

Figure 3. Plot of resistance versus geometrical ratio of ZnO micro/nanorods.

Figure 4 shows the resistance versus temperature (RT) plot of one of the four samples used in the I-V curve analysis. The exponential decay nature of the plot illustrates the semiconducting property of ZnO micro/nanorod sample. This is because for typical semiconductors, the resistance decreases exponentially with increasing temperature. This is due to the fact that electrons are free to move at higher temperatures as a result of thermal energy and this contributes to the lowering of the resistance. At a lower temperature however, electrons are frozen due to deficiency of thermal energy, making the resistance rise significantly.

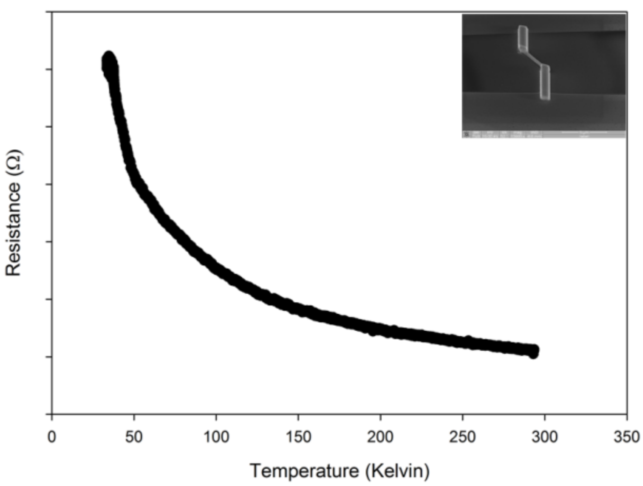

Figure 4. Resistance versus temperature curve of an individual ZnO micro/nanorod using Sample D (inset).

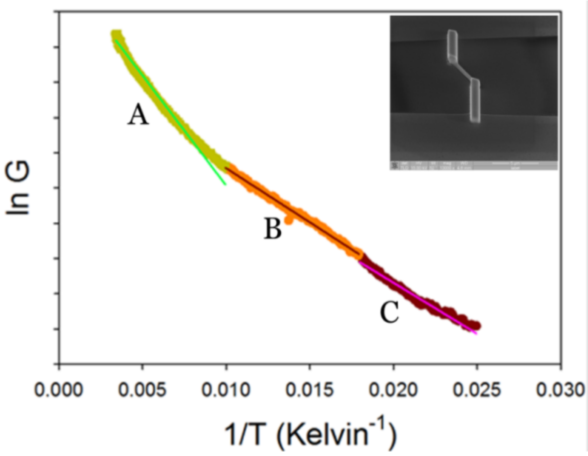

Figure 5. Conductance plot with temperature of an individual ZnO using Sample D (inset).

Shown in Figure 5 is the plot of the conductance G as a function of 1/T using the ZnO micro/nanorod grown from the 0.009 M sample. It can be observed that the plot can be divided into three regions or transitions. The slopes of the lines give information on the nature of the electronic transitions, whether it is from the valence band or from impurity levels within the band gap. It is worthwhile to mention that the RT plot's temperature range is limited only up to room temperature, thus eliminating the possibility of a direct valence to conduction band transition, in which case the slope would give the band gap energy. ZnO is an n-type semiconductor intrinsically, and thus the majority carriers are electrons. The slopes mentioned above would then give us the idea that these transitions are actually due to electrons trapped in impurity levels, which may be shallow or deep as measured from the conduction band. The three different slopes obtained point to the energy positions of these impurity levels.

Focusing on the transitions of the sample, the activation energy $E_{impurity}$ of the electrons can be known using Equation 2

$$slope = \frac{-(E_c - E_d)}{2.3k} = \frac{-E_{impurity}}{2.3k} \qquad \text{Equation 2}$$

where k is the Boltzmann's constant. From these data, the energy for the impurity level from the conduction band is computed to be 24.6 - 24.9 meV for transition A, 12.1 - 12.3 and 11.1 - 11.8 meV for transitions B and C, respectively. These activation energies from the conduction band have the same order of magnitude for a Zn impurity (Look and Hemsky 1999, Reddy et al. 2008). There has been a consensus that Zn impurities form shallow levels measured from the conduction band, and a range of plausible positions of these levels were reported in (Look and Hemsky 1999, Reddy et al. 2008), although there is no general agreement as to what are the exact positions of these levels. Electrical characterization of a single ZnO micro/nanorod is of importance especially in minute electrical circuitries as each individual ZnO electrical properties could affect the overall performance of the whole device. Previous works have done similar fabrication technique and measurements (Choi et al. 2010), albeit they used metal seed with template in growing ZnO structures and constructed ZnO rods array in their electrical characterization, thus rendering their measurements as ensemble averages (piezoelectric response characteristics) that could possibly neglect the potential unique electrical properties (defect centers and Ohmic characteristics) of each constituent ZnO rods that might be of importance in overall actual performance. In summary, these results have demonstrated the capability of our techniques in the electrical characterization of a single ZnO micro/nanorod, and thus could be of immense significance in the future of atomic-scale device fabrication.

TABLE 2. Summary of activation energy obtained from the sample grown using 0.009 M concentration.

Region	E_a (meV)
A	24.6 – 24.9
B	12.1 – 12.3
C	11.1 – 11.8

CONCLUSION

Synthesis of free-standing ZnO micro/nanorods was successfully done using a low temperature, seedless hydrothermal synthesis technique, and the grown ZnO structures were investigated in terms of structural morphology and electrical properties. XRD results show that the method produces highly crystalline ZnO with no signs of other chemical impurities from the solution. For further electrical characterizations, ZnO-electrode system utilizing a single ZnO micro/nanorod was successfully constructed. The I-V characteristic curves of the grown samples were obtained, and it can be concluded that the measured resistance is proportional to the aspect ratio of the samples. Also, each ZnO micro/nanorod I-V curve follows an Ohmic behavior. Furthermore, the RT curve of the samples using two-point probe method showed the semiconducting behavior of individual ZnO micro/nanorod. The slopes represent the activation energies for thermal-assisted conduction persisting in the samples. These results are of importance in the further development of nanoelectronics using a single micro/nanorod as key components, and thus would help in the proliferation of true single nanostructure circuitries for device applications.

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CONFLICT OF INTEREST

None to indicate.

CONTRIBUTION OF INDIVIDUAL AUTHORS

Alexandra B. Santos-Putungan
Ms. Santos-Putungan did the fabrication of the samples, analysis and write-up of the results gathered.

Leonalyn M. Bambao
Ms. Bambao did the I-V and RT measurements and helped in the analysis for the electrical characterizations.

Roland V. Sarmago
Dr. Sarmago formulated the problem, helped in the analysis of the results.

REFERENCES

Bill J, Gerstel P, Hoffmann RC, Jeurgens LPH, Lipowsky P, Wildhack S, Aldinger F. Bio-inspired evolution of zinc oxide-based materials directed by amino acids and peptides. Mater Res Soc Symp Proc 2005; 873E.

Choi J, You X, Kim C, Park J, Pak JJ. Power generating characteristics of zinc oxide nanorods grown on a flexible substrate by a hydrothermal method. Journal of Electrical Engineering & Technology 2010; 5: 640-645.

Kim JB, Byun D, Ie SY, Park DH, Choi WK, Choi JW, Angadi B. Cu-doped ZnO-based p-n hetero-junction light emitting diode. Semicond Sci Technol 2008; 23.

Liu WJ, Zhang J, Wan LJ, Jiang KW, Tao BR, Li HL, Gong WL, Tang XD. Dielectrophoretic manipulation of nano-materials and its application to micro/nano-sensors. Sensors and Actuators B 2008; 133: 664–670.

Look DC, Hemsky JW. Residual native shallow donor in ZnO. Physical Review Letters 1999; 82.

Mahmoodi SR, Raissia B, Marzbanrada E, Shojayia N, Aghaeia A, Zamani C. Dielectrophoretic assembly of ZnO nanorods for gas sensing. Procedia Chemistry 1 2009; 947-950.

Reddy NK, Ahsanulhaq Q, Kim JH, Hahn YB. Well-aligned ZnO nanorods for device applications: synthesis and characterization of ZnO nanorods and n-ZnO/p-Si heterojunction diodes. Europhysics Letters 2008;81.

Sakurai M, Wang YG, Uemura T, Aono M. Electrical properties of individual ZnO nanowires. Nanotechnology 2009; 20: 155-203.

Schlenker E, Bakin A, Postels B, Mofor AC, Wehmann HH, Weimann T, Hinze P, Waag A. Electrical characterization of ZnO nanorods. Phys. Stat. Sol. (b) 2007; 244:1473–1477.

Wu WY, Ting JM, Huang PJ. Electrospun ZnO nanowires as gas sensors for ethanol detection. Nanoscale Res Lett 2009; 4:513–517.

Yoon SW, Seo JH, Kim KH, Ahn JP, Seong TY, Lee KB, Kwon H. Electrical properties and microstructural characterization of single ZnO nanowire sensor manufactured by FIB. Thin Solid Films 2009; 517: 4003-4006.