



# Facile aqueous growth of 150 nm ZnO nanowires for energy harvester: Enhanced output voltage using Pt sputtered electrode



Mansoor Ahmad<sup>a,\*</sup>, Janice Kiely<sup>b</sup>, Richard Luxton<sup>b</sup>, Musarrat Jabeen<sup>a</sup>, Muhammad Khalid<sup>c</sup>

<sup>a</sup> Department of Physics, University of Punjab, Lahore, Pakistan

<sup>b</sup> Institute of Bio-Sensing Technology, UWE, Bristol, UK

<sup>c</sup> Department of Physics, NED University of Engineering & Technology, Karachi, Pakistan

## ARTICLE INFO

### Article history:

Received 1 October 2015

Received in revised form 17 December 2015

Accepted 21 December 2015

### Keywords:

ZnO nanowires

Piezoelectric potential

Energy harvester

Piezoelectric potential

Pt sputtered electrode

## ABSTRACT

Facile aqueous growth technique was adopted to grow diameter controlled 150 nm ZnO nanowires on an ITO (indium tin oxide) coated PET (poly ethylene terephthalate) substrate. Prior to nanowire growth, a pure wurtzite structured ZnO seed layer was grown on PET substrates. Surface morphology and elemental composition were investigated by SEM (scanning electron microscopy) and EDS (energy dispersive spectroscopy) respectively. An enhanced output piezoelectric potential of 1.858 with an output power density 215.4 mW/cm<sup>2</sup> was achieved using a Pt sputtered electrode. We have obtained enhanced values of output voltage compared to our previously reported voltage values of 1.34 V (Ahmad et al. 2014).

© 2015 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

ZnO is multifunctional semiconductor. It has excellent electrical and optical properties which make it a more prominent material in the electronic and optoelectronic industries. It has a wide band gap (3.37 eV), is environment friendly (nontoxic) and is an inexpensive material [1–2]. It provides a wide range of crystal growth technologies, is quite stable in air and its abundant occurrence makes it a more versatile material for commercial applications. Its existence in a one dimensional nanostructure enhances its usability in optoelectronic [3–4] devices and especially in energy harvesting devices. For energy harvesting applications, the semiconductor and piezoelectric properties of ZnO are of main importance. ZnO based piezoelectric nanogenerators have great compatibility with biologically flexible substrates and they can be integrated with different biological and organic materials. ZnO based nanogenerators can be used with flexible devices. They can be used in stretchable and portable devices [5–7].

To generate energy for nanoscale systems, ZnO based piezoelectric nanogenerators are an ideal source, especially in the case of small size and low power consumption batteries with a long life time. For a sustainable independent operation, a continuous power source is required and for this type of operations the energy source must be self powered. ZnO based nanostructures can harvest energy from external sources.

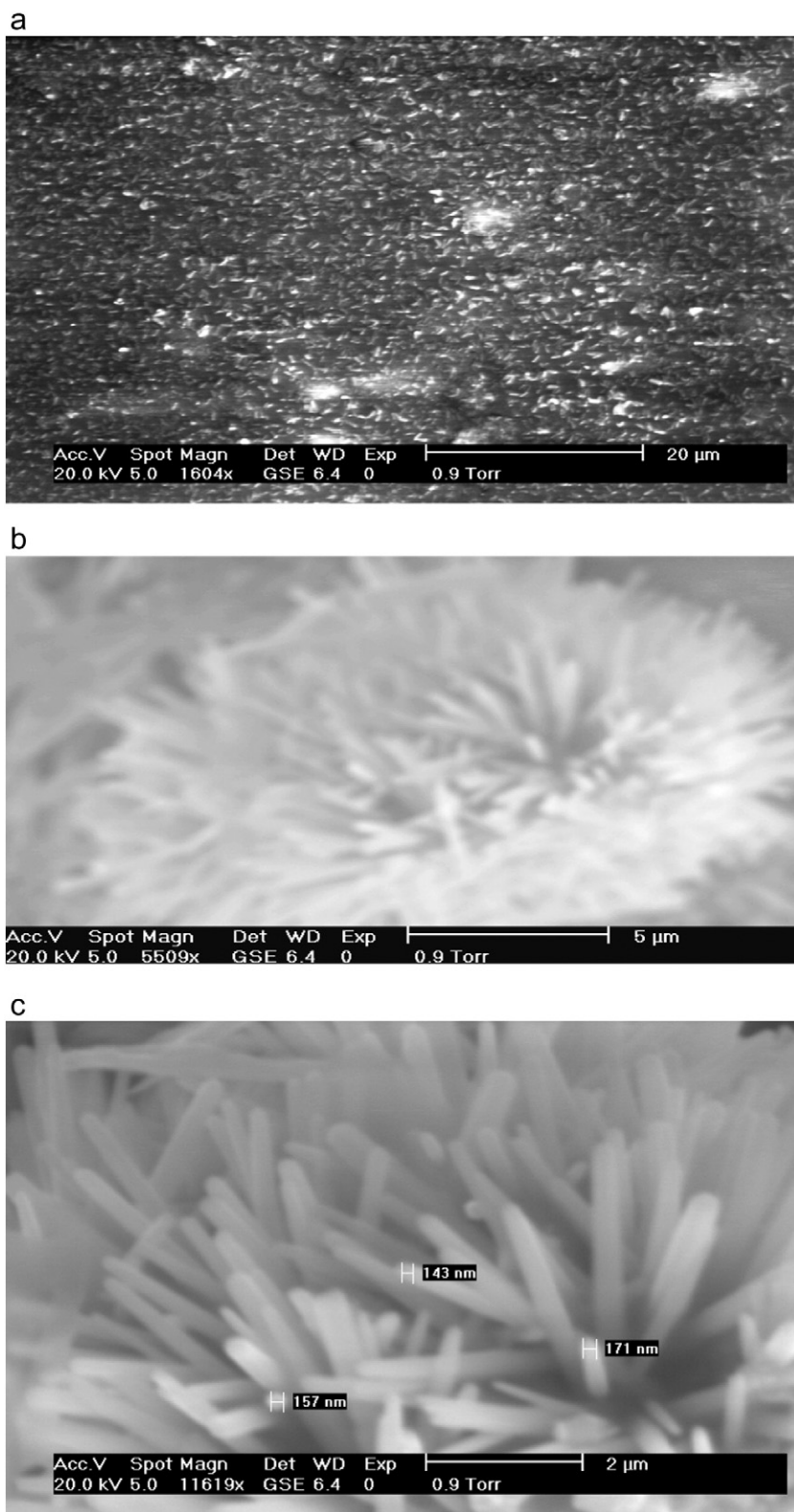
These may include the stretching of muscles, blinking of an eye, joint movement, and expansion and contraction of blood vessels [8–11].

In this work we have used Pt as a sputtering electrode material rather than gold. In our previous work [12] we have sputtered gold to act as the top electrode and we have studied output voltage graphs with 2.5 nm, 5 nm and 7 nm thick sputtered layers. We have used Pt in this study due to its high work function (6.1 eV). External applied force is nearly 50 nN as in an earlier reported work [12].

## 2. Materials and methods

Zinc acetate dehydrate [Zn (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O], hexamethylenetetramine (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>), zinc nitrate hexahydrate [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] and solvents of analytical grades with no further purification were used for synthesis. All reagents were purchased from Sigma Aldrich. An ITO coated PET substrate was ultrasonically cleaned with deionized water and then with acetone for 15 min then dried in air for 30 min. A droplet of 10 mM zinc acetate was coated on PET substrates to grow a seed layer. Coated PET substrates were dried in the air for 20 to 30 min. A well adhered and wurtzite structured ZnO seed layer was obtained by repeating the coating step two to three times then annealed at 60 °C for an hour. Growth of well aligned ZnO nanowires was carried out in an equimolar nutrient solution of hexamethylenetetramine and zinc nitrate hexahydrate in a reaction flask. A 300 mL nutrient solution was prepared and seed layer coated PET substrates were immersed upside down for 2.30 h at 95 °C. Substrates were removed from solution and for cleaning purposes they are rinsed with deionized water and dried

\* Corresponding author.



**Fig. 1.** (a) Top SEM image of ZnO nanowires. (b) SEM image of ZnO nanowires, at low magnifications, lens elevation at 80°. (c) SEM image of 150 nm ZnO nanowires grown on PET substrates, lens elevation at 60°.

in the air for 30 min. ITO coated PET substrates have a resistivity of 10 M  $\Omega$ /sq, and their device structure is similar to that used in our earlier published work i.e. an ITO coated PET substrate has acted as a base electrode; it works as a bottom electrode due to its conductive coating. The middle portion is comprised of vertically grown ZnO nanowires

and the upper electrode is a Pt sputtered electrode using Emscope SC 500 having an internal pressure of Ar 0.1 Torr. A nutrient solution of HMTA ( $C_6H_{12}N_6$ ) and zinc nitrate hexahydrate [ $Zn(NO_3)_2 \cdot 6H_2O$ ] was prepared in a canonical flask with a volume of 300 mL; it is an equimolar solution and the molarity of the solution was adjusted by using a

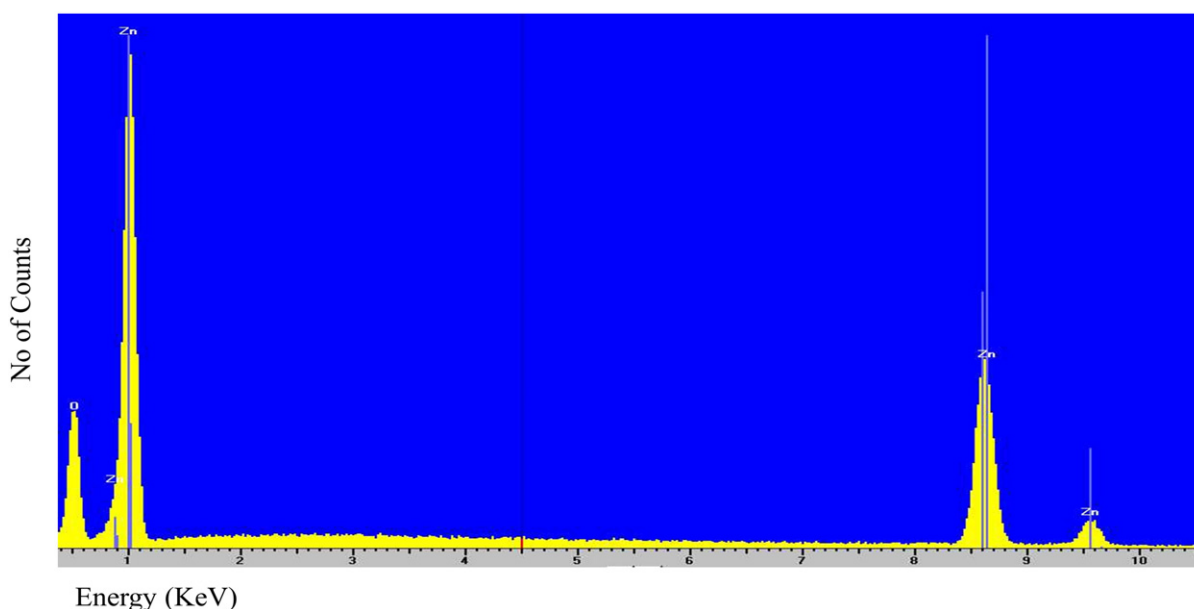


Fig. 2. Energy dispersive X-ray spectroscopy of ZnO nanowires.

chemical relation

$$C = m/V \times 1/MV. \quad (1)$$

where  $C$  is the molar concentration in mol/L,  $m$  is the mass of solute dissolved in a solvent of  $V$  liters and  $MV$  is the molecular weight in g/mol of the solute dissolved in solvent. The size of the device was around 500 nm, and pure copper wires are connected to both the top and bottom electrodes by silver paste. Measurement of voltage and output power density was acquired by Picoscope 6204 (PC based instrument) i.e. we have recorded our voltage values by connecting our nanostructure with a picoscope and the picoscope to our computer.

For the growth of ZnO nanowires  $Zn^{+2}$  was provided by zinc nitrate salt hexamethylenetetramine which acted as a weak base and gradually produced  $OH^-$ . This slow release of  $OH^-$  was found crucial for the proper growth of nanowires; if the release was fast then nutrient solution would have been consumed quickly and the further growth of nanowires would be stopped. The growth of nanowires was dependent on reaction parameters like temperature, time and the concentration of the precursor. The density of nanowires on the substrate was controlled by controlling the concentration of reactants in the precursor. We have carried out a series of experiments by varying the concentration of zinc salt and hexamethylenetetramine and found that they should be equimolar. In initial stages of growth, nucleation growth was the deciding factor for the density of nanowires. These nuclei grew with the passage of time and initially converted in nanorods and then gradually transformed in nanowires. After initial stages the density of nanowires were not affected by further nuclei and these late coming nuclei were dissolved in a solution. Initially rod like structures were grown as reported [12] but we have grown a long wire structure by giving more and more time to a weak base so that it can slow down the growth process in the nutrient solution and wires can grow along their length.

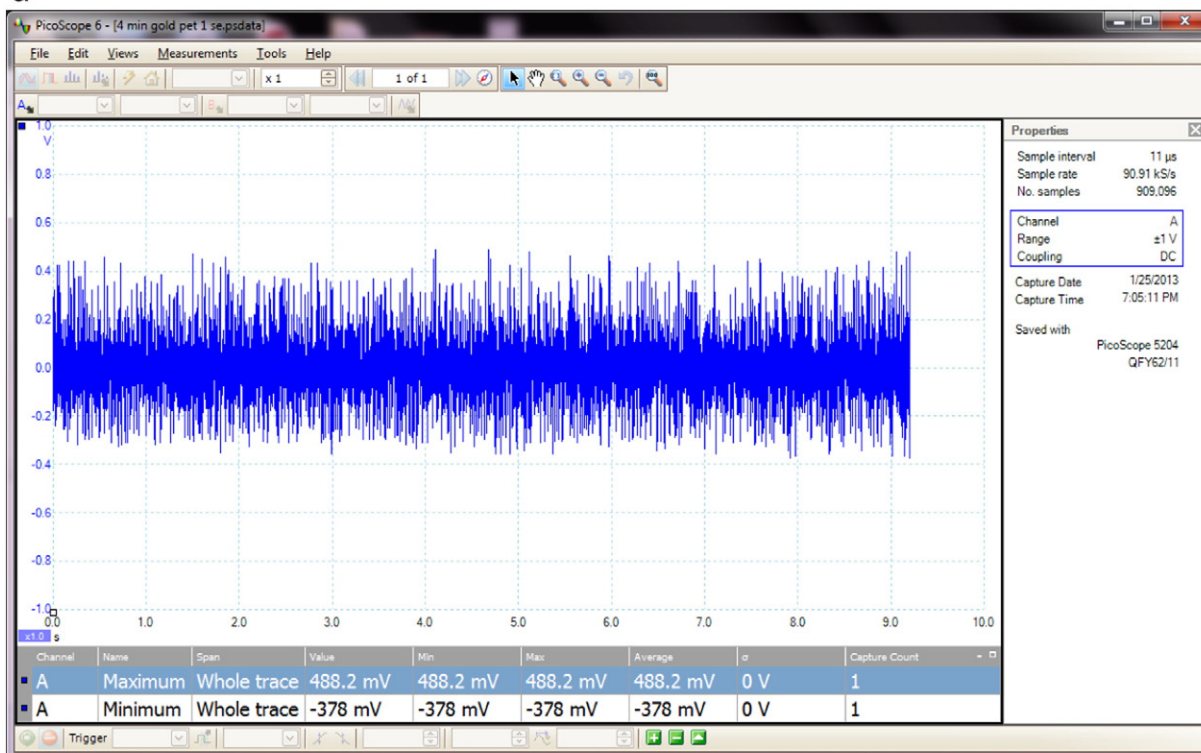
### 3. Results and discussions

Fig. 1 (a,b,c) show SEM images of ZnO nanowires grown on a PET substrate, and a hexagonal wurtzite structure is evidenced in Fig. 1(c). Fig. 1 (a,b,c) are taken at an elevation of  $90^\circ$ ,  $80^\circ$  and  $60^\circ$  respectively. Images have shown well oriented nanostructures having a diameter of around 150 nm and the narrow spacing between them was also achieved by controlling the concentration of the nutrient solution. In

Fig. 2 EDS images are obtained from ESEM Philips XL30 and energy (KeV) is represented along x-axis and the arbitrary no. of counts are taken along the y-axis. The image has shown the elemental composition of nanowires, i.e. Zn and O, and most importantly no other elemental peaks are visible showing contamination of free structure. Fig. 3(a) represents the output piezoelectric potential generated by ZnO nanowires having a 2.5 nm top electrode thickness; obtained voltage peaks were not as periodic as in the case of a 7.5 nm thick sputtered electrode.

We have acquired periodic voltage peaks with a maximum voltage of 1.858 V. In Fig. 3(b) the upper half (scope 1) represents voltage and the lower part (spectrum 1) represents an output power density of  $215.4 \text{ mW/cm}^2$ . Time is taken along the x-axis and voltage along the y-axis. Novelty of research work is that by reducing the diameter of nanowires from 350 nm [17] to 150 nm we have acquired high voltage values; the reason for high voltage values is that by a decrement in the diameter of nanowires, a more pronounced edge effects phenomenon is caused within nanowires which caused enhanced scattering within nanowires and due to this increase in scattering, reverse leakage current through nanowires has been reduced considerably and all piezoelectric potential has appeared in the output stages of the device. Output power density for a 2.5 nm thick Pt sputtered electrode has been recorded but not included due to an insignificant value however in the case of a 7.5 nm thick Pt electrode we have acquired a high output power density of  $215.4 \text{ mW/cm}^2$ . We have already shown in our earlier work [13] that a 7.5 nm thick gold electrode has produced the maximum possible value of voltage with periodic voltage peaks. We sputtered a Pt electrode for 1 min and 3 min to obtain 2.5 nm and 7.5 nm thick layers respectively. A 7.5 nm thick layer of an electrode has previously shown the ideal Schottky contact. A Schottky contact is essential for piezoelectric potential and electron affinity of a semiconductor which should be less than the work function of sputtering metal [14]. Earlier we have reported 1.34 V with a 7.5 nm sputtered gold electrode and now we have obtained 1.858 V with a Pt sputtered electrode of the same thickness of 7.5 nm. It clearly indicates that a sputtered electrode with a high work function has produced high output voltage. Gold has a work function of 5.1 eV while Pt has 6.1 eV [15], and low output values in the case of gold are due to a reverse leakage current that has been reduced in the case Pt. Not only has a sputtered electrode played a role in producing high voltage but also a decrement in diameter of nanowires also has a vital role in the reduction of reverse leakage current that is due to "Edge effects"

a



b

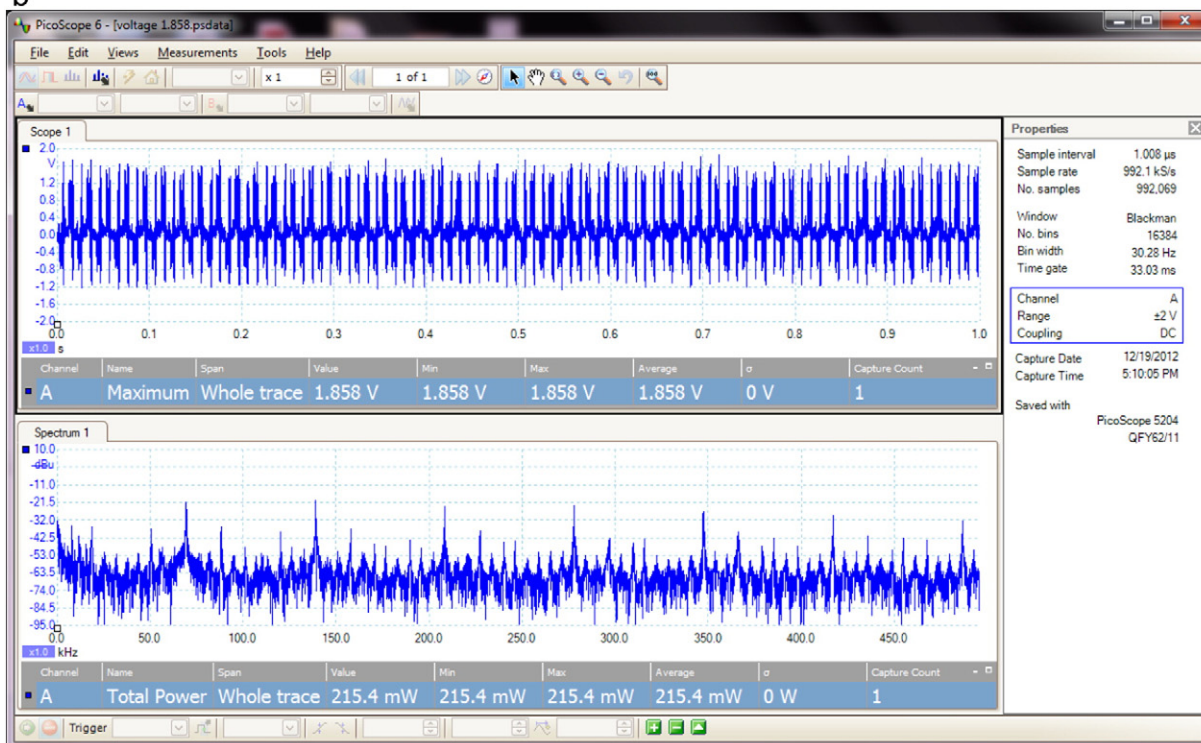


Fig. 3. (a) Output voltage graph using Pt sputtered electrode of 2.5 nm thickness. (b) Output voltage graph using Pt sputtered electrode with 7.5 nm thickness.

present in nanowires. Electrons suffer huge scattering due to these edge effects which cause poor conductivity through nanowires [16]. Earlier with 350 nm ZnO nanowires we have reported voltage values of 1.65 V and now voltage has been enhanced up to 1.858 V with 150 nm diameter which shows a reduction in reverse leakage current

hence an increase in output voltage. An external force of  $\sim 50$  nN was applied by using an extremely light roller on top of the Pt electrode. As we have discussed in our earlier work, such external force could not deform nanowires permanently because once the force is removed they will regain their original position due to the high elasticity [17–18].

#### 4. Conclusion

A highly densely packed structure of ZnO nanowires were grown on ITO coated PET substrates. Prior to the growth of ZnO nanowires a ZnO seed layer was grown on a PET substrate at low temperature values. Surface morphology has been studied by SEM and EDS results.

High voltage values (1.858 V) have been obtained with a 7.5 nm thick Pt electrode. The values have been improved by our previously reported voltage values. We have obtained improved results by reducing the diameter up to 150 nm and by substituting the top Gold electrode by a Pt electrode. We have also achieved a high output power density of 215.4 mW/cm<sup>2</sup> with low noise values.

#### Acknowledgements

The research work has been fully supported by the Higher Education Commission, Pakistan with

Support initiative Grant No. IRSIP 21 Ps 04. I would like to thank the Department of Applied sciences of UWE, Bristol, UK for providing access to their lab facilities.

#### References

- [1] B. Kumar, S.W. Kim, *Nanoenergy* 1 (2012) 342–355.
- [2] S. Xu, Z.L. Wang, *Nano Res.* 4 (2011) 1013–1098.
- [3] Z.L. Wang, *J. Mater. Chem.* 15 (2005) 1021–1024.
- [4] Y. Wei, C. Xu, S. Xu, C. Li, W. Wu, Z.L. Wang, *Nano Lett.* 10 (2010) 2092–2096.
- [5] B. Weintraub, Y.G. Wei, Z.L. Wang, *Angew. Chem. Int. Ed.* 48 (2009) 8981–8985.
- [6] Z.L. Wang, J.H. Song, *Science* 312 (2006) 242–246.
- [7] X.D. Wang, J.H. Song, J. Liu, Z.L. Wang, *Science* 316 (2007) 102–105.
- [8] R. Yang, Y. Qin, C. Li, G. Zhu, Z.L. Wang, *Nano Lett.* 9 (2009) 1201–1205.
- [9] X. Wang, J. Liu, J. Song, Z.L. Wang, *Nano Lett.* 7 (2007) 2475–2479.
- [10] Z. Li, Z.L. Wang, *Adv. Mater.* 23 (2011) 84–89.
- [11] Z. Li, G. Zhu, R. Yang, A.C. Wang, Z.L. Wang, *Adv. Mater.* 22 (2010) 2534–2537.
- [12] L. Lin, H. Watanabe, M. Fujii, M. Takahashi, *Adv. Powder Technol.* 20 (2009) 185–189.
- [13] M. Ahmad, M. Iqbal, J. Kiely, R. Luxton, M. Jabeen, *Ind. J. Eng. Mater. Sci.* 21 (2014) 672–676.
- [14] <http://hyperphysics.phy-astr.gsu.edu/hbase/tables/photoelec.html>
- [15] S.M. Zee, *Physics of Semiconductor Devices, Their Edition*, Wiley, 2013.
- [16] [wikipedia.org/wiki/Nanowire](http://wikipedia.org/wiki/Nanowire).
- [17] M. Ahmad, M. Iqbal, J. Kiely, R. Luxton, M. Jabeen, *Int. J. Eng. Res. Technol.* 2 (2013) 2751–2757.
- [18] X. Sheng, Q. Yonq, X. Chen, W. Yaguang, Y. Rusen, Z.L. Wang, *Nat. Nanotechnol.* 28 (2010) 366.