Retraction

Electrical properties of an individual ZnO micro/nanorod

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Published 20 October 2015

It has come to the attention of IOP Publishing that this article should not have been accepted by the editors due to its earlier publication in the International Journal of Philippine Science and Technology (Alexandra B. Santos-Putungan, Leonalyn M. Bambao, and Roland V. Sarmago International Journal of Philippine Science and Technology 2015 Vol. 8 Issue 1 Pages 43-45). Consequently, this paper has been retracted by IOP Publishing.
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, indicating good semiconducting properties. Finally, three different theranly-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 on nanoelectronics and nanocircuitries.

1. 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 bound 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 [1-6]. 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 [7-9] 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

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patterned substrate through an Ohmic contact connection, and subsequently its I-V curve characteristics and RT measurements are obtained and analyzed.

2. Methodology
The synthesis of ZnO structures was done using the hydrothermal method, in which zinc acetate dihydrate $\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}$ and hexamethylenetetramine (HMTA : $\text{C}_6\text{H}_{12}\text{N}_4$) 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

$$\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Zn}^{2+} + 2\text{CH}_3\text{COO}^- + 2\text{H}_2\text{O}$$

$$\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} \leftrightarrow 4\text{NH}_3 + 6\text{HCHO}$$

$$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$$

$$\text{Zn}^{2+} + 4\text{OH}^- \leftrightarrow \text{Zn(OH)}_4^{2-}$$

$$\text{Zn(OH)}_4^{2-} + \text{heat} \leftrightarrow \text{ZnO} + 2\text{H}_2\text{O} + 2\text{OH}^-$$

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 in Si substrate was washed with water to remove residual salts, air dried and annealed at 500°C for 20 minutes.

Electrical characterization of the ZnO samples were divided into two parts: the current-voltage measurements (I-V measurement) and the resistivity versus temperature (RT) measurements. Preliminary sample preparation was done for the electrical characterizations. ZnO rods were sonicated in ethanol and was dispersed using a micropipette on prefabricated chips with electrodes. Platinum was deposited using Focused Ion Beam (FEI NOVA 600) to form contacts with the ZnO rods and the electrodes. The I-V characteristic curves were measured using four-point probe, while RT measurements were done using the two-point probe method. A 10mA current source was used to supply current and the voltage output was measured afterwards for the RT measurements.

3. Results and discussions
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 (1010) growth direction. It can also be noticed that the reaction indeed produced ZnO in different growth directions as the other peaks show. Other notable peaks are 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.

For the electrical characterization, the samples grown using 0.009 M growth parameter were used. Figure 2 shows the 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 a Schottky type that results to potential drops and thus deteriorates the electrical properties. This finding is of importance in the utilization of ZnO micro/nanorods as key materials in the fabrications of nanoscale electronics. 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 10³ Ohms, which implies that the samples are highly resistive.
The geometrical ratio of each sample were obtained and summarized in Table 1. For sample A, the geometrical ratio is $3.35 \pm 0.78 \mu m^{-1}$, and the calculated resistance is $3.3 \, k\Omega$. On the other hand, for sample B having geometrical ratio of $7.98 \pm 0.45 \mu m^{-1}$, a higher value for the resistance was obtained, which is $5.8 \, k\Omega$. Furthermore, for the remaining samples C and D with geometrical ratios of $10.72 \pm 0.85 \mu m^{-1}$ and $17.23 \pm 4.78 \mu m^{-1}$, the computed resistances are $8.3 \, k\Omega$ and $9.9 \, k\Omega$, respectively. Thus, it was illustrated that higher geometrical ratio amounts to higher resistance, which is a signature property of classical Ohmic device.

The resistivity of the samples, $\rho$, is obtained statistically following Ohm’s law behaviour relating the resistance $R$ to its aspect ratio, given by

$$R = \rho \frac{L}{A} \quad \text{(1)}$$
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           |

From the samples considered above, the resistivity of the ZnO micro/nanorods is calculated to be equal to $4.83 \times 10^{-2} \, \Omega \cdot m$.

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 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 lower temperatures however, electrons are frozen due to deficiency of thermal energy, making the resistance rise significantly.

Figure 5 is the plot of the conductance G as a function of $1/T$ using the ZnO micro/nanorods grown from the 0.009 M sample. It can be observed that the plot can be divided into three regions of 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 bandgap. It is worth while 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 of the electrons can be known using equation (2)

$$E_{impurity} = 2.3k$$

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 - 24.9meV for transition A, 12.1 - 12.3 and 11.1 - 11.8 meV for transitions Band C, respectively. These activation energies from the conduction band have the same order of magnitude for a Zn impurity [10, 11]. There has been a consensus that Zn impurities form shallow levels measured from the conduction band, although there is no general agreement as to
what are the exact positions of these levels. Look and Remsky (1999), and Reddy et al. (2008) reported values that form a range of plausible positions of the levels, in which this work's calculated values fit in [10, 11].

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

4. Conclusion

Synthesis of ZnO micro/nanorods was successfully done, and the grown ZnO structures were investigated. Free-standing ZnO micro/nanorods were effectively produced using a low-temperature method of fabrication, the hydrothermal method. XRD results show that the method produces highly crystalline ZnO with no signs of other chemical impurities in the solution. The I-V characteristic curves of the grown ZnO micro/nanorods were obtained, and it can be concluded that the resistance of the ZnO micro/nanorods is proportional to the aspect ratio of the samples. Also, the grown ZnO micro/nanorods electrical properties follow an Ohmic behavior. Furthermore, the RT curve of the samples using two-point probe method showed the semiconducting behavior of the ZnO micro/nanorods. The slopes represent the activation energies for thermal-assisted conduction persisting in the samples.

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Acknowledgement

We would like to acknowledge the Emergent Science and Technology grant from the University of the Philippines Office of the Vice President for Academic Affairs (OVPAA).