

# Diameter controlled synthesis of ZnO nanowires for energy harvester: Effect of sputtered coated platinum electrode on ZnO nanowires.

Mansoor Ahmad<sup>(a)</sup> Muhammad Azhar Iqbal<sup>(b)</sup> Janice Kiely<sup>(c)</sup> Richard Luxton<sup>(d)</sup>

Musarrat Jabeen<sup>(e)</sup>

<sup>(a)</sup> Department of Physics, university of Punjab, Lahore, Pakistan.

<sup>(b,e)</sup> Department of Physics, University of the Punjab, Lahore, Pakistan.

<sup>(c,d)</sup> Institute of Bio-Sensing Technology, University of the West of England, Bristol, UK.

## Abstract

We have successfully synthesized diameter controlled (350 nm) ZnO nanowires. First we have grown seed layer on ITO coated PET substrate then in second step well aligned ZnO nanowires were grown on seed layer. Crystallinity, morphology and growth rate of nanowires were controlled by controlling synthesis parameters. Grown nanowires have adopted the same pattern as of the seed layer. Surface morphologies, crystallinity and elemental composition were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) respectively. Pure hexagonal (wurtzite) structure ZnO nanowires were grown along (002) direction. We have also investigated the effect of platinum electrode on top of ZnO nanowires. High output voltage of 1.654 volts demonstrated the potential to convert mechanical energy into electrical energy.

Keywords: ZnO nanowires, energy harvester, schottkey contact, piezoelectric potential.

## Introduction

In nanotechnology, the three most studied one dimensional nanostructures are silicon nanowires [1-4], carbon nanotubes [5-9] and zinc oxide nanowires [10-12]. ZnO due to its wurtzite structure is one of the most dominant materials used in nano piezotronics. ZnO is wide band gap material (3.37 eV), which is transparent to visible light, non toxic and biocompatible and which has high binding energy (60 MeV). Due to its versatility and variety of configurations in nanostructures, it is being used in numerous applications like optoelectronics, spintronics, sensors, actuators, nanogenerators [13]. ZnO nanowires have shown potential for the fabrication of nanogenerators and nano piezotronic devices [14].

ZnO crystal structure lacks the central symmetry. It can easily be understood by considering  $Zn^{+2}$  and  $O^{+2}$  are arranged in a tetrahedral structure along the c-axis. Interestingly the unit cell of ZnO is neutral but cations and anions can arrange themselves to create special polar surfaces. These polar surfaces are negatively and positively charged. These oppositely charged ions create a dipole moment along c- axis. In normal conditions the charges are not mobile and non-transferable because the ions arrange themselves in such a way as to minimize the electrostatic energy [15-16]. But when an external stress is applied, charge centers (cations and anions) are disturbed which results the creation of dipoles. This piezoelectric field is created due to external pressure and it is preserved as long as external

pressure is sustained. Potential created due to these poles are called piezoelectric potential [14]. The creation of this potential is the basis of Piezogenerators. For a mechanical energy harvester, several types of external energies can be utilized such as breathing, muscle contraction and expansion, heart beating, wind energy etc. depending upon the requirement. For instance first bio medical energy harvesting, human finger was used. The flexible nanogenerator was fixed on moving joint and external energy is provided by the movement of joint [17-20]. In this study a roller was used to apply small force to create piezo electric potential.

Various methods have been reported for the growth of well aligned ZnO nanowires for instance, pulsed laser deposition [21], electrochemical bath deposition [22], sol-gel method [23], spray pyrolysis method [24], hydrothermal method [25], etc. Among all these methods, hydrothermal method has significant advantages such as cheaper in cost, environment friendly, low synthesis temperature and large area deposition. It also provides opportunity to control diameter, length and density of nanowires by controlling synthesis parameters. So it would be a good choice to grow well oriented ZnO nanowires for energy harvesting purposes. We have grown controlled diameter ZnO nanowires on ITO coated PET substrate covering an area of  $1 \text{ cm}^2$ . Vertically grown nanowires were then used to produce piezoelectric potential under a minute continuous mechanical pressure. Nanowires growth was carried out at low temperature. We have also studied first time effect of sputtered coated platinum electrode on ZnO nanowires and these nanowires have generated high output voltage of 1.654 volts.

## Experimental Details

All reagents were used of analytical grade with no further purification. All of them are purchased from Sigma Aldrich. First we have cleaned the substrates through detergent then afterwards by isopropyl alcohol and acetone for 15 minutes respectively then substrates were dried in air for half an hour. 20 mM solution of Zinc Acetate was prepared to grow the seed layer. Droplets of solution were used to grow a seed layer on each substrate. The seed layer was annealed at  $100^\circ \text{C}$  for 2 hours. Indium tin oxide coated PET substrates ( $10\Omega/\text{sq}$ ) have shown good results for ZnO seed layer.

To grow well aligned ZnO nanowires on seed layer, nutrient solution zinc nitrate hexahydrate and hexamethylenetetramine was used. 400mL equimolar solution was prepared in conical flask. ITO coated substrates were immersed in nutrient solution up-side down for 3 hours at  $90^\circ \text{C}$ . Generally it is observed that cleanliness is quite a major issue in these types of procedures so we have rinsed it with deionised water to avoid any contaminations and then dried in air at  $60^\circ \text{C}$ .

whole procedure was repeated by varying different parameters to observe any significant change in the outcome of experiment. Well aligned ZnO nanowires with diameter of around 350 nm and length about 1  $\mu\text{m}$  were synthesized on flexible substrates. To make an energy harvester, we made a sandwich like structure with ZnO nanowires in between top and bottom electrode. To ensure a schottkey contact between top of ZnO nanowires and top electrode, we have used platinum electrode. We have also investigated the different thickness values of platinum electrode on top of nanowires to observe change in piezoelectric potential. Schottkey contact is vital for piezo electric potential. When external pressure is applied piezoelectric potential is developed inside the nanowires and the difference of potential between two ends of nanowire allows electrons to flow through external circuit. Due to schottkey barrier between nanowire and top electrode, electrons could not pass through the interface and tend to flow through external circuit. In our case, we have used picoscope 5204 to measure piezoelectric voltage.

## Results and Discussions

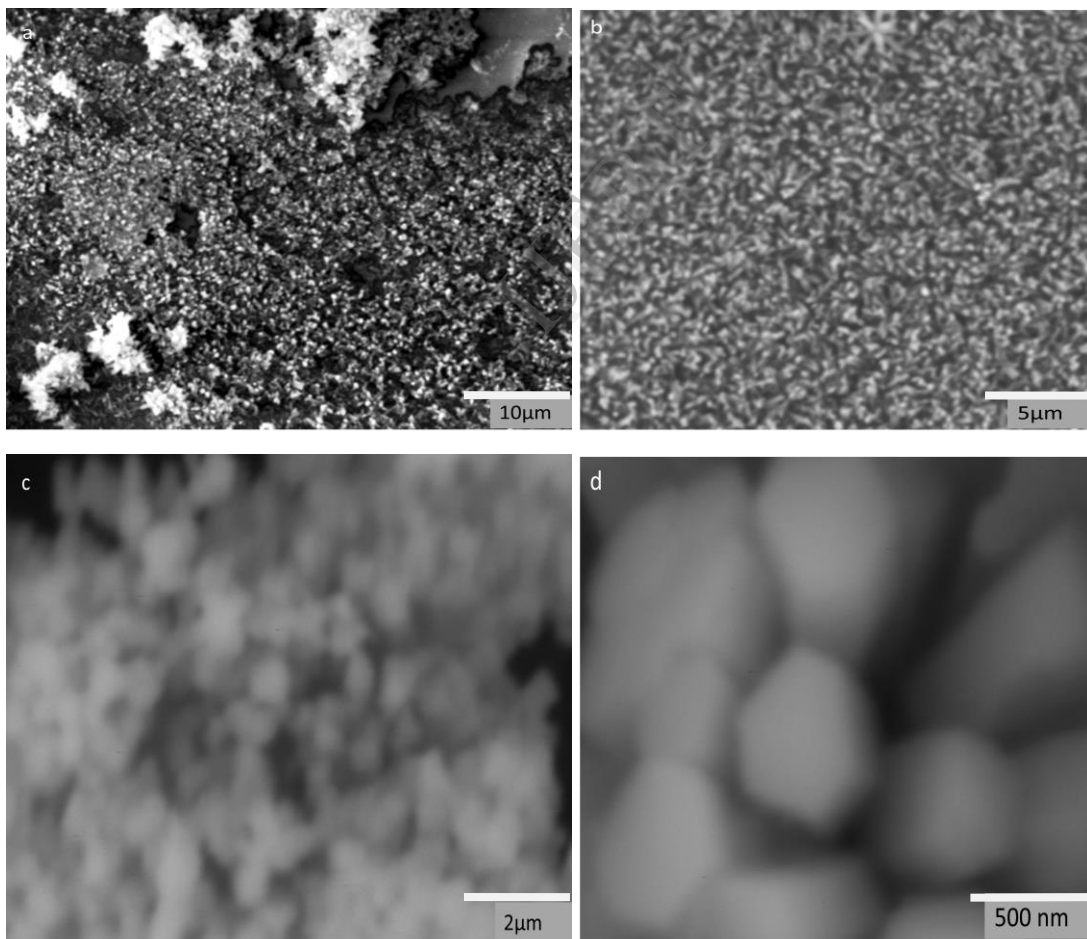


Fig.1 SEM images for ZnO nanowires (a,b) at low magnification, (c,d) at high magnification.

Surface morphologies of ZnO nanowires grown on ITO coated PET substrates are illustrated in fig.1 Fig.1(a) at 4000 times magnification and (b) at 8000 magnification showed

distribution of nanowires on entire sample, this also showed better growth of seed layer on flexible substrates. Fig.1(c) at 17,000 and (d) at 30,000 magnification have shown pure hexagonal structure of ZnO nanowires with average diameter of 350 nm. All nanowires were grown vertical from substrates and there was also narrow spacing between them which was necessary for producing piezoelectric potential. SEM images have shown all nanowires grown are properly adhered with seed layer. The morphology and structure shown the molarity of precursor was adjusted properly. We have used ESEM Philips XL30 having a resolution 4nm to obtain SEM images.

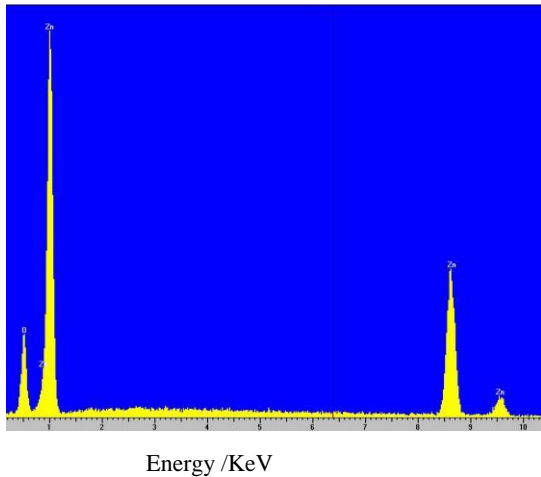


Fig.2 EDS results of ZnO nanowires.

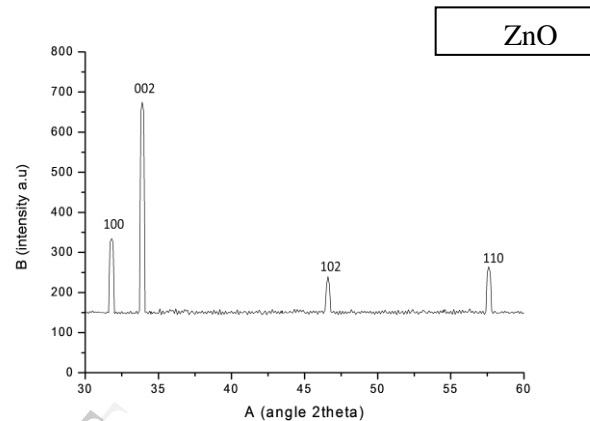


Fig.3 XRD patterns of ZnO nanowires

Fig.2 represented energy dispersive spectroscopy of grown ZnO nanowires indicating the presence of Zn and O and also verified that there were no other impurities were present. EDX ISIS 3.2 was used to obtain energy dispersive spectrum of ZnO nanowires. While fig.3 represents XRD patterns of vertically grown nanowires taken from Bruker D8 using CuK $\alpha$  radiation of wavelength 0.1454nm. Strong sharp peaks in XRD pattern indicated high crystallinity of ZnO nanowires. All peaks were matched by standard ZnO wurtzite crystal structure peaks. XRD pattern indicated vertical growth orientation of nanowires. High diffraction peak along (002) direction indicated the growth orientation along c-axis, however comparatively weak peaks along (100), (102) and (110) have shown some other orientations as well but not as strong as along (002) direction. Pure hexagonal wurtzite structure of ZnO nanowires as shown in Fig.1 were totally in agreement with XRD patterns. Vertical growth orientation and crystallinity of nanowires both were necessary for producing piezoelectric potential which was evidenced in XRD and SEM results.

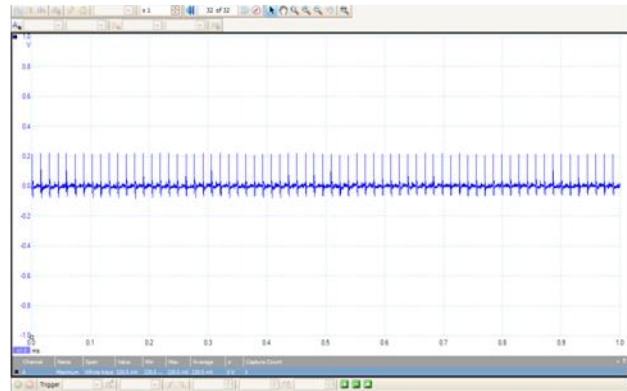
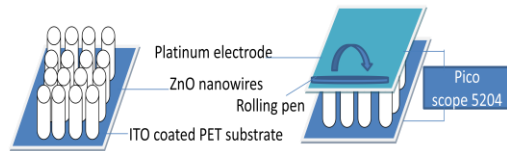


Fig.4 schematic diagram ZnO nanowires based energy harvester. Fig.5(a) output voltage graph with 2.5nm thick Pt electrode.

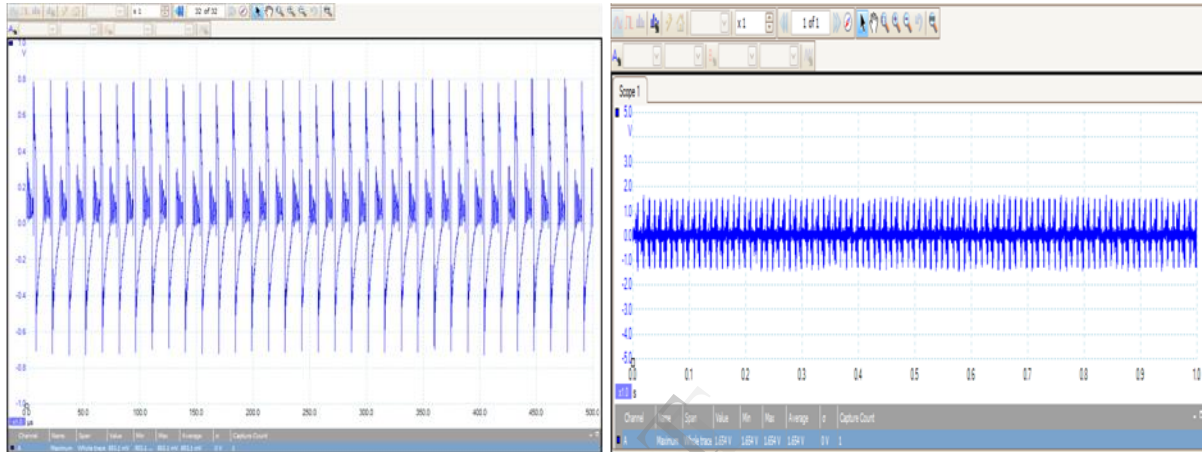


Fig.5(b) output voltage graph with 5nm thick Pt electrode. Fig.5(c) high output voltage graph with 7.5nm thick Pt electrode.

Well aligned ZnO nanowires on ITO coated PET substrate with top electrode (platinum) sputtered by sputtering unit SC500 were shown in schematic diagram. We have created a schottky contact between ZnO nanowires and top electrode by using platinum as top electrode. As we have discussed earlier that schottky contact is quite crucial for piezoelectricity.

These nanowires rely on piezoelectric property of ZnO need small gap in between them especially near the tips of nanowires to get sufficient bending when an external pressure is applied. We have applied a minute external pressure through a rolling pen on top electrode. We have also investigated the different thickness of sputtered coated Pt electrode on top of nanowires.

We did it by varying sputtering time. 2.5nm thick platinum electrode has produced an output voltage of 220 mV. For 2 minutes sputtering time, 5nm thick Pt layer has produced 803mV. For three minutes sputtering time 7.5nm thick Pt layer has produced a high output voltage of 1.654 volts. Further increase in the thickness of Pt, resulted in no further increase in output voltage. It was concluded that for high output voltages the coating must be uniform and should cover all nanowires completely but excessive thickness was unnecessary.

These vertically grown nanowires have shown excellent results as compared to previously reported nanostructure results [26-28]. Previously reported data has given the evidence only that these nanostructures can convert mechanical energy into electrical energy. Single wire nanogenerator

attached to a human finger joint has produced a voltage (15mV to 20mV) during stretching and bending, similarly nanogenerator attached to running hamster produced 70mV voltage [29]. So far maximum output voltage peak reported by a large array of ZnO nanowires was 1.2 volts [30]. We have enhanced output voltage up to 1.654 volts.

### **Conclusion**

We have successfully synthesized 350nm ZnO nanowires on ITO coated PET substrates. Vertically grown ZnO nanowires have shown excellent epitaxial relationship with seed layer. Strong diffraction peaks along (002) direction have given evidence of the growth along c-axis. SEM results have shown pure hexagonal structure. They were totally in agreement with XRD results. We have first time investigated the effect of platinum electrode on top of nanowires in generating piezoelectric potential. Different thicknesses of platinum on ZnO nanowires were tested and 7.5nm thick platinum layer has produced a high output voltage 1.654 volts. The high output voltage was achieved when all nanowires were covered by platinum electrode completely. Periodic voltage peaks have also shown that these ZnO nanowires have produced sustained self bias voltage under a continuous a mechanical pressure.

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