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PAPER

Adsorption effect of oxygen on ZnO Nanowires (100 nm) leading towards pronounced edge effects and voltage enhancement

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Abstract

Here, we report high output piezoelectric voltage generation from oxidized ZnO nanowires (100 nm). Periodic high output voltage peaks were observed during series of oxygen exposure experiments. Gradual rise in piezoelectric potential from oxidized ZnO nanowires is being evidenced for the very first time. Sharp voltage peaks 464 mV, 803 mV, 1.354 V, 1.795 V and 2.44 V are observed for an exposure of oxygen for 1 h, 2 h, 3 h, 4 h and 5 h respectively in a sealed chamber at 50 ppm. It has been observed maximum output value has been saturated after 5 h of O exposure. Enhanced piezoelectric potential appearing at output stages is due to the adsorption of oxygen molecules on long ZnO nanowires, giving rise to 'Edge Effects' and consequently reducing reverse leakage current through nanowires and enhancing output voltage. SEM images revealed the surface morphology ZnO nanowires, diameter range was found around 100 nm. XRD pattern verified vertical growth orientation of ZnO nanowires on ITO (indium Tin oxide) coated PET (poly ethylene terephthalate) substrates. Minute external force ~50 nN is used to produce piezoelectric potential within nanowires.

1. Introduction

In the recent era of nanotechnology, ZnO is becoming the most promising material due to striking properties like direct wide band gap (3.37 eV), high exciton binding energy of (60 MeV) and most importantly combined piezoelectric and semiconducting property known as Nanopiezotronics. Nanopiezotronics is one of the promising research phenomenon emerged in nanotechnology in last decade or so. Nanopiezotronics, covering wide range applications including nanogenerators, nanoscale field effect transistors, bio sensors, diodes, mechanical energy harvesters, tiny transducers and self powdered devices. By coupling piezoelectric and semiconducting properties, various external forces can be used to generate piezoelectric potentials, like bending of muscles, minute rolling forces, wind energies, small vibrations and etc [1–5].

Versatility of ZnO structures in nanotechnology is being exhibited by various morphologies like nanowires, nanobelts, nano helix, nano belts, nanosprings and nanotubes, all these nanoscale structures grabbing the attentions of the researchers, due to high elasticity and showing endurance to fatigue, which really enhances the lifetime of self powered nano devices and the other impressive feature is its low cost growth techniques having control on morphologies and density, by using a variety of substrates make the researcher's favorite material [6–9]. Scavenging mechanical energy into electrical energy by using ZnO based nanogenerators [10–18] is one of the salient features of ZnO nanostructures, due to its numerous applications in electronic industries, various structures like LING (lateral integrated nanowire generator) [14], VING (vertically integrated nanowire generator) [12] and NEG (Nanocomposite electric nanogenerator) have been fabricated. VING structure combines both piezoelectric and semiconducting properties. In VING, when nanowires are subjected under uniaxial strain, the charge distribution symmetry is disturbed and resulting piezoelectric potential gradient along the length of the nanowire. Large array of vertically aligned ZnO nanowires under the strain give rise to macroscopic piezoelectric potential behavior. Under uniaxial strain upper schottky contact act as negative charge source and bottom ohmic contact as positive charge source and current starts flow through an external circuit. Essential schottky contact stops the flow of electron from the metal semiconductor interface, leading the accumulation of electrons to the bottom electrode unless the potential is fully depleted and new equilibrium stage is reached and external strain is removed, the piezoelectric potential inside nanowires disappears by neutralizing all the accumulated electrons at the bottom electrode through external circuit move towards upper electrode and pulse in opposite direction is appeared at output stages [19, 20].

The base of nanogenerator lies in the production of piezoelectric potential. In an unstrained ZnO nanowires, charge distribution is balanced i.e. cations and anions are coincided but when an external mechanical stress is applied charge distribution disturbs and results in electric dipole formation, electric dipole formation last only as long as an external strain is there, potential created by these dipoles on either side of the structure is piezopotential or piezoelectric potential. ZnO wurtazite structure posse's intrinsic property of lack of symmetry which is crucial for mechanical to electrical energy conversion [21, 22].

Our earlier reported values using VING structure with Au sputtered electrode 1.354 V. In this study, we have achieved high output voltage of 2.44 V by using oxidized ZnO nanowires, we have thoroughly investigated oxidized ZnO nanowires in 1 h, 2 h, 3 h, 4 h and 5 h exposure of oxygen at 50 ppm in the locally made chamber. Our results are significantly improved by using oxidized ZnO nanowires.

2. Materials and methods

All reagents are of analytical grade, without any further purification. To ensure the clean and smooth surface of the PET substrates, they are ultrasonically cleaned by deionised water and IPA (Isopropyl alcohol) respectively and dried at room temperature for 30 min.

Synthesis of ZnO wires have been carried out in two steps. In first step, seed layer is grown on Ultrasonically cleaned PET substrate and annealed for 30 min at 60 °C then in second step annealed PET substrates are immersed upside down in nutrient solution. Vertical growth of ZnO nanowires is found to be closely dependent on growth of seed layer. The precursor solution (Zinc acetate dehydrate $[Zn\,(CH3COO)_2{\cdot}2H_2O]$) of 0.01M is used for the growth of seed layer on PET substrate . Droplets of precursor solution are used to coat the substrate at approximately 50 °C. Coating step is repeated until the growth of thick white seed layer. ITO coated PET substrates are annealed at 60 °C for 30 min. Seed layer coated substrate is immersed upside down for 2 h and 15 min at 90 °C in equimolar solution (500 ml) of zinc nitrate Hexahydrate $[Zn(NO_3)_2\,{\cdot}6H_2O]$ hexamethylenetetramine $(C_6H_{12}N_4)$. Finally, sample is dried at room temperature for 30 min. The aspect ratio of ZnO nanowires is strictly dependent on growth time in nutrient solution and Density of the nanowires is controlled by adjusting the concentration of nutrient solution.

Emscope SC 500 is used to sputter Au electrode on top ZnO nanowires to produce schottky contact. 2 kV is the operating voltage to initiate irradiation process in the presence Ar at an internal pressure of 0.1 torr. An external force approximately ~50 nN is applied on top of nanowires by light plastic roller. Applied external force is well below to the Elastic limit of ZnO nanowires. Theoretically 6% maximum tensile strain is the value after Which wire can get fractured [19]. Picoscope 5204 is used to obtain piezoelectric voltage.

3. Results and discussions

Figures 1(a)–(d) are at low and high magnifications respectively, indicating pure hexagonal wurtazite structure. Dense structure of nanowires is being controlled by the concentration of nutrient solution. Narrow opening in between nanowires is necessary for bending during the application of external force for piezoelectric potential.

Figure 2 shows VING structure, comprising of ITO coated PET substrate as bottom electrode, Gold sputtered electrode as top electrode and ZnO nanowires as intermediate vertical Structure. Figure 3 revealing the XRD pattern of vertically grown ZnO nanowires on PET substrate. Sharp XRD have shown crystalline structures and all peaks at particular angles are closely in agreement with previously reported values, [23, 24]. Most of the nanowires have got the preferred growth orientation along *c*-axis. Results depicted the majority of the ZnO nanowires have grown vertically upward from substrate, however few nanowires had other orientation but not of much significance because numerous vertically grown nanowires were contributing in piezoelectric voltage generation. Diffracted peaks from ZnO nanowires at an angle 33.456, 35.212, 47.423 and 56.65 corresponding to crystal planes (002), (101), (102) and (110) are observed. All observed values are compared with standard file

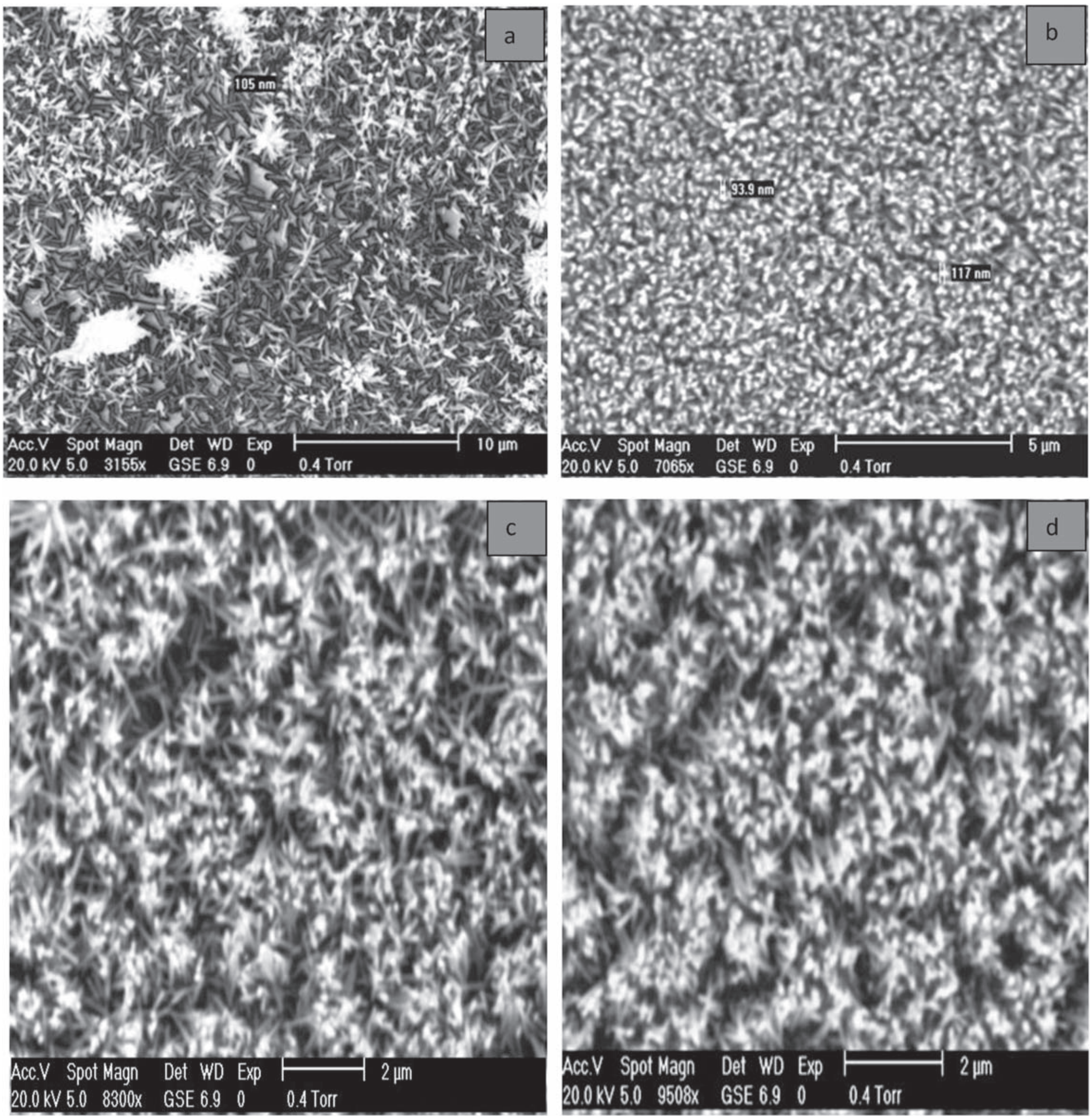

Figure 1. (a)–(d) SEM images of ZnO (100 nm) nanowires grown on ITO coated PET substrates at 3100×, 7065×, 8300×, 9508 magnification respectively.

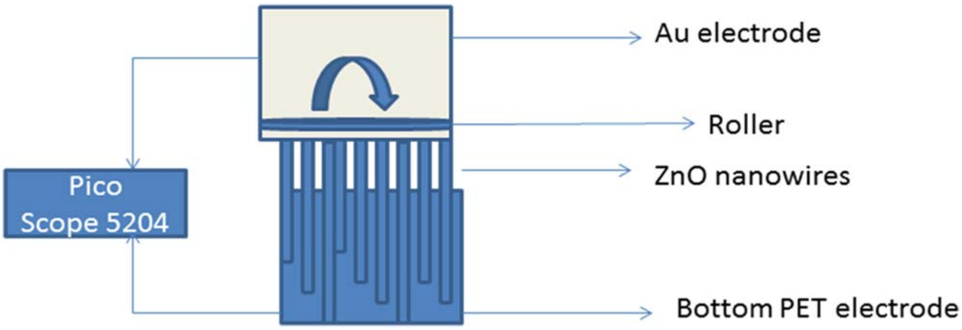

Figure 2. Schematic diagram of ZnO nanowires based nanogenerator.

(JCPDS 36-1451). It is clear from diffracted pattern that preferred growth orientation of ZnO nanowires are along the *c*-axis. The prominent peak intensity along crystal plane (002) has verified the argument.

Figure 4(a) shows the voltage graph obtained from the VING, periodic voltage peaks indicating the production of schottky contact in between ZnO nanowires and gold sputtered top electrode. The schottky contact at least on one end of VING structure is essential [10]. Electron affinity of ZnO nanowires is around

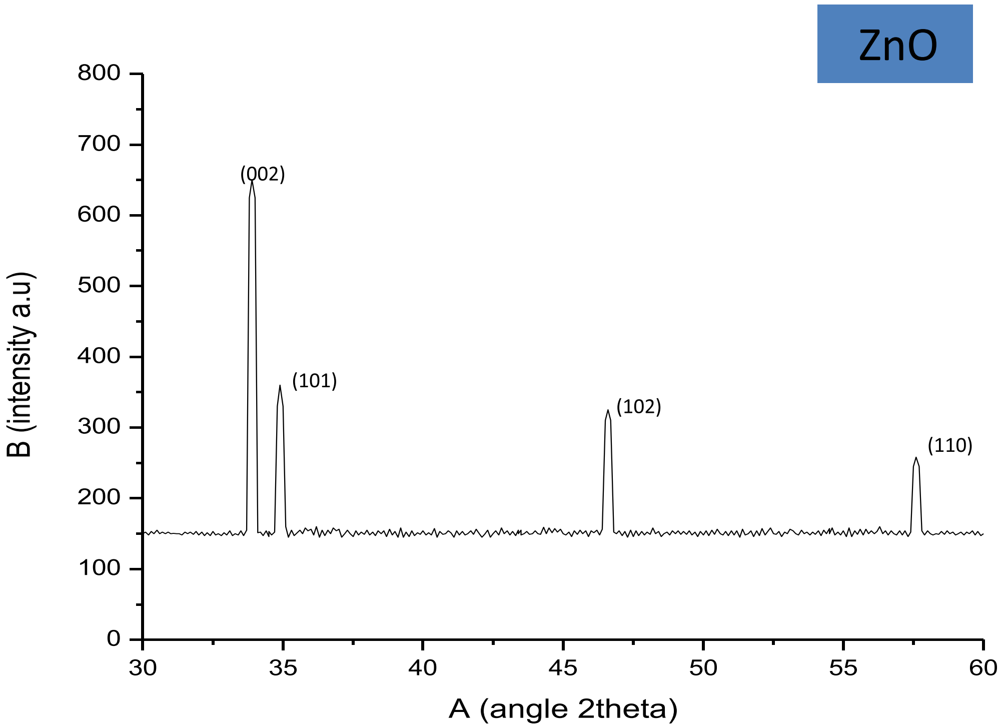

Figure 3. XRD pattern of vertically grown ZnO nanowires on ITO Coated PET substrates.

4.5 eV and work function of Au is 5.1 eV, so creating an interface which stops the flow of electron through the nanowires. The gradual rise in the piezoelectric potential as evidenced from figures 4(b)–(f) is after 1, 2, 3, 4 and 5 h exposure of oxygen in gas chamber at 50 ppm. The rise in output voltage is due adsorption of oxygen molecules on the long ZnO nanowires. ZnO NWs have also an intrinsic property of oxygen vacancies on its surface called 'surface defects', Oxygen molecules adsorbed on surface defects has given rise to the 'Edge Effect' phenomenon, due to which the conductivity through the nanowires is reduced. As already very few conducting channels are available in the NW for conducting purposes [12]. To reduce the conductivity through the nanowires, the reverse leakage current through the nanowires needs to be reduced so that high piezoelectric potential can be obtained at the external output stages of the nanogenerator. Oxygen molecules adsorbing on the surface defects of ZnO nanowires attain free electrons to form the ions $O_2 + e^- \rightarrow O_2^-$ [18, 25] due to which free electrons within nanowires are reduced and hence reduction of the reverse leakage current through the nanowires. ZnO nanowires exhibiting large aspect ratio (length to diameter ratio) provide more oxygen vacancies on the surface [26] which will cause more O_2^- ion formation leading towards more reduction in reverse leakage current and consequently enhanced piezoelectric potential is appeared on picoscope voltage spectrum.

Gradual rise in piezoelectric potential in various voltage spectrum for different oxidation exposure intervals is due to the accumulation of more and more number of oxygen molecules adsorbing on ZnO nanowires surfaces and squeezing the conducting channels $G = e^2/2h$ [27] available in nanowires. Minimizing the reverse leakage current through diameter thinning has already been reported in our earlier studies [12]. In this study we have reported significant voltage rise of around 2 volts with maximum voltage of 2.24 volts with maximum output power density of 321.2 mW cm^{-2}, high output power density exhibits its usage in self sustainable nanoscale devices. As shown in figure 4(g), it has also been observed that output voltage is saturated after 5 h of oxygen exposure. This verifies the occupation of all oxygen vacancies available on ZnO nanowires. Earlier [10], our maximum reported values with 100 nm ZnO nanowires is around 1.354 V and now with oxidized ZnO wires voltage is being elevated up to 2.24 V, so an overall rise of 65% in output voltage is achieved by using 100 nm ZnO nanowires under ambient conditions. Oxidized ZnO nanostructure have produced far superior results as compared to several previously reported values like maximum 1.26 V is achieved during a continuous fast stretching and fast releasing nanogenerator grown on Au substrate [28]. Flexible nanogenerator attached on finger has yielded a maximum voltage of 100 mV during bending and stretching [14]. similarly, ZnO nanowires grown on Kapton film, during fast stretching and fast bending has produced an output voltage of 20–50 mV [29]. ZnO nanogenerator attached at back of hamster, was used to have piezoelectric potential during its running and stretching has yielded a maximum voltage of 70 mV [30]. ZnO based woven nanogenerator fabricated on paper sheet has produced an open

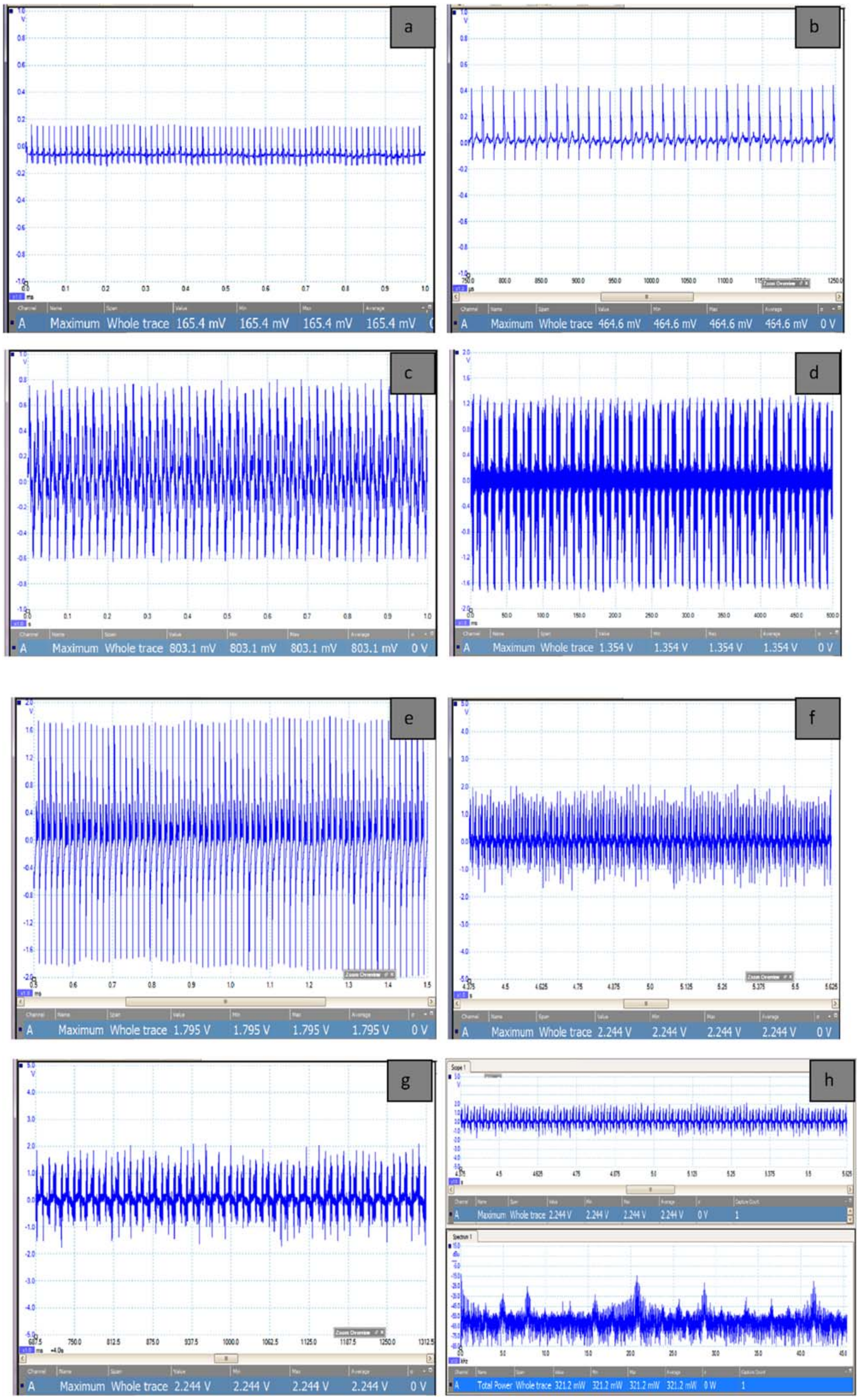

Figure 4. (a) Output voltage of 165 mV with Au sputtered electrode, (b)–(g) Maximum Output voltage of after 1 h, 2 h, 3 h, 4 h, 5 h, 6 h of oxygen exposure, (h) maximum output power density 321.2 mW cm^{-2} after 5 h of oxygen exposure.

circuit voltage 1.5 V and perturbed with air flow produce a voltage of 1.2 mV [31]. Several other complex and expansive routes, like lateral integrated nanowire generator, involving lithographic technique for masking nanowire and electrode patterns for thousands of horizontally grown nanowires has produced a maximum voltage of 1.2 V [32]. So, our obtained voltage values through oxidized ZnO nanowires via low cost and hassle free technique are quite compatible with above mentioned values.

4. Conclusion

We have successfully grown 100 nm ZnO nanowires on ITO coated PET substrates by using low cost hydrothermal route. We have thoroughly studied the behavior of ZnO nanowires for 1 h, 2 h, 3 h 4 h, 5 h of oxygen exposure at 50 ppm and observed a significant rise in output piezoelectric potential from 460 mV to 2.24 V. Further oxygen exposure has not produced any rise in the piezoelectric potential showing that all intrinsic surface defects present on ZnO nanowires are being captured by oxygen molecules and no further vacancies were present to enhance the edge effect phenomenon which could enhance the voltage furthermore. Maximum output voltage of 2.24 V with high power density of 321.2 mW cm^{-2} is achieved. We purpose these high output voltage producing Oxidized ZnO nanowires for self powered Nanodevices.

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