Effects of grain size and temperature, on the output voltage generation of Energy harvester using ZnO nanowires (oxidized with O2).

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Abstract

Here, we report high output voltage generation via oxidized ZnO nanowires. A thorough study has been carried out to observe the behavior of ZnO nanowires under reduced grain size and high temperature conditions. Study has revealed that piezoelectric output voltage generated by ZnO based VING (vertically integrated nanowire generator) has been gradually increased, as the diameter of nanowires is decreased. Secondly, it has also been observed that maximum peak voltage has been further enhanced, if nanowires are oxidized at high temperature. ZnO nanowires ≈ 200 nm have produced maximum peak voltage 2.283 V at room temperature and if oxidized at 200o C then output voltage has been further raised to 2.638 V Having output power density 365.7 mW/cm2, similarly ≈ 100 nm ZnO nanowires have produced maximum voltage of 2.598 V At room temperature and at 200o C the value is elevated to 2.835 V and ≈ 50 nm ZnO nanowires have generated 3.38 V at room temperature and when oxidized at 200o C voltage has been raised to 3.465 V with power density of 511.3 mW/cm2. The values have been significantly improved by our earlier reported values.

1. Introduction

ZnO nanowires are considered most exciting structure in the world of nanotechnology due to their exceptional electrical and optical properties. The versatility of ZnO nanowires is evident from their numerous applications in optoelectronic industry [1,2] biomedical applications [3,4] piezoelectric applications [5-7] and also in gas sensing applications [8-10]. ZnO nanowires have shown excellent results to be considered as the ideal candidate for self powered nano-scale devices [11-14].

ZnO nanowires based nanogenerators has always been our area of interest, especially vertically integrated nanowire generators (VING). We have not only used VING to produce high piezoelectric voltages but also exposed the surface of ZnO nanowires surface to various oxidizing gases to generate further high piezoelectric voltage [15-17]. To understand the mechanism of VING, the role of schottky barrier is very crucial. When an external force is applied on top electrode of VING, the charge symmetry of crystal is disturbed and dipoles within structure are created. The dipole formation inside nanowires structure is the basis of piezoelectric potential. Piezoelectric potential created can only be delivered to the output stage, if one end of the VING is a schottky (metal-semiconductor) contact. Schottky contact ensures the flow of electrons in one direction only i.e. from top to bottom electrode. Schottky contact worked as barrier for the electrons, electrons having sufficient only energy can surpass the barrier. Electron affinity of ZnO (Ea = 4.5 eV) which is less than the work function of Au (φ = 5.1 - 5.4 eV), that means reverse leakage current through the nanowires have been minimized by using an Au as top electrode [18, 19].

ZnO has been used for gas sensing applications in past [20-23]. Seiyama et al has observed the changing behavior of metal oxide in the presence of various gases. The electrical properties were being closely monitored in gaseous ambience and observed change in conductivity of metal oxide with the change of gases composition present in the atmosphere. It has been also observed by the researchers that

sensitivity and response of various metal oxides including ZnO can be further improved by suitable dopants [24,25], reducing grain size [26] and operating temp.[27, 28] at which a particular gas is being sensed. The salient feature of the recent study is that in contrast to conventional orthodox behavior of sensing, we have used oxidized ZnO nanowires for energy harvesting purposes and generated high piezoelectric voltage. Not only this but we have improved our results by squeezing the diameter of the ZnO nanowires and oxidized them at high temperature. Both modifications have yielded considerable rise in output voltage. REDOX (Reduction-Oxidation) mechanism occurring on ZnO nanowires surface has been used to obtain the desired results.

2. Materials And Methods

All reagents of analytical grade (98 %) are purchased from Sigma Aldrich and they have been used without further purification. ITO (indium tin oxide) coated PET (poly ethylene terephthalate) are cleaned through ultrasonically bath by using IPA and acetone for 10 min. each respectively then dried in the air.

Zinc acetate dihydrate [Zn $(CH_3COO)_2 \cdot 2H_2O$] has been used to grow seed layer on ITO coated PET substrate. 10 mM solution of zinc acetate dihydrate has been used to grow the seed layer on the substrate by drop by drop method and the procedure was repeated to three times. Substrates were annealed at 50^o C for 20 min. Equimolar (1:1) solution of zinc nitrate hexahydrate [Zn $(NO_3)_2.6H_2O$] and hexamethylenetetramine (HMTA) [$C_6H_{12}N_4$] has been prepared to place the PET substrate upside down. Equimolar nutrient solution was kept at 90^o C.

It was observed through experiments that density of the nanowires can be controlled by the adjusting concentration of nutrient solution. The density of nanowires is quite crucial in our case.

To generate piezoelectric potential from ZnO nanowires, there must be narrow opening in between the top ends of nanowires so that when an external force is being applied there must be some bending space for them. Similarly, the diameter of nanowires could be controlled by time duration of growth in nutrient solution. Both factors have been well explained in our earlier reports [5-7]. Owing the information from earlier results, we have grown ~ 200 nm, ~ 100 nm and ~ 50 nm ZnO nanowires on separate substrate (sample1, sample2, sample3). Each sample has been exposed to Oxygen in a sealed chamber at 100 ppm at 100^o C, 150 ^{o} C, 200 ^{o} C, and 250 ^{o} C. The idea behind the exposure of the samples at high temperature is to get more molecules adsorbed on ZnO surface. ZnO nanowires exhibit large aspect ratio of 10^3 so surface to volume ratio is very high. High surface to volume ratio enabled us modify ZnO nanowires surface to achieve the desired high output piezoelectric voltage.

VING is composed of ITO coated substrate (bottom electrode), central ZnO nanowires and Au sputtered top electrode. Minute external force ~100 nN is applied on top of VING to produce piezoelectric potential within nanowires. Piezoelectric potential is being detected by versatile picoscope 5204. Schematic diagram of VING has been shown in Fig.1

3. Results And Discussion

Philips XL 30 has been used to investigate the surface morphology of ZnO nanowires grown on PET substrates. It has been observed that majority of the nanowires are grown vertically upward from substrate in and results are well supported by XRD pattern. Fig. 3(a, b, c) clearly indicated that strongest peak along (002) at an angle 34.34^{o} was present in all three results. It confirmed that preferred growth orientation is along c-axis. XRD data represented peaks along (100), (002) and (110) planes at 31.63^{o}, 47.48^{o} and 56.65^{o} respectively but sharp peak along (002) plane was prominent. It has also been observed that there is narrow spacing in between nanowires, which was required and crucial for piezoelectric voltage generation.

Two sharp peaks at 529.5 eV and at 531 eV in the XPS spectrum of O 1s is shown in

Fig. 4(a). The peak appeared at 529.5 eV is related to O^{2-} ion in ZnO structure [29] and peak located at 531 eV is related to hydroxyl (OH) group adsorbed on ZnO nanowire surface [30]. Similarly, XPS spectra of Zn 2p in Fig.4 (b) clearly indicated two peaks of Zn $2p_{3/2}$ at 1021 eV and Zn $2p_{1/2}$ at 1041 eV are accordance with standard values of Zn 2p states [31]. Difference in peaks of 20 eV is in agreement with reported values of Zn 2p states for ZnO nanowires, however slight shift is in the peaks is due to surface morphology of ZnO nanowires [32].

Owing the facts from our earlier reported [15-17] values of oxidized ZnO nanowires at room temperature. Maximum satureated output voltage from ZnO nanowires have been generated. 2.598 V has been achieved which is exactly in agreemenet with the pevious results. To ensure that the generated output votage peaks are a true signal of ZnO nanowires. rigorous testing has been carried out which is depected in histogram in fig.4 (b). positive value peaks and negative value peaks are exaclty in the same voltage reang as shown in Picoscope graph fig.4 (a).

The mechanism of adsorption of oxygen is quite clear from eq.1. As oxygen has got high electronnagitivity of around 3.6 make it very easy to get adsorbed on ZnO nanowire surface by just accepting the electron. ZnO nanowites intrinsically *n-type* material has lots of free electrons available on its surface. At room temperature O_2 gets ionized quickly by adsorbing on surface site defects on ZnO nanowires. Intrisically, ZnO nanowires are *n-type* material and these unintetional defects act as shallow donors. Role of shallow donors at high tempertaure becomes more significant [33, 34]. The pheneomenon of adsorption of O_2 on ZnO nanowire surface and its implecations on the output voltage of nanogenerator has been well explained in our earlier study [15].

$$O_2 + e^- \rightarrow O_2^- \qquad (1)$$

It has been observed that with the increase of exposure time oxygen at room temperature the piezoelectric voltage generated by ZnO nanowires has been increased by 2.24 V. Rise in output voltage has been due to the adsorption O_2 molecules on ZnO naowires exhibiting large surface-to-volume ratio. Adsorbed O_2 molecules has captured free electrons and due to decrement of electrons, conduction through the nanowires is reduced. As the working pricipal of ZnO nanogenerator is based on piezolectric voltage generation. Current flowing through nanowires is a bad factor for nanogenerators. O_2 molecules adsorbed on ZnO nanowires surface have produced “Edge effects” due to which internal scattering within nanowires has also increased. Internal resistance has increased the internal resistace of the nanowires, which is highly desired for high output voltage through nanogenerators .The phenomenon is being evident in the output voltage spectra. O_2 molecules while adsorbing on nanowire surafces from a receptor layer on metal ZnO n it also helps other molecules to get adsorbed on surface. During the process of gaining the electrons from nanowire surface, an ionic layer is developed and O_2 molecules get ionized O_2^- . Formation of layer rises the potential barrier by increasing the space chrge width of the barrier [17]

	100^o C	150^o C	200^o C	250^o C
Output volatge generated by ZnO Nanowires (200nm) modified with O_2	2.283 V	2.598 V	2.638 V	1.795 V
Output volatge generated by ZnO Nanowires (100nm) modified with O_2	2.599 V	2.677 V	2.835	1.858 V
Output volatge generated by ZnO Nanowires (50nm) modified with O_2	3.386 V	3.425 V	3.465	2.244 V

Table1. output voltage values generated by ZnO nanowires at different temp.

ZnO nanowires have been oxidized at high temperature because at high temperature, it has got tendency of accepting more electrons as compared to room temperature [35].

It is quite evident from Fig.8 (a, b) that rise in temperature has caused the reduction in reverse leakage current. Reduction of reverse leakage current is due to the enhancement of depletion layer. Depletion width enhancement is bad factor for the current flow and it has caused hindrance for leakage current through the nanowires. Argument has been well justified by the output piezoelectric voltage spectra, voltage has been increased as the oxidation temperature has been raised. It can also be seen that trend is uniform for all three cases. Initially, voltage has shown upward trend and after 200^o C the voltage has been degraded. Voltage decrement above 200^o is due to initialization of desorption process. Desorption

of O_2 molecules from ZnO nanowire surface have caused two factors, one is reduced “Edge effects” and second reduction in depletion width within nanowires. During desorption process, captured electrons by O_2 has been released back to ZnO nanowires. Release of electrons again initiated the conduction process through the nanowires; consequently piezoelectric output voltage has been reduced. Leakage current through nanowires tend to diminish piezoelectric potential of nanowires. Piezoelectric potential developed during an external pressure must be delivered at output stages trough external load only, not through the nanowires. Desorption of O_2 molecules at elevated temperature has reduced the population of O_2 molecules on surface of ZnO nanowires, which depleted the edge effects. Edge effects have increased the internal resistance of nanowires during adsorption and helps piezoelectric potential to be preserved within nanowires. By the removal of O_2 from ZnO nanowires piezoelectric potential tend to deplete through nanowires and output voltage has been reduced.

Sensitivity phenomenon of various gases on ZnO surface has been reported by many researches around the globe. Some have used additives/dopants [35-36], some have reduced the grain size and some have used variation in temperatures but the novelty of recent finding is that it’s being used for the enhancement of piezoelectric potential. No impurity has been added to the structure because as by doing so internal dipole creation during the application of external force would have been affected and piezoelectric potential may have not produced. Working principle of ZnO based energy harvester is dependent on the generation of piezoelectric potential. In ZnO wurtzite structure O^{2-} and Zn^{2+} are arranged in layer by layer fashion one over the other in balanced condition but when balance is disturbed by an external agent (force) then cations and anions separate with each other hence the creation of dipole in the structure and potential due to this dipole moment is called as piezopotential [37].

Chemiresistive nature of metal oxides have effected the space charge width, during adsorption of strong oxidizing gases and it worked as barrier for electrons to travel through the nanowires. chemisresistance property has been used for gas sensing applications [38] but salient feature of the study the use of chemiresistive property of ZnO nanowires to produce high output voltage. ZnO nanowires based mecanical transducer has produced high piezoelectric voltages by using surface modificatied ZnO nanowires. Surface modification process neither require any catalyst nor high vacuum temperature conditions. As far as coventional sensing purpose is concerned, researcher has added dopants to stabbalize the REDOX mechanism [39,40], by doing so stability is achieveed only at room temperature and failed to keep the process under cotrol at slightly high temperature. Our recent results are quite competitive as we have achieved high piezoelectric voltage by oxidizing the ZnO structure at elavated temperature. Stucture has not shown any abnormal behavior at high temperatures. It has been achieved due to purity of single crystal structure. It has been observed that added impurity may yield required result in ceratin operating condition but it gets unpredictable, as the operating conditions are slightly changed. Stable and consistent output has always been the first priority of the nanogenerators for selfpowered nanodevices, which is being achieved.

The results are quite competitive not only for certain optimal temperature range but also otherwise. Wang [41-43] reported piezoelectric output voltages using nanogenerators like LING (lateral integrated nanowire generator) attached to finger joint has produced 1.2 V during finger bending, LING attached on running hamster has generated 70 mV, Woven nanogenerators in the fabric have generated 3 mV during fabric friction but recently reported values are quite high as compared to above mentioned values. High voltage values are quite encouraging not only at nano-scale level but also on micro and macro level as well. Obtained voltage values are double to voltage of AA batteries and AAA batteries used in commercial applications.

4. Conclusions

We have successfully grown ZnO nanowires on ITO coated PET substrates. VING structure has been employed to produce high output voltage generation using oxidized ZnO nanowires. The study has been focused from a diameter range ≈ 200 nm to ≈ 50 nm. By reducing the grain size of ZnO nanowires, net rise of 1.142 V has been achieved. Furthermore, oxidized ZnO nanowires have produced more prominent results and net increase of 1.82 V has been recorded. Raise of 0.347 V has been recorded In the case of ≈ 200 nm nanowires, Raise of 0.237 V has been recorded In the case of ≈ 100 nm nanowires, Raise of 0.85 V has been recorded In the case of ≈ 50 nm nanowires. So is the case, in power densities. ZnO nanowires has been oxidized in a sealed camber (100 ppm) at 250^{o} C but the optimal range for maximum output was around 200^{o} C. Afterwards, mainly due to the desorption process, voltage tends to drop. We have deduced from our experimental findings that considerable rise in output voltage has been produced by reducing the grain size of ZnO nanowires and by oxidizing them at 200^{o} C. We propose highly efficient and low cost VING for self-powered nanoscale devices.

Declarations

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Figures

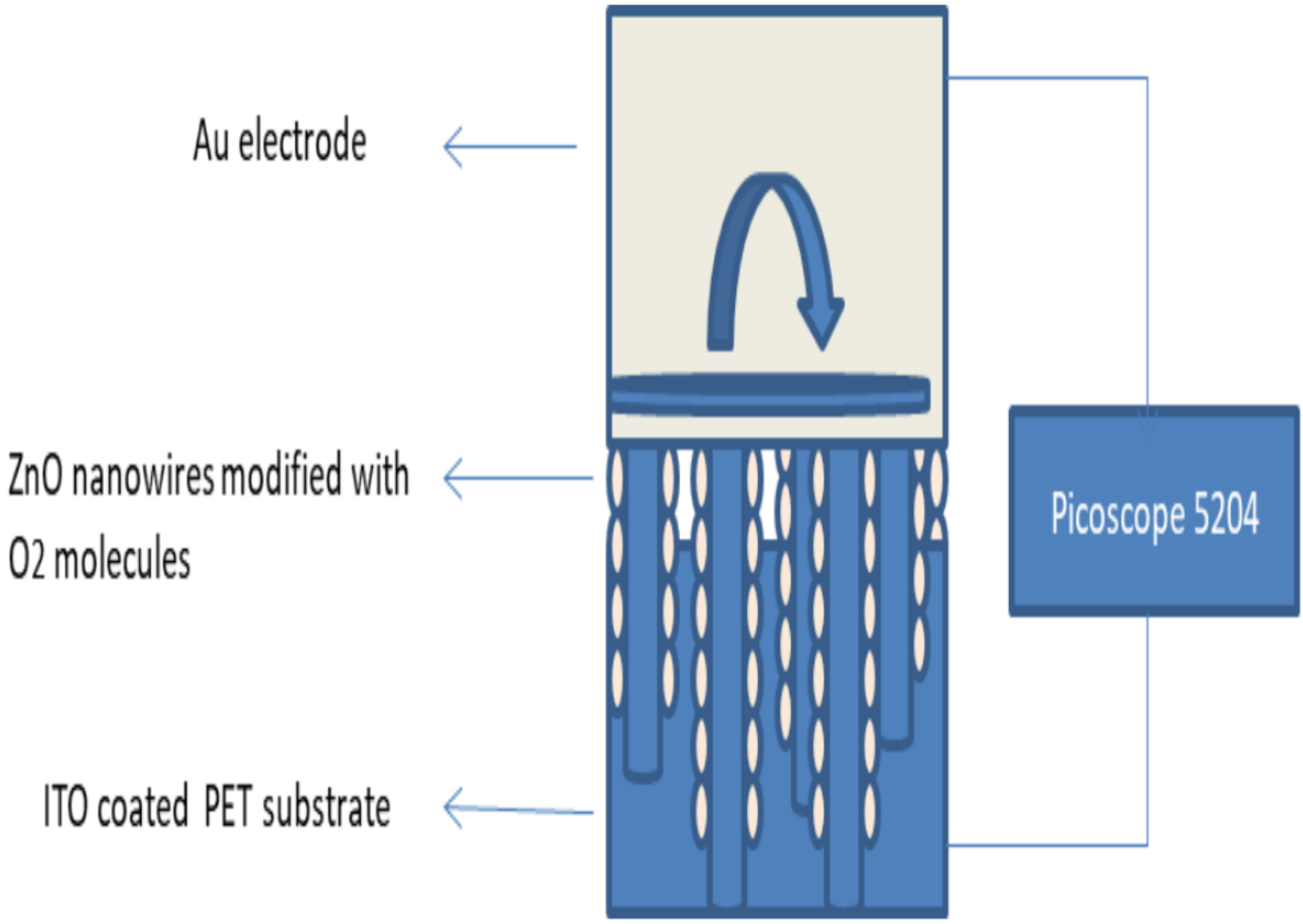

Figure 1

Schematic diagram of ZnO nanowires based nanogenerator.

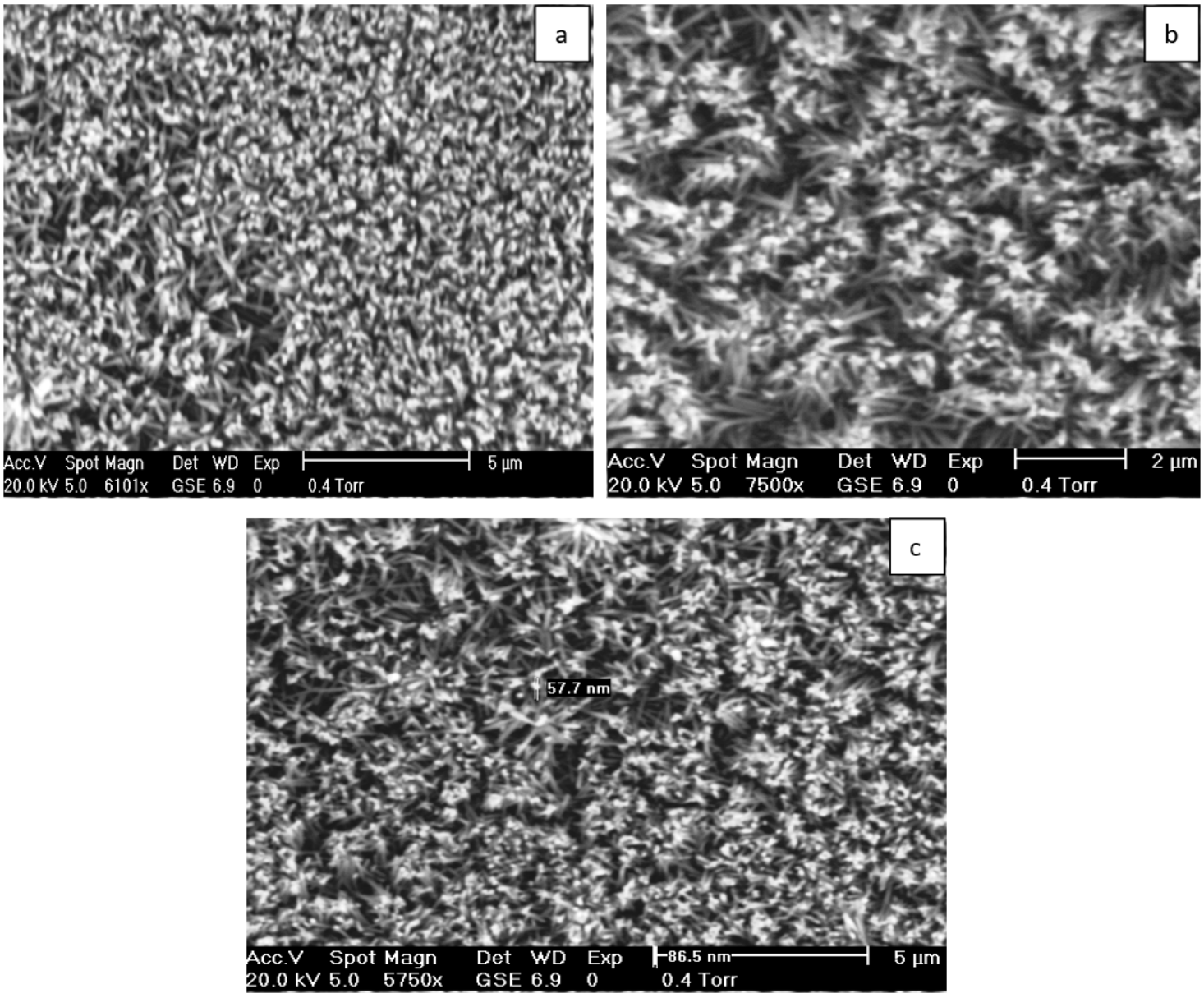

Figure 2

SEM images of ZnO nanowires grown on ITO coated PET substrates, (a) diameter ≈ 200 nm, (b) ≈ 100 nm, (c) ≈ 50 nm

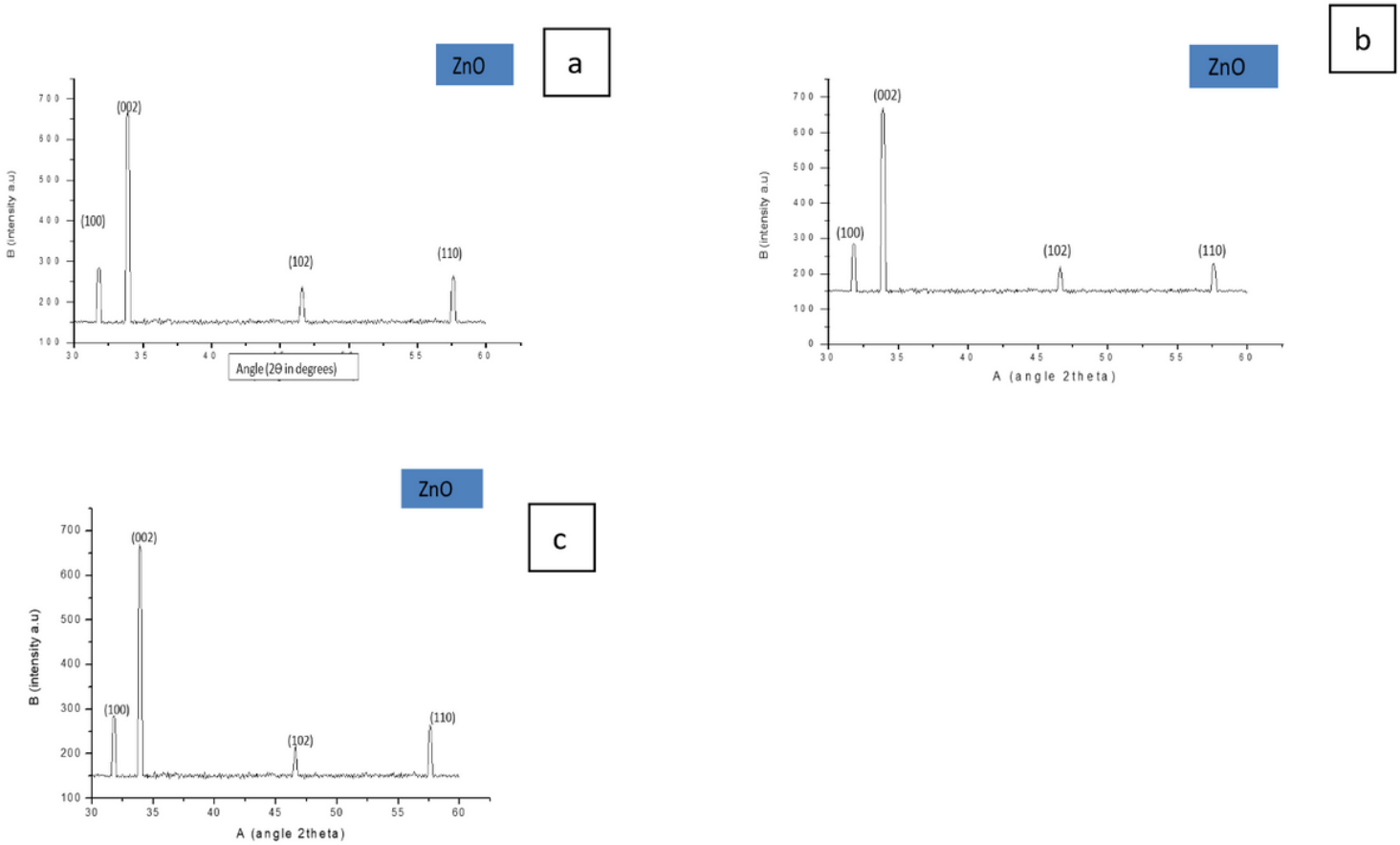

Figure 3

XRD pattern of vertically grown ZnO nanowires, (a) sample, (b) sample, (c) sample 3.

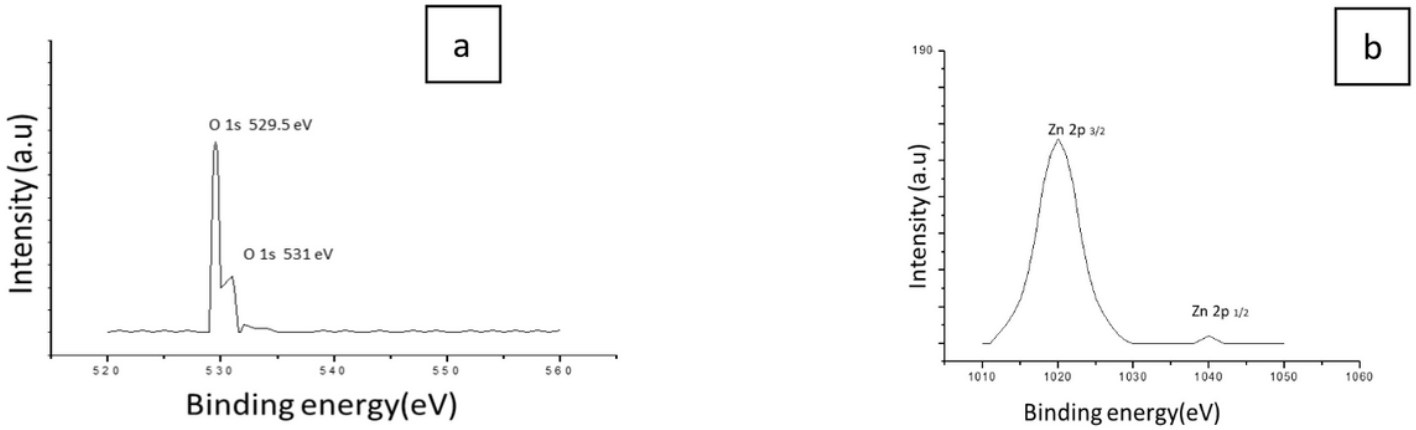

Figure 4

XPS spectra, (a) O 1s, (b) Zn 2p

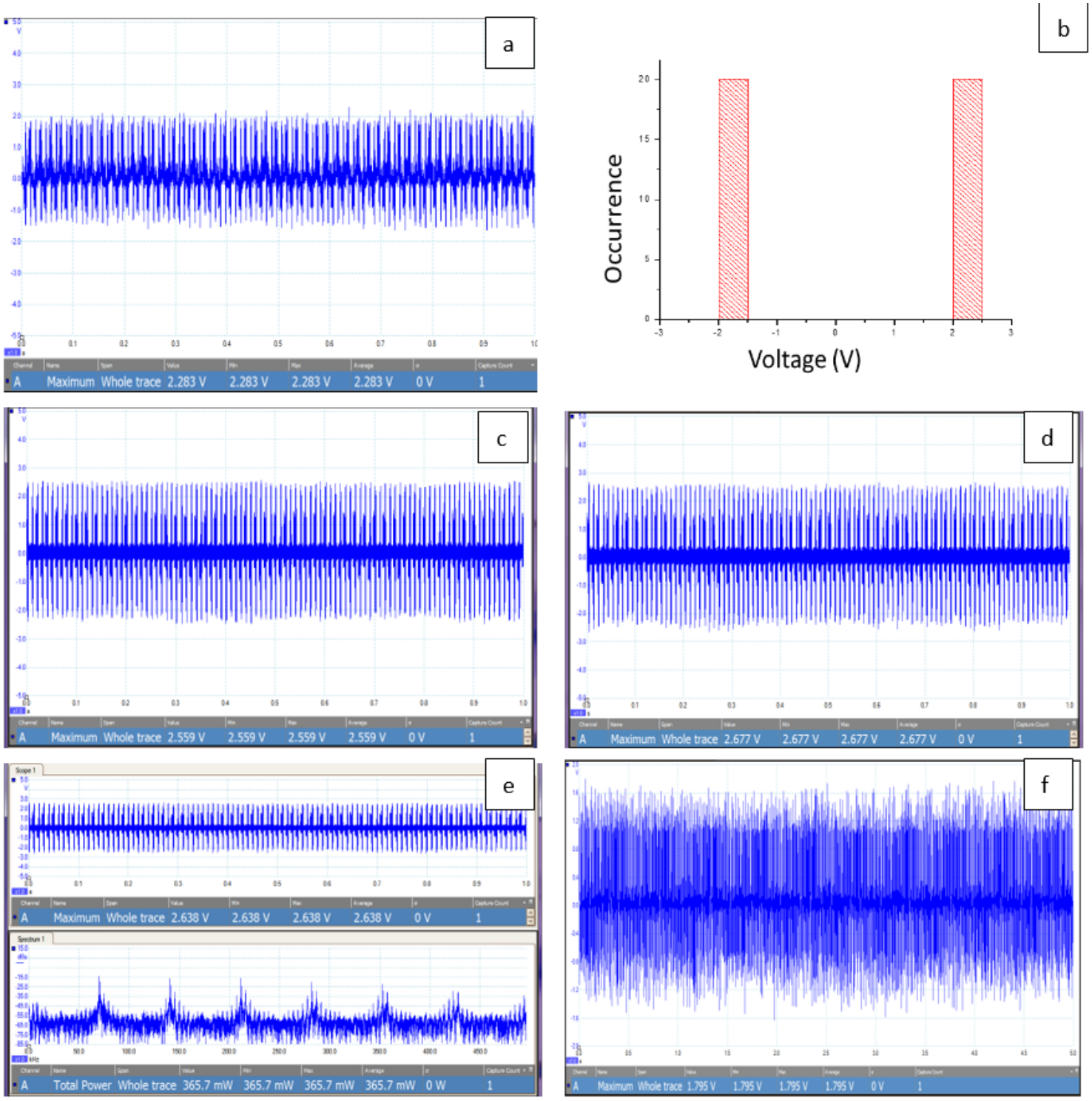

Figure 5

output voltage generated by ▯ 200 nm ZnO nanowires, (a) at 100o C, (c) at 150o C, (d) at 200o C, (e) at 250o C, (f) power density 365.7 mW/cm2, (b) voltage occurrence histogram.

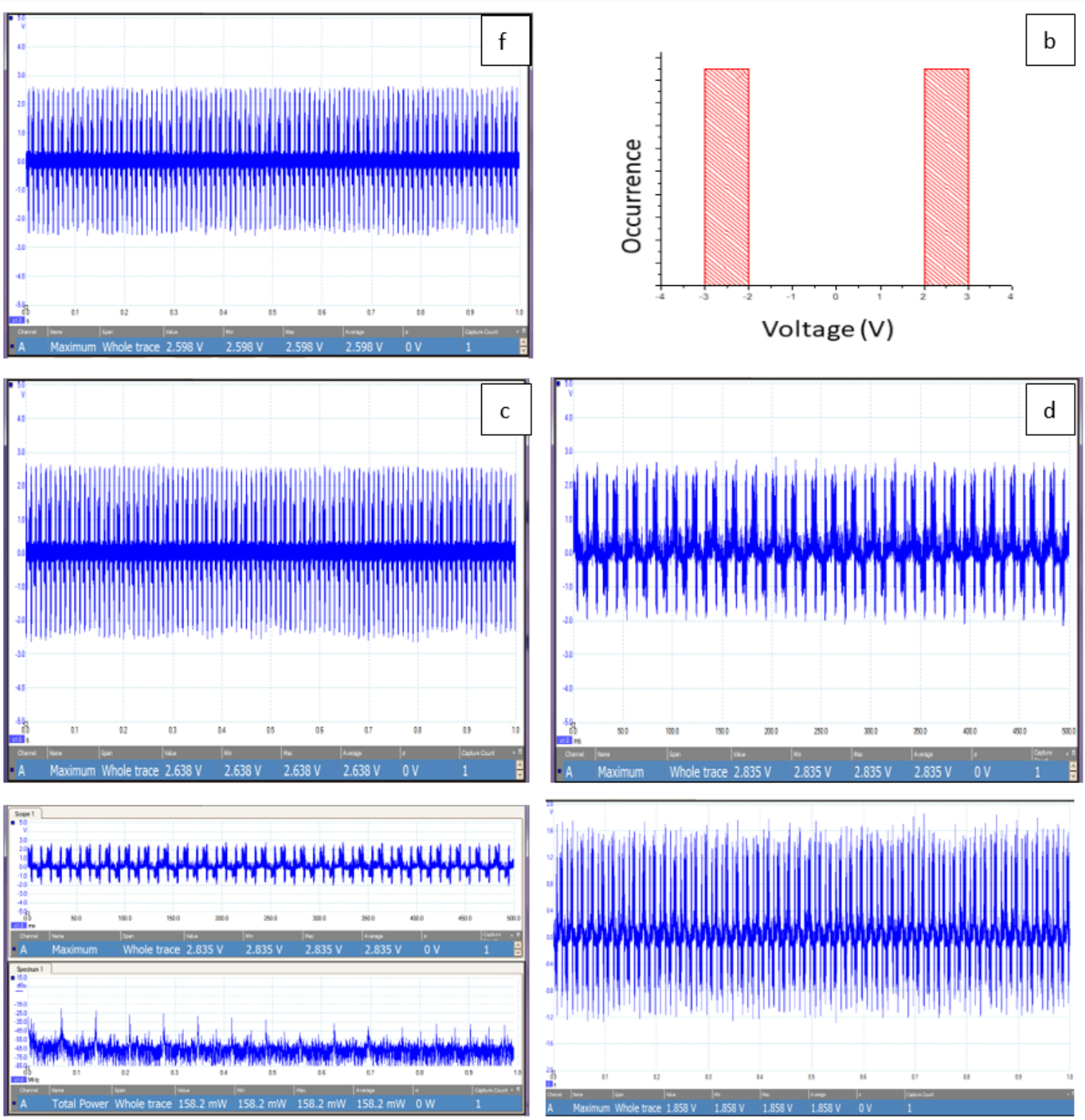

Figure 6

output voltage generated by 100 nm ZnO nanowires, (a) at 100o C, (c) at 150o C, (d) at 200o C, (e) at 250o C, (f) Power density 158 mW/cm2, (b) voltage occurrence histogram.

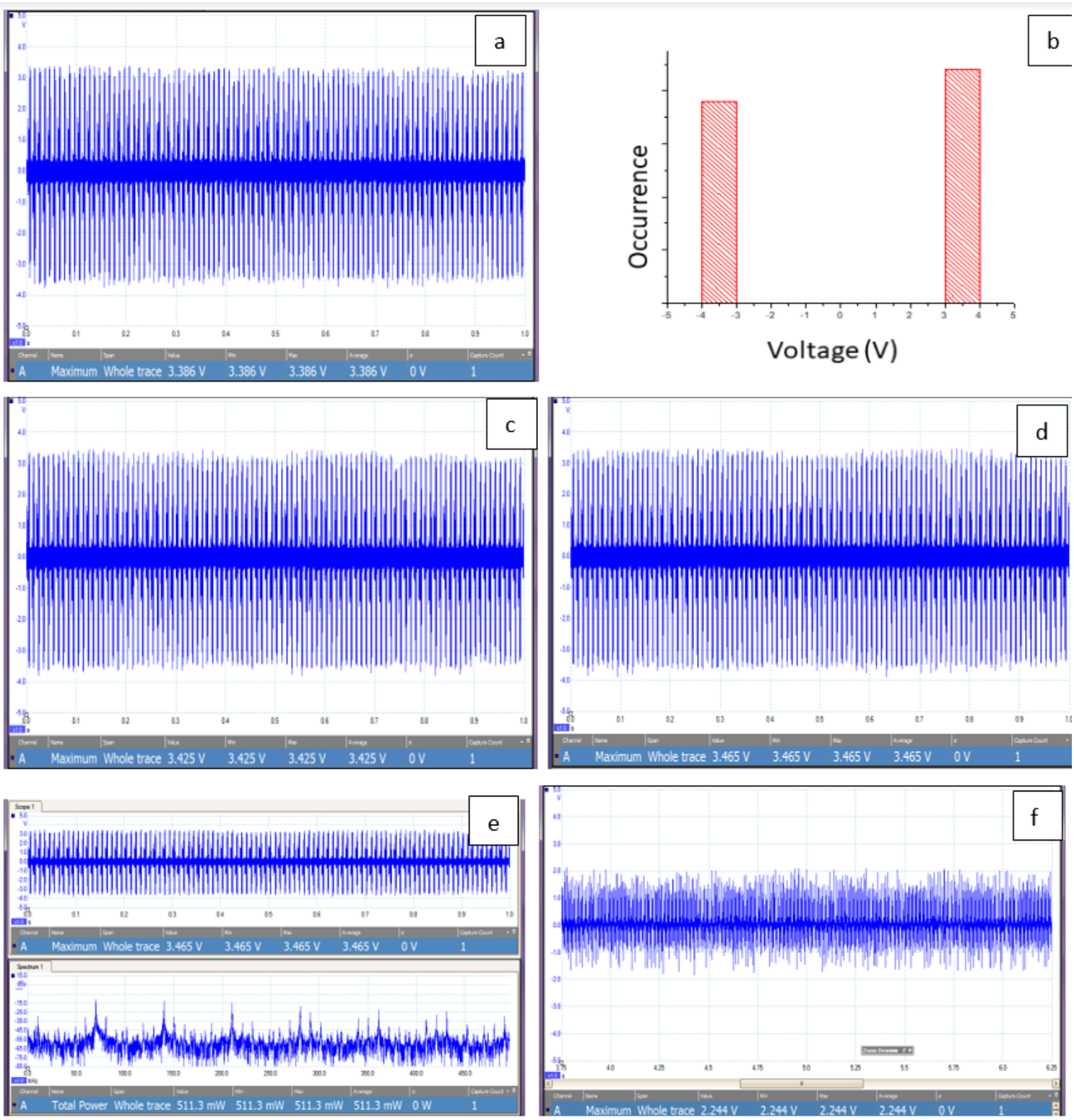

Figure 7

output voltage generated by □ 50 nm ZnO nanowires, (a) at 100o C, (c) at 150o C, (d) at 200o C, (f) at 250o C, (e) power density of 511.3 mW/cm2, (b) voltage occurrence histogram.

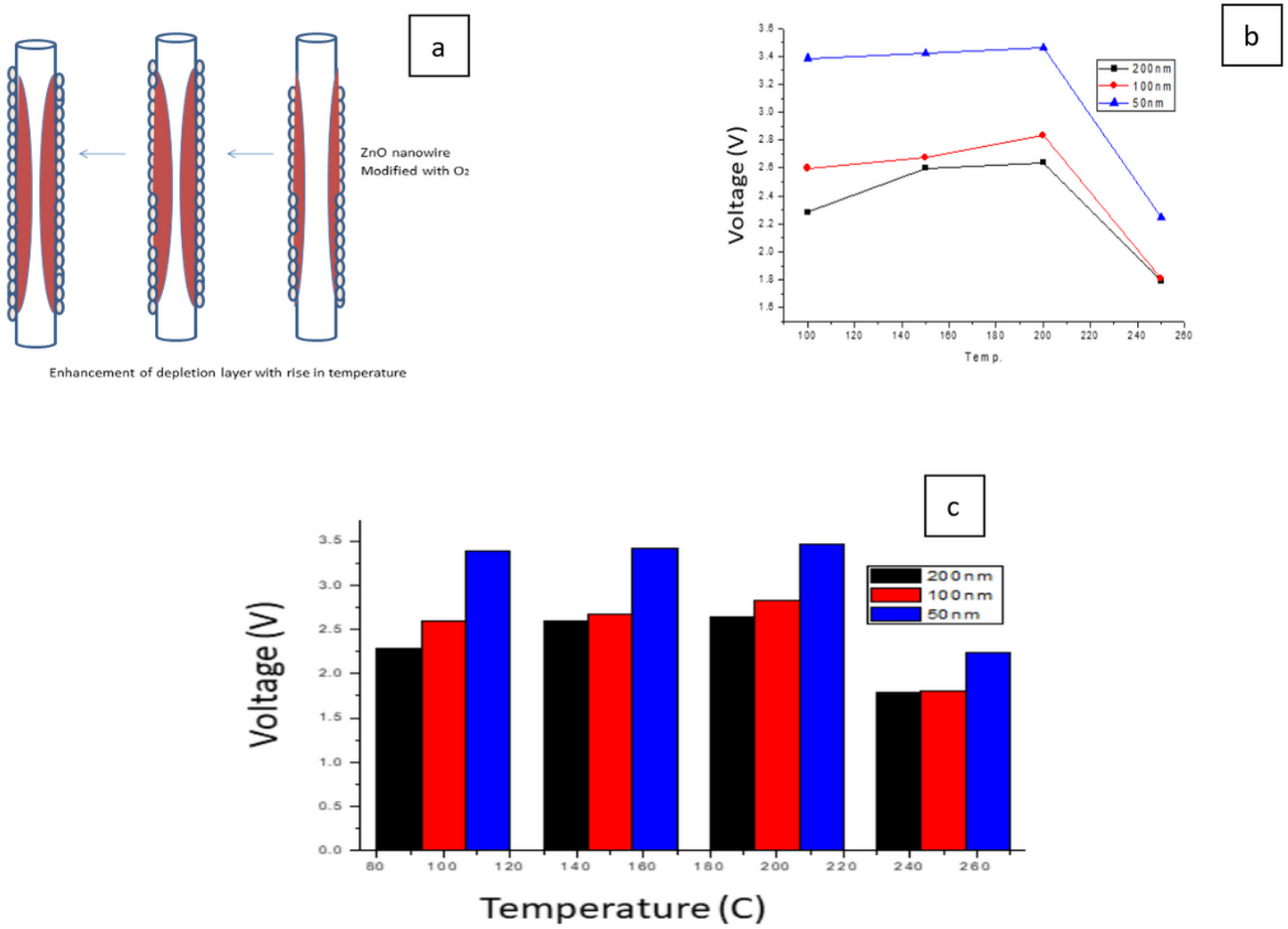

Figure 8

(a) schematic diagram of enhancement of depletion layer with the rise in temp., (b) graph showing trend of oxidized nanowires at Different temp., (c) comparison of output voltages generated by ZnO nanowires.