Enhanced output voltage generation via ZnO nanowires (50 nm): Effect of diameter thinning on voltage enhancement

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Abstract

50 nm ZnO nanowires were grown on indium tin oxide (ITO) coated poly ethylene terephthalate (PET) substrates by adapting facile aqueous growth technique using low temperature and vacuum conditions. Prior to growth of ZnO nanowires, pure hexagonal wurtzite structured seed layer was grown on flexible substrates. Surface morphology of nanostructure has been examined by scanning electron microscopy (SEM). Vertical growth orientation has been evidenced in XRD patterns. Minute external mechanical force (~50 nN) has produced periodic voltage peaks. 2.5 nm and 7.5 nm thick sputtered Pt electrode have been tested to obtain output voltages. 50 nm ZnO nanowires has produced a maximum output voltage of 2.717 volts having an output power density of 397.1 mW/cm2. By squeezing the diameter, we have reduced reverse leakage current through nanowires and enhanced output voltage.

Introduction

After carbon nanotubes [1–3] and silicon nanowires [4–6], ZnO nanostructures have attracted researchers due to its wide range of applications in electronics and optoelectronic industry. ZnO is an important semiconductor material having a direct bandgap of 3.34 eV; due to its wide band gap it has got numerous applications in optics, sensors, spintronics, actuators and biomedical sciences [7]. ZnO possesses wurtzite and blend structures which Zn+2 and O−2 are arranged in layer by layer manner along vertical axis, due to the lack of central symmetry in its structures it exhibits piezoelectric properties that can be used in all mechanical energy harvesting devices, current modulated devices, MEMS based sensors and in surface acoustic waves. The Production of Piezoelectric potential is vital in nanogen-erators and in strain sensors and piezoelectric potential can be created or controlled by a Schottky contact in between metal and semiconduc-tor. Earlier in our work, we have used Au sputtered top electrode to work as schottky contact with ZnO nanowires but in this study we have explored the role of Pt sputtered electrode [8–10]. ZnO nanostructures also exhibit robust properties which make them promising candidate to be used in mechanical-electrical energy conversion devices [11]. ZnO, due to its semiconducting and piezoelectric properties, it is considered highly favorable in UV lasering [12], UV sensors [13], light emitting diodes [14], gas sensors [15,16] and solar cells [17].

ZnO nanostructures became more prominent due to their use as tiny transducers which can be implanted in nanoscale electronic, optoelectronic and in-vivo biomedical systems; the best way to use these nanoscale transducers is to trigger them with external ambient energy. Interestingly,

harvesting of energy can be selected according to the application for instance; human body has lot of mechanical systems that can impart their mechanical energy to nanoscale systems im-planted in human body, due to their dimensions in nanoscale billions of tiny transducers can be accumulated on a single substrate of one centimeter. In our case piezoelectric property of ZnO was used to convert external force of 50 nN to produce an output voltage of 1.34 V, each nanowire grown on a substrate covering an area of 1 cm2 worked as nano transducers [8,18–20]. There are few methods reported for the growth ZnO nanowires for instance Sol-gel [9,21], spray pyrolysis [22], chemical bath deposition [23] but hydrothermal growth was found cheapest from all and most importantly it does not require high vacuum and high temperature conditions [8]. The technique has got a significant feature that it provides morphology and density control of ZnO nanowires without any catalyst.

Materials and methods

All Reagents used were of analytical grade of 98% purity with no further purification. Initially ITO coated PET(10 Ω/Sq) substrates were washed and dried in air then cleaned ultrasonically with deionised water and acetone respectively for 15 min each and then dried. Prior to ZnO nanowires growth pure wurtzite structured seed layer was grown on PET substrate. 10 mM solution of zinc acetate dihydrate [Zn (CH3COO)2·2H2O] was used to grow a seed layer, to obtain pure wurtzite structure of seed layer process was repeated two to three time. Seed layer annealing was carried out at 60 °C for 2 h, growth orienta-tion was closely related to seed layer annealing. Seed layer annealing was found quite critical step in growth of nanowires [24,25]. Nutrient solution (500 mL) of HMTA [C6H12N4] and Zinc nitrate hexahydrate [Zn(NO3)2.6H2O] was prepared to grow ZnO Nanowires of controlled diameter. Annealed substrates were immersed in nutrient solution upside down for two hours. Growth time was found crucial for controlled diameter growth of NW however density of the wires were controlled by the concentration of HMTA and [Zn(NO3)2.6H2O].

Our previous work led us to grow controlled diameter growth of nanowires which enabled us to study the effect of diameter on output voltage generation [8,26]. ITO coated PET substrates acted as base electrode and upper electrode has been sputtered by using sputtering unit Emscope SC 500.

Ar was present in the chamber exerting an internal pressure of 0.1 torr; 2 kV voltage was used to initiate charge irradiation process in the chamber, we have sputtered 2.5 nm and 7.5 nm thick Pt layers on top of ZnO nanowires. Extremely light plastic roller is used to apply ~50 nN force on top of nanowires to produce piezoelectric potential. Structure of the energy harvester is shown in later part of the paper, lower part consist of PET substrate on which ZnO nanowires were grown, which acted as base electrode, the intermediate part comprises of ZnO nanostructure and upper part is sputtered Pt electrode. Plastic roller was rolled on to obtain the output voltage values recorded by Picoscope 5204. Plastic roller was not attached on upper electrode; it was rolled on upper electrode externally.

Results and discussion

SEM images in Fig. 1(a) shows uniform growth of ZnO nanowires on ITO coated PET substrate, density of nanowires on substrate were controlled by adjusting the concentration of nutrient solution. Dense packed structure of nanowires eliminated one fabricating step, which made it economical technique, otherwise polymer matrix would have been required to fill intermediate

space in between nanowires so that it could not be short during Pt coating. Fig. 1(b) and (c) have shown the diameter range was about 50 nm, diameter control was achieved by closely monitored growth time in the nutrient solution. Our earlier reported results [8] were closely in agreement with our recent results, we have obtained improved morphology and density control by controlling synthesis parameters such as growth time in solution and more dense structure was achieved by increasing the concentration ratio of HMTA [C6H12N4] and zinc nitrate hexahydrate [ZnO3·6H2O] in solution. Narrow opening near the tips of ZnO nanowires were desired to get sufficient bending for piezoelectric potential. Our reported values were closely in agreement with reported values [27]. Fig. 2 represented well oriented growth of ZnO nanowires along c-axis, all peaks were matched from ZnO (JCPDS card no 36-1451). Sharp peak along (002) direction has given evidence that most of nanowires were grown vertically upward from substrate however some weak peaks along (101), (102), (110) and (100) showing other orientation as well but not of much significance which was also evidenced in reported value [28]. Fig. 3 shows the schematic configuration of energy harvester that we have used in our study. Bottom substrate acted as one conducting electrode, central vertical structure of ZnO NW and upper electrode was Pt sputtered electrode and minute external force of ~50 nN was applied by an external roller to provide external mechanical energy. We have used Pt electrode instead of Au electrode to improve our results, as Au has a work function of (5.1–5.4 eV) while Pt has a work function of (6.1 eV) which is far greater than the electron affinity of ZnO of (4.5 eV) which means by doing so we have reduced the chances of reverse leakage current to minimum and consequently increasing output voltage across external circuit through picoscope 5204. Picoscope was found suitable instrument to measure minute voltage to its perfection along with other features like output power density harmonic distortion band width and etc.

The results described in the research article are an extension and improvement of our previously reported work [8,23,29], in which we have synthesized 100 nm ZnO nanowires and studied its output voltage using gold sputtered electrode. To improve our results, 50 nm ZnO nanowires were grown to achieve high voltage values by blocking the reverse leakage current through the nanowires. All of piezoelectric potential generated by minute external force of ~50 nN must be obtained at output stages and by reducing the diameter of nanowires we have reduced the possibility of the current to pass through the channels available in nanowires. As reduction of diameter of nanowires have minimized the conducting channels in nanowires which are multiples G=e2/2h [32]. We have achieved high voltage as quantized energy channels have been reduced which caused a considerable increment of 1.063 volts.

Fig. 4(a) shows periodic output voltage peaks of 1.071 V with 2.5 nm thick gold electrode, we have used specific thickness in our earlier reported results to ensure the production of piezoelectric potential and our earlier work has clearly indicated that 7.5 nm thick electrode has produced maximum piezoelectric potential so we have used 7.5 nm thickness without analyzing any intermediate thickness in between 2.5 nm and 7.5 nm. We have also obtained output power density of maximum generated voltage as it has the significant value 397 mW/cm2. Periodic voltage peaks in voltage in Fig. 4(a) has indicated formation of schottky contact between the tip of ZnO nanowire and Pt top electrode. Schottky contact at one regulates the flow of current through external circuit while Ohmic contacts at both ends cannot generate power [20].

Earlier [29], we have reported voltage generation via ZnO nano-wires having diameter range ~350 nm; piezoelectric potential produced by them was 1.654 volts but in this study we have reduced diameter upto ~50 nm and considerably enhanced piezoelectric potential was achieved. One schottky contact is essential for the piezoelectric potential; Au and Pt both have been used for the same purpose [20,29,30].Infirst stage, where 2.5 nm thick top layer is grown has given the evidence

of schottky contact between nanowires and top electrode like mentioned in our earlier results [8]. Au sputtered electrode for schottky contact has been reported earlier [31] and ITO coated bottom electrode has also been used in the study which acted as bottom electrode however the previous study was focused on RF sputter coated seed layer and its effects on piezoelectric potential but top and bottom electrode structure was quite close the experimental approach that we have discussed in our results. The evidence of schottky contact has also been reported for AFM contact mode, where investigation of piezoelectric voltage has been carried out, AFM tip has produced minute external pressure in contact mode that we have produced by an external roller [32], as contact mode AFM has its own limitations and AFM tip has to be changed after every now and then that makes it more expensive and non viable approach.

In this study we have transformed external mechanical energy in electric energy that can be used to power numerous nano electrical devices without batteries. Minute external force of ~50 nN is applied by extremely light plastic roller to produce piezoelectric potential within nanowires. Applied mechanical force has produced strain 0.15% which is quite less than maximum tensile strain 6% which is theoretically predicted value for ZnO nanowire after which the wire gets fractured [33].

We have used minute external force to develop piezoelectric potential inside nanowires, in the absence of external force the charge centre of cations and anions coincide with each other but as external force is applied the charge centre disturbs and electric dipole is created which results piezoelectric potential, piezopotential is conserved in strained nanowires. We opted VING (vertical nanowire integrated nanogenerator) for mechanical energy harvesting, due to its low cost synthesis while LING (lateral integrated nanowire nanogenerator) involves expansive steps like Au or Pt layer needs to be sputtered on the substrates to act as electrodes then a mask is involved for patterned growth of ZnO nanowires with in sputtered electrodes and for mask patterning lithographical lift-off processes are also involved likewise NEG (nanocomposite electric nanogenerator) involves filling requires filling solutions with in nanowire matrix which makes it more expensive and complicated to opt [34,35].

Schottky contact at one end of the nanowire is essential for piezo potential, which is created at the top of nanowires moreover 2.5 nm thick Au and Pt electrode has been sputtered and corresponding output voltage has been analyzed Au having low work function than Pt has created less piezoelectric potential similarly 5 nm and 7.5 nm thick Au and Pt electrodes thick electrodes have also been tested in our previous work [8,26]. Our previous results confer that maximum output voltage has been achieved with 7.5 nm thick sputtered electrode. In this study, we have only used 2.5 nm thick Pt electrode just to ensure the formation of schottky contact in between nanowires and top electrode. We have enhanced output voltage by thinning of diameter upto ~50 nm which reduced the reverse leakage current through nanowires but piezoelectric potential without having metal contact is not possible as we have discussed earlier and in numerous reported results [36–38] have verified that one end metal contact is essential. Schottky contact at one end device prevents the electrons to flow through nanowires ZnO nanowire work as charge pump and electrons flow the through external circuit. As the external force is applied, negative piezoelectric potential rises up at the top of nanowires relative to the bottom and so the Fermi level, consequently electron flow from top to bottom through external circuit and tends to accumulate at bottom until the equili-brium is reached, when external force is removed piezoelectric potential in nanowire vanishes electrons move from bottom electrode to top electrode via external circuit and voltage peak in opposite direction is achieved. Periodic potential peaks exhibits the formation of schottky contact in between ZnO nanowires and top sputtered elec-trode. It's a manifestation of piezotronic effect i.e. coupling piezo-electric and semiconducting properties [30].

As mentioned above extremely light plastic roller is used to apply ~50 nN force on top electrode for the production of piezoelectric potential. Thinning of diameter enhances scattering phenomenon within nanowires which causes poor conductivity through nanowires. In our case, high piezoelectric potential was required and it is achieved by reducing reverse leakage current through nanowires. Maximum piezoelectric potential could be delivered at output stages only if the reverse current through nanowires is reduced. Electrons suffer huge deflection to pass through the nanowire in small diameter ranges; 50 nm ZnO nanowires have shown poor conductivity of reverse leakage current which can be seen in Fig. 4(a) exhibit periodic output voltage peaks with 2.5 nm thick Pt electrode while Fig. 4(b) representing output voltage peaks with 7.5 nm think Pt electrode and Fig. 4(c) showing high output power density of 397.1 mW/cm2 is achieved.

Conclusions

By squeezing the diameter of ZnO nanowires up to 50 nm, we have achieved high output voltage of 2.717 V with an output power density of 397.1 mW/cm2. Piezoelectric potential was generated by applying minute external pressure. Due to high work function (ϕ=6.1 eV) of Pt, it was used as top electrode. Low cost aqueous route has been adopted for the synthesis of ZnO nanowires, their morphology has been controlled by adjusting physical growth parameters and growth has been carried out in a catalyst free environment. ITO coated PET substrates have acted as conducting base electrode, central nanostruc-ture was grown in two steps, in first step hexagonal wurtzite seed layer was grown on PET substrates and in second step vertical growth of nanowires has been carried out in nutrient solution. Picoscope 5204 has been use to record output potentials of structure. XRD pattern revealed vertical growth of nanowires along c-axis and surface mor-phology was evidenced in SEM images.

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Figures

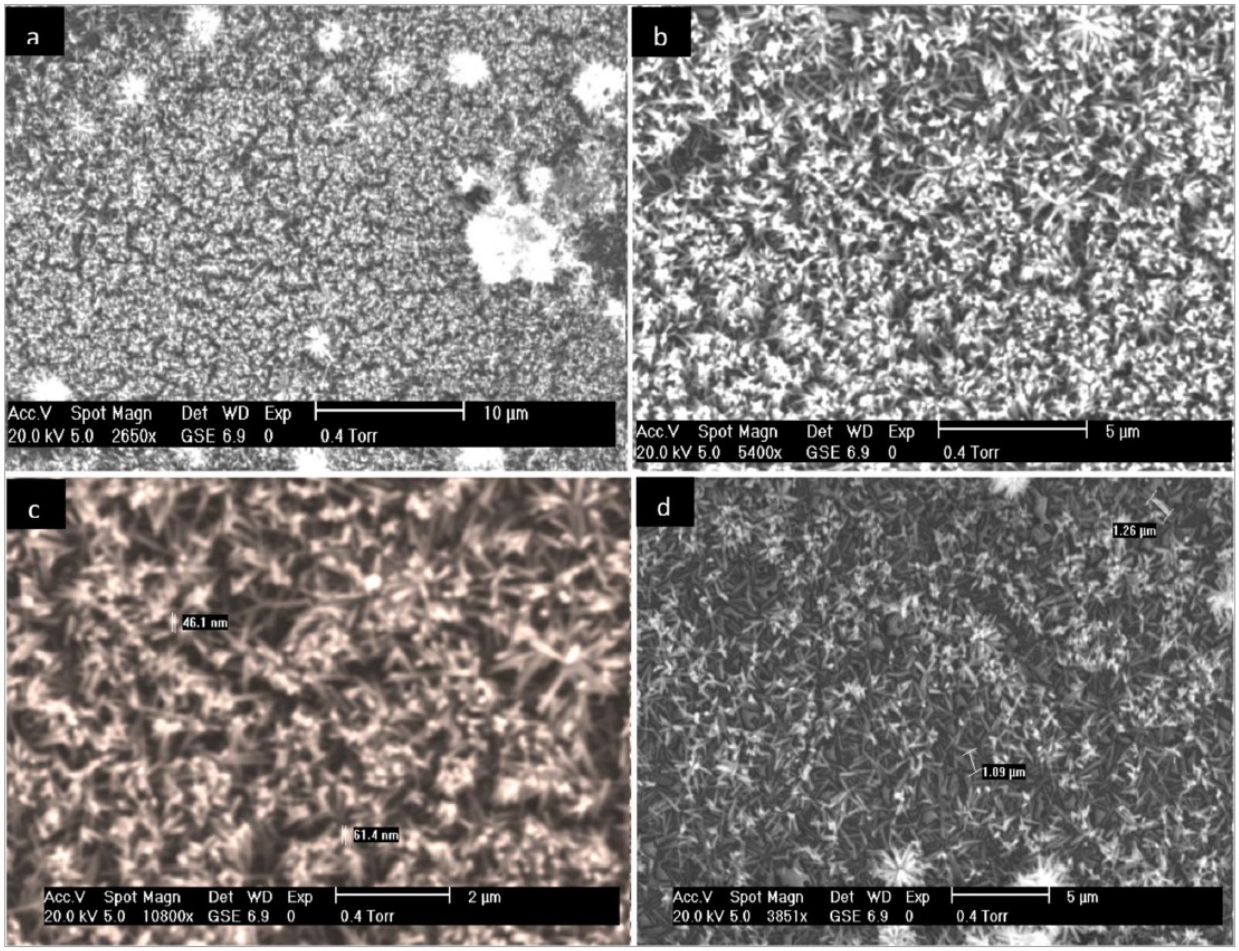


Fig. 1. (a, b, c) SEM image of 50 nm ZnO nanowires grown on PET substrate at low and high magnification respectively and (d) SEM image of 1 µm long ZnO nanowires.

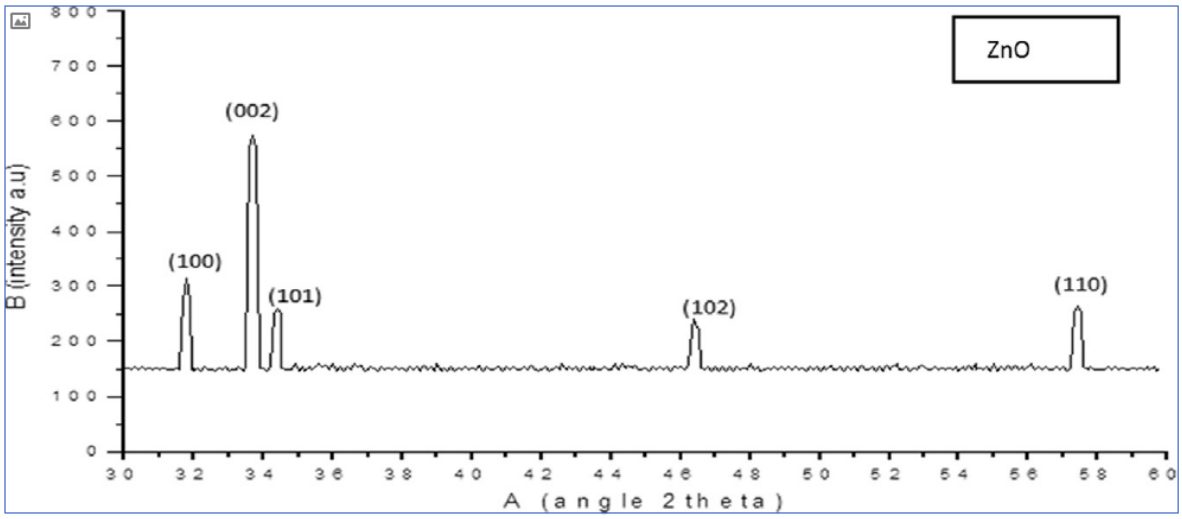


Fig. 2. XRD pattern of ZnO nanowires grown on PET substrate annealed at 60 °C for 30 min.

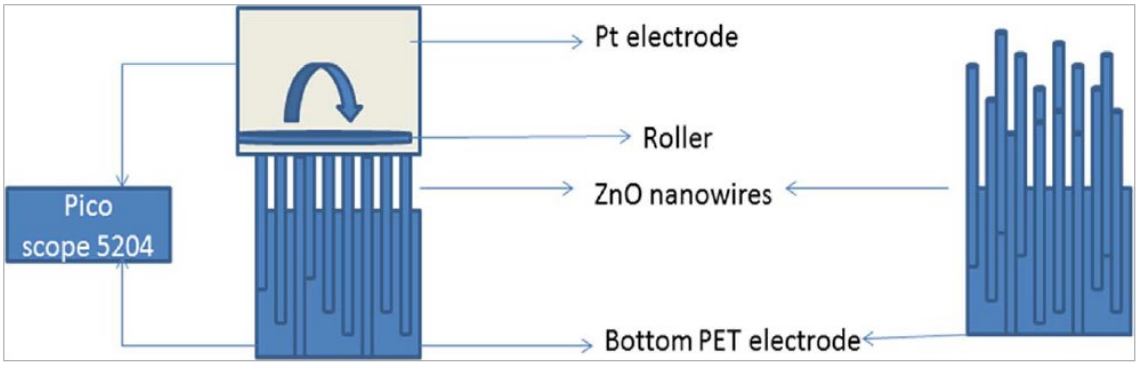
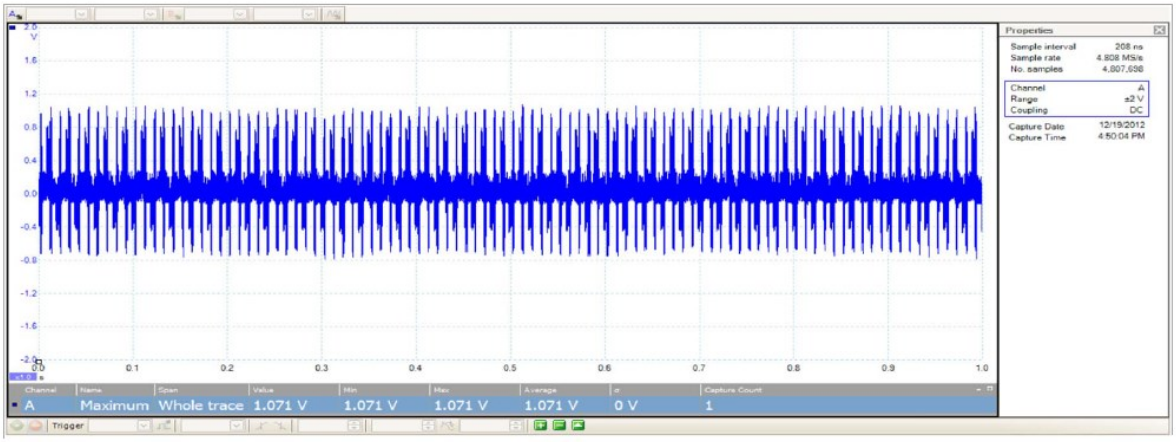
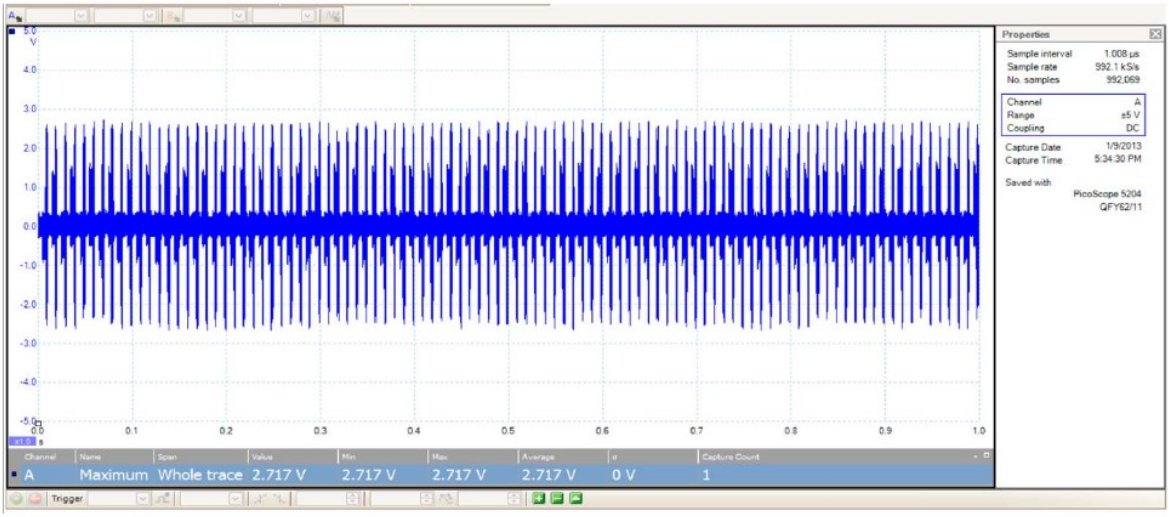


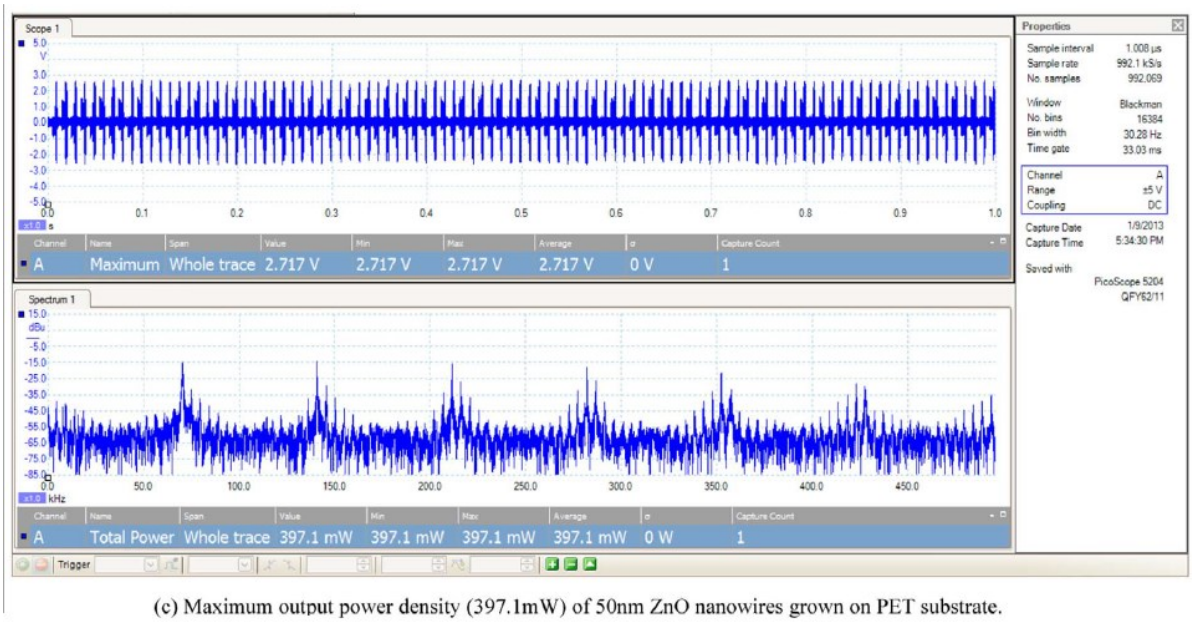
Fig. 3. Schematic diagram of energy harvester.



(a) Output voltage using 2.5nm thick Pt sputtered electrode.



(b) Maximum output voltage (2.717V) using 7.5nm thick Pt sputtered electrode.



(c) Maximum output power density (397.1mW) of 50nm ZnO nanowires grown on PET substrate.

Fig. 4. (a) Output voltage using 2.5 nm thick Pt sputtered electrode. (b) Maximum output voltage (2.717 V) using 7.5 nm thick Pt sputtered electrode. (c) Maximum output power density (397.1 mW) of 50 nm ZnO nanowires grown on PET substrate.