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# Temperature dependant high output voltage generation via mechanical transducer by using surface modified ($O_2$, $CO_2$, $NO_2$) ZnO nanowires

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ABSTRACT

Here, we report high output piezoelectric voltage generation using ZnO nanowires oxidized at high temperature. The study has been carried out to observe behavior of ZnO nanowires in the presence of strong oxidizing gases (O, $CO_2$, and $NO_2$) at elevated temperature. The focus of the research was to generate high piezoelectric voltage by using surface modified ZnO nanowires. VING (vertically integrated nanowire generator) has been exposed to oxidizing gases. ZnO nanowires oxidized with $O_2$ have shown maximum high output voltage of 3.36 V at 200$^o$ C, showing net rise of 0.762 V as compared to voltage generated at room temperature. Similarly, ZnO nanowires modified with $CO_2$ molecules have generated piezoelectric voltage of 2.589 V at 200$^o$ C, exhibiting a rise of 0.778 V as compared to the values recorded at room temperature and ZnO nanowires modified with $NO_2$ have generated maximum output voltage of 3.307 V at 150$^o$ C, indicating net rise of 0.59 V to the voltage values achieved at room temperature.

## 1. Introduction

ZnO in its hexagonal structure is one of the most promising semiconductor materials. It has got direct wide band gap of 3.7 eV, exciton binding energy of 60 meV and refractive index higher than 2 [1–3]. Due to its versatile nature it has been extensively used in wide range of applications like UV lasers [4], Photodetectors [5], dye-sensitized solar cells [6,7], light emitting diodes [8], Bio-sensors [9–11], nanogenerators [12–18] and self-powered devices [19–22]. ZnO is being is the first choice of researchers due to its various morphologies for numerous nano-scale applications like nanobelts [23], nanorods [24], nanorings [25], nanohelixes [26], nanotubes [27] and nanowires [28,29].

ZnO nanostructures have been extensively used for gas sensing applications [30–32]. Intrinsically, it is n-type material [25] and provides charge carriers for conducting purposes. At nano-scale, where aspect ratio is high, it also provides large surface area for gas molecules to get adsorbed. Adsorption of gas molecules on surface of ZnO nanostructures change their electrical properties which is being used by researchers for various gas sensing purposes [33–36]. We have used surface modified (oxidized) ZnO nanowires to generate high piezoelectric potential using VING [37–39]. Surface modified ZnO based VING is being used very first time for high piezoelectric voltage generation. Working principal of oxidized ZnO nanowires is based on chemiresistive nature of metal oxide semiconductor. Adsorption of gas molecules on ZnO nanowires is being carried out either by donating electrons or by accepting electrons of a particular gas. The behavior is termed as REDOX (Reduction-Oxidation) mechanism [40]. Gas adsorption phenomenon is being influenced by many factors like type of sensing material used [41], additives used in base material [42], grain size [43], and operating temperature [44].

In the recent study, we have thoroughly investigated the behavior of oxidized ZnO nanowires at elevated temperature. Chemiresistive nature of ZnO nanowires has generated high piezoelectric voltage under the ambience of various oxidizing gases. $O_2$, $NO_2$, and $CO_2$ have been selected due to their strong tendency of accepting the electrons from ZnO nanowire surface and oxidizing them quickly. It has been observed that surface modified ZnO nanowires oxidized at high temperature have generated high piezoelectric output voltage. However, it has been also observed that ZnO nanowires loaded with $O_2$ and $CO_2$ have shown

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downward trend after 200$^o$ C and for $NO_2$, the process has initiated above 150$^o$ C. It was due to initialization of desorption process. At high temperature, charge kinetics is increased and so as the scattering within nanowires. Adsorbed molecules on surface of ZnO nanowire surface tend to dissociate from surface by releasing electrons back to ZnO nanowires that increases the leakage current through nanowires. Consequently, reducing the output piezoelectric voltage, as leakage current through nanowires is a bad factor VING [45].

The deliverence of potential at output stages could be achieved by using metal-semiconductor (schottky) contact at one end of the VING. In VING, when external stress is applied on top electrode, negtive potential rises and the conduction band and fermi level both are eleavated relative to bottom elctrode. Due to a potential gradient in between top and bottom elctrode current starts to flow through the external circuit. Schottky contact at the top electode is found very cruicial, as it allows electrons to flow only through external load and stops the electrons (leakage current) to flow back through the nanowires. Electrons accumulating at the bottom elctrode rises up the femi level at the bottom electrode as well. The flow of electrons continues, unless an equilibrium is achieved in between upper and lower electrode. Piezoelectric potential develped due to external pressure has been compltely screened out. External pressure is removed, piezoelctric potential developed inside nanowires tend to collapse and all the accumulated electrons at the bottom start to flow back towards top electrode to maintain the charge neutrality in balanced condition. The phenomenon of creating piezoelctic potential and its deliverenece at output stages was made possible by the schootky contact, because if the contact has not acted as barrier in between ZnO nanowires and metal contact all the accumulated charge would have been depleted through the the nanowires and there would be no output voltage [46].

Its is very first time that surface modified ($O_2$,$CO_2$, $NO_2$) ZnO nanowires have generated high piezoelectric output voltage, when oxidized at high temperature.

## 2. Material and methods

All reagents (analytical grade 98%) are purchased from sigma Aldrich. We have fabricated VING structure by using ITO (indium tin oxide) coated PET (poly ethylene terephthalate)substrate as bottom electrode ZnO nanowires an intermediate part and Au electrode as upper electrode. PET substrates cleaned with deionized water and acetone respectively. Synthesis of ZnO nanowires has been carried out in two steps. First, seed layer is grown and then in second step vertical growth of nanowires was achieved. 10 mM solution of zinc acetate dihydrate (CH3COO) $_2{\cdot}2H_2O$] was used to grow seed layer on PET substrates. After seed layer growth, substrates were annealed at 60$^o$ C for 30 min. PET substrates are placed upside down for 3 h at 90$^o$ C in equimolar nutrient solution of Hexamethylenetetramine [$C_6H_{12}N_4$] and Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$]. Density of ZnO nanowires on the substrates is controlled by the adjusting the concentration of HMTA and zinc nitratehexahydrate. Aspect ratio of nanowires has been controlled by the adjustment of physical parameters like optimal temperature range at which nutrient solution has kept and growth time in nutrient solution. Control on Surface morphologies and density of nanowires has been well explained in our earlier reports [9–11]. We have grown three samples of same size $1 \times 1$ $cm^2$ in size and growth condition were kept same for all the samples to get the uniformity. Sample 1 was exposed to $O_2$, sample 2 exposed $CO_2$ and sample 3 to $NO_2$ at various temperature ranges from 100$^o$ – 250$^o$ C. samples have been exposed to all three gases at 100 ppm in a sealed chamber. ITO coated PET substrates are used as bottom electrode and Au sputtered electrode as upper electrode. Schematic diagram of mechanical transducer has been shown in Fig. 2 (d). Emscope SC500 is being used to sputter gold electrode on top of ZnO nanowires. Ar gas pressure inside the chamber was 0.1 Torr; the operating voltage to start charge irradiation process is of 2 kV. ZnO nanowire based nanogenerators is supposed to harvest mechanical energy into useful electrical energy by applying 100 nN force on top electrode using plastic roller. Piezoelectric output voltage has been recorded by versatile Picoscope 5204. Surface morphologies of structures have been studied by ESEM Philips XL30. (See Fig. 1.)

~100 nN force is applied on top electrode to generate piezoelectric potential within nanowires. it has been observed that movement of cations and anions within ZnO nanowire only requires minute external force, charge center disturbs and $Zn^{+2}$ and $O^{-2}$ tend to accumulate on either ends of the crystal and hence and electric dipole is being developed within nanowires. It is basically the bases of piezoelectric based nanogenerators. it has been tested that most the cations and anions are displaced to either ends of the nanowires by applying minute external force. It was indicated by the output voltage spectra that values are saturated at a given applied force. After, saturation of voltage at a particular applied force, increment of force becomes meaningless. Applied stress is quite less than the maximum tensile strain predicted for ZnO nanowires before it gets fractured. The value is only 6% of the maximum predicted safe value [47]. But yes, the factors, which can minimize the reverse leakage current through nanowires, hold the key of enhancement of output voltage.

## 3. Results and discussions

Environmental SEM Philips XL 30 has been used to study the surface morphology of ZnO nanowires. It has been observed that dense ZnO nanowires have been grown having slight interspacing in between their tops. Slight gap between top of nanowires is essential for piezoelectric nanogenerators. The difference between the voltages of as grown ZnO nanowires and surface modified ZnO nanowires have ensured that not only reverse leakage current through nanowires have been decreased but screening effect has also been reduced. Screening effect is a bad factor for ZnO nanowires based VING [48]. During a mechanical stress, n-type ZnO nanowires having excess of electrons in the conduction band have a tendency to get attracted towards positive charge center of the electric dipoles of adjacent nanowires and weak the piezoelectric field, hence depletes the piezoelectric potential. By surface modification of ZnO nanowires, screening effect has been minimized, adsorbed gas molecules on outer surface of nanowires worked as barrier for any charge transportation.

ZnO nanowires based Nanogenerators require narrow spacing at top end for bending during the application of external force. Piezoelectric potential developed inside nanowires is due to the creation of dipoles developed at two ends of nanowires during an external pressure. When an external force is applied that charge centre of wurtzite ZnO nanowires is being perturbed and negative charge tend to accumulate at anyone end of the nanowires and opposite charge to the other end of the wires. Dipole creation under external force is the working principal of mechanical nanogenerators [45].

In Fig. 2 XRD peaks are exactly in agreement with SEM images. ZnO nanowires have been grown vertically upward from ITO coated PET substrates. Diffracted peaks from ZnO nanowires at angles 31.63, 34.42, 47.49 and 56.65 corresponding to crystal planes (100), (002), (102) and (110) have been observed. All observed values have been compared with standard file (JCPDS 36–1451). It is evident from the obtained diffracted pattern that preferred growth orientation of ZnO nanowires is along the c-axis. The prominent peak intensity along plane (002) has been observed in the values obtained from all three samples.

Two sharp peaks at 530.1 eV and at 532 eV in the XPS spectrum of O 1 s is shown in Fig. 3(a). The peak appeared at 530.1 eV is related to $O^{2-}$ ion in ZnO structure [49] and peak located at 532 eV is related to hydroxyl (OH) group adsorbed on ZnO nanowire surface [50]. Similarly, XPS spectra of Zn 2p in Fig. 3 (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 [51]. 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 [52].

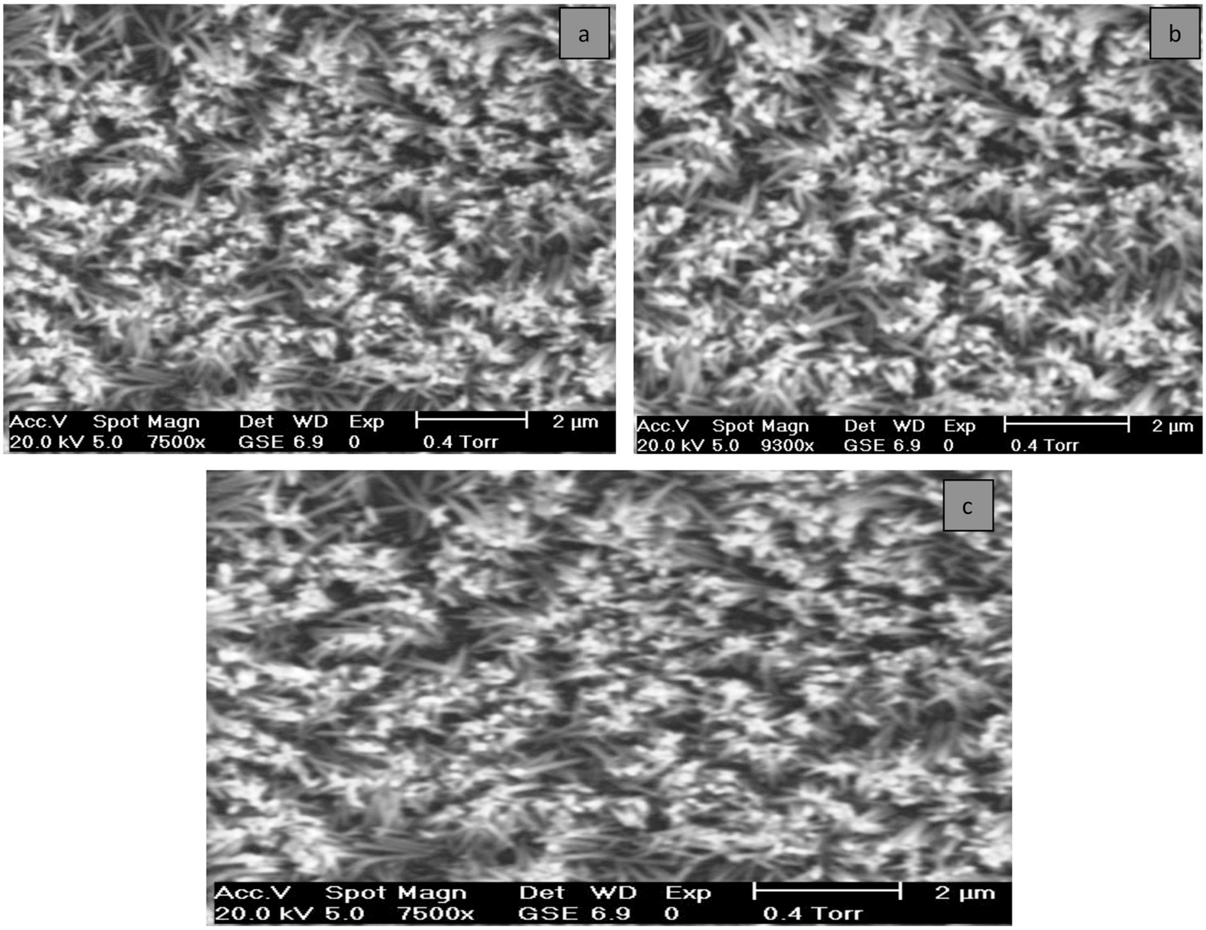


**Fig. 1.** SEM images of ZnO nanowires grown on ITO coated PET substrates, (a) Sample1 for $O_2$ exposure, (b) Sample 2 for $CO_2$ Exposure, (c) Sample3 for $NO_2$ exposure.

The FTIR analysis has been performed over arrange of 4000–400 $cm^{-1}$. The adsorption of $O_2$ is quite clear from 720 $cm^{-1}$ band. The In-situ FTIR study revealed the adsorption of $O_2$ on surface on ZnO nanowires while peak around 490 $cm^{-1}$ is related to ZnO nanowires. An absorption band of ZnO is located in the range of 510–420 $cm^{-1}$. The peak is around 500 $cm^{-1}$ is correlated to wurtzite zinc oxide [53,54]. The other weak peak is around 450 $cm^{-1}$ is related to the stretching vibration mode of ZnO bonding [55]. EDS results have been obtained from from ISIS 3.2 and the presence of Zn and O are clear and exactly in agreement with FTIR spectra, shown in Fig. 4 (a, b).

Owing the facts from our earlier reported [37–39] 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. 5 (b). positive value peaks and negative value peaks are exaclty in the same voltage reang as shown in Picoscope graph Fig. 5 (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 [56,57]. 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 [44].

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

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 urface-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 results. $O_2$ molecules while adsorbing on nanowire surafces from a layer on metal oxide structure, 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 [39]. It has been also observed that fuction of ionized layer is enhanced at elavated temperatures. We have exposed Oxidized structure at high temperature and adsorbed layer $O_2^-$ captures two or more electrons from ZnO naowire surface and shallow donors level can donate more electrons and during the process electron

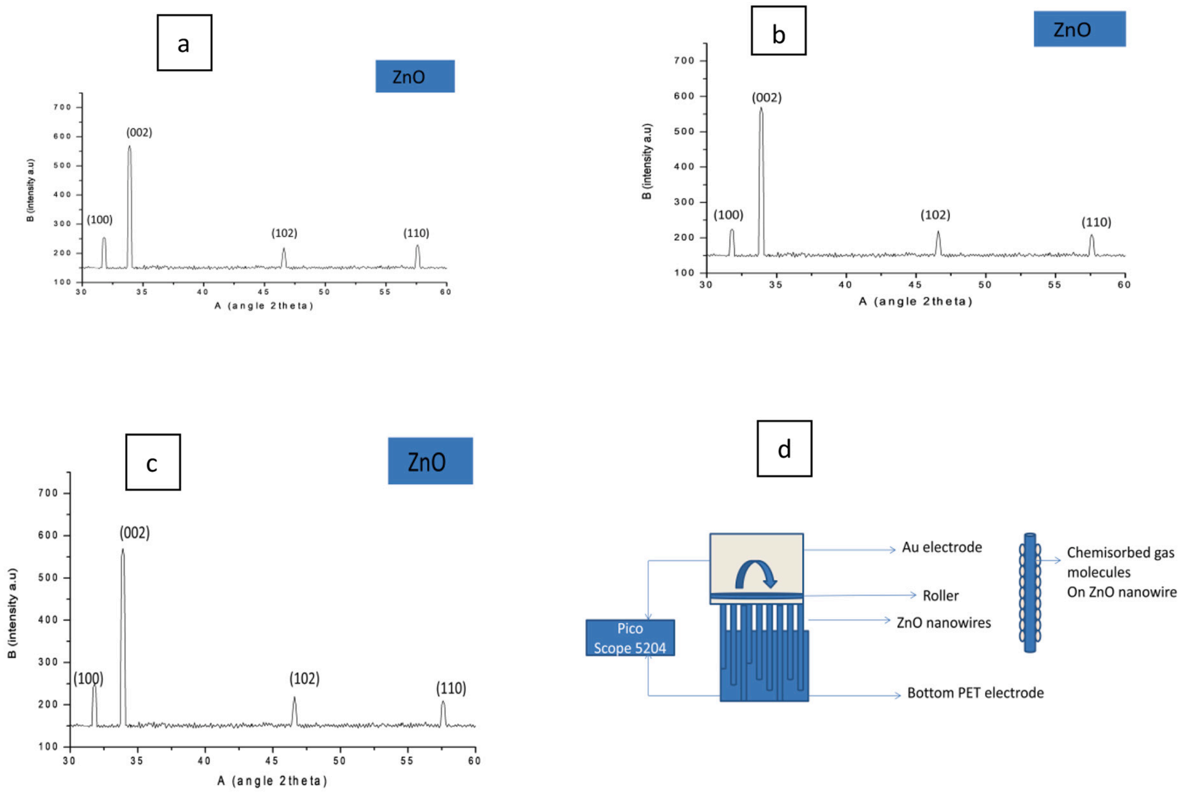


**Fig. 2.** XRD pattern of vertically grown ZnO nanowires, (a) sample1, (b) sample2, (c) sample 3, (d) Schematic diagram of ZnO based nanogenerator and ZnO (oxidized) nanowires.

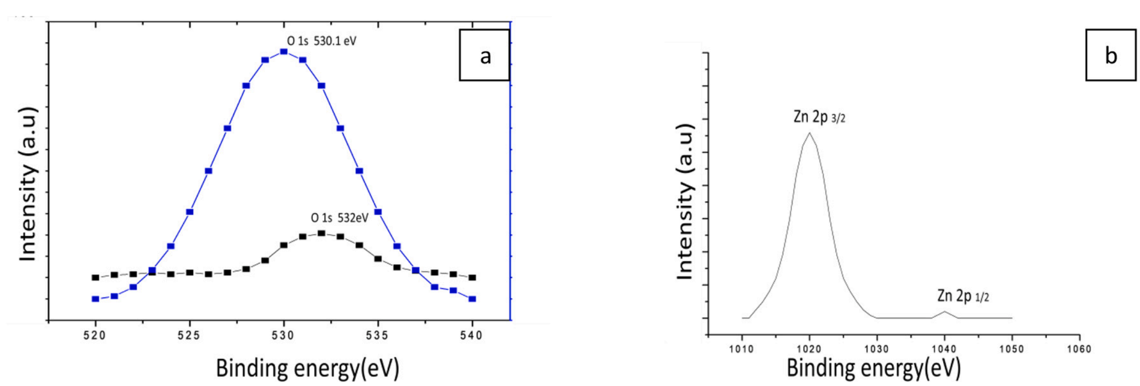


**Fig. 3.** XPS spectra, (a) O 1 s, (b) Zn 2p.

popoulation within nanowires is reduced. By reduction of elctrons reverse leakage current through nanowires is reduced. That is main reason of enahnced output voltage peaks at elevated temperatures. It has been observed that piezoelectric volatge was increased above 200$^{o}$ C and saturates but after that voltage tend to decrease. It could be due to many reasons, one prominent reason was initalization of desorption process of $O_2$ molecules from ZnO surface. It would have initiated transfer of electrons back ZnO naowires. Space charge width would have been reduced and so as the depletion width. The conduction of the electrons through naowires would have been increased and consequently piezoelectric potential would was decreased.

$$O_2 + 2e^- \rightarrow 2O^-$$

Or

$$O_2^- + e^- \rightarrow 2O^-$$

The process of adsorbing two electrons at high temperature is being explained by the above reactions [40,58] and It is quite consistent with the recent reported piezoelectrric output potential.

Stability test of VING has been carried with and without surface modification of ZnO nanowires and in both the case, output voltage was found consistent through a longer period of time. Histogram in Fig. 5(b, f) has shown the occurrence of the output voltage is consistent and stable for longer time and the results are exactly in agreement with theoretically predicted values in which it has been revealed that ZnO nanowires have generated piezoelectric voltage for a longer time without being cracked [59]. Theoretically, elasticity has been associated with fine nanostructures and it has been the salient feature of ZnO nanowires based nanogenerators that they are fatigue free [60]. It has been already predicted theoretically that even 35 billion cycles at resonant frequency would not fatigue ZnO nanowires and generated output voltage remains consistent [61]. Stability test of VING for 1200 cycles has already been

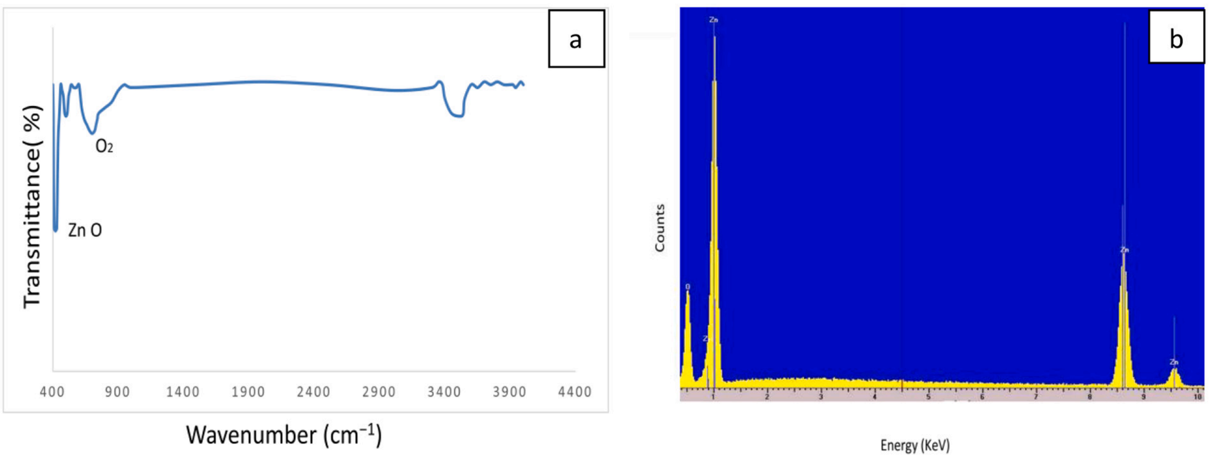


**Fig. 4.** (a) FTIR spectra of ZnO nanowires and adsorbed O, (b) corresponding EDS spectra of ZnO nanowires.

reported [62] and voltage was found unchanged.

Open circuit voltage of VING has been monitored, during change of the load resistance.

(2 to 12 MΩ) and corresponding output voltage is gradually increased. It has been observed in the results shown in Fig. 6 (a, b) that voltage enhancement pattern remains the same in both the cases whether it is surface modified nanowires are at room temperature or at elevated temperature (200$^{o}$ C). Applied load resistance is same for both the cases and are totally in agreement with theoretically predicted values [63]. Load resistance test authenticates the stability of the device in both conditions.

Current density of VING has been plotted in Fig. 7 (a, b). Fig. (a) is the current density of as surface modified (oxidized with $O_2$) ZnO nanowires at room temperature and fig. (b) is current density of ZnO nanowires at elevated temperature (200$^{o}$ C). It is exactly in agreement open circuit voltage spectra of nanowires. (See Figs. 8 and 9.)

From our previous results [38], it has been obserevd that ZnO nanowires modified with $CO_2$ molecules have generated an output voltage of 1.7 V at room temperature. it has been evidenced that $O_2$ layer works as receptor function for the other gas molecules to get adsorbed on metal oxide surface. It has been discussed earlier that the tendency of adsorbing electrons from ZnO nanowires surface increases at higher temperature. Mechanism of adsobing of electron and at room temperatre is represented by Eq. (3). By reduction of conducting elctrons form ZnO nanowires, the reverse leakage current trough nanowires has been reduced. Consequently, output piezoelectric voltage has been increased. At high temperatures adsorption pheneomenon of $CO_2$ molecules on metal oxide semiconductor has enhanced and it explained by Eq. (4). $O_2$ ionic layer works as good receptor fuction and $CO_2$ molecules directly interacts with ionic layer to form $CO_3^{2-}$ [64]. The pheneomenon of reduction of electrons during the processs is being well justified through output voltage (1.811 V) at 100$^{o}$ C. Piezoelectic voltage incremenet is due to reduction of population of electrons in ZnO nanowires. Less number of electrons ensured less leakage current through nanowires. Gradual rise in temp. Has shown rise in piezoelectic voltage, with the rise in temperature $CO_2$ molecules have given rise to more oxidation phenomenon and increased the internal resistane of ZnO nanowires.

$$CO_2 + e^- \rightarrow CO_2^- \quad (3)$$

$$CO_{2+}\ O_2^- \rightarrow CO_3^{2-} \quad (4)$$

The process of absorbing of more electrons at higher temperature is being explained [65,66] earlier but the REDOX mechanism has been used to enhance the sensitivity of the metal oxoide for gas sensing purpose. The unique feature of the recent study is to generate high piezoelectric voltage via surface modified ZnO naowires oxidized at high temperaure.

At room temperature, ZnO nanowires modified with $NO_2$ molecules have exhibited maximum voltage peak of 2.717 V, which is exactly in agreement with earlier reporeted results [38]. At elavated temprature, at 100$^{o}$ C Piezoelectric voltage has been increased and maximum voltage peak of 3.307 was recorded. At 150$^{o}$ C,200$^{o}$ C, 250$^{o}$ C output voltage was 3.307, 2.44 V and 1.339 V was recorded respectively. Decrement in the voltage at high temperature range could involve number of reasons. The dominent reason could be desorption process of $NO_2$ molecules from ZnO nanowire surface. The kinetics of charge acrriers at high temperature would have been increased and the scttering pheneomenon inside the nanowires would has also been incresased. Intrestingly, desoption pheneomenon is being evident in all strong oxidizing gases but the phenomenon has initated at different temperature. Like, for $O_2$ and $CO_2$ the voltage decline appeared above 200$^{o}$ C but for $NO_2$ gas it started at above 150$^{o}$ C. It signifies the fact the adsorption and desoprtion pheneomenon is related to temperature values [40]. ZnO nanowires modified with oxidizing gases could generate high piezoelectric vlotage but keeping the safe the operating temperature range in consideration.

$$NO_2 + e^- \rightarrow NO_2^- \quad (5)$$

$$NO_2 + O_2 + 2e^- \rightarrow NO_2^- + 2O^- \quad (6)$$

Mechanism of adsorbing electron from ZnO surface and at high temperature is represented by Eq. (5) and Eq. (6) respectively. It has mentioned earlier that O forms ionic layer on metal oxide surface and becomes conductive for other gas molecules to get adsorbed.". Behavior of $NO_2$ is different from $CO_2$, it could be adsorbed on ZnO surafece with or without O layer due to its strong oxidation behavior [22].

As, $NO_2$ has got high electron affinity than O, when it adsorbs on ZnO surface it removes the O from the.

Surface. The oxidized ZnO nanowires structures have been used earlier [67–69] for gas sensing purposes and pheneomenon of sensitivity response was decreased sharply at high temperature. One of the main reasons, is the desorption prcoess taking place at high temperature. The other reason could be, it has been observed earlier [70] that at NO2 while reacting with ZnO nanowires turn in NO leaving one O atom that get adsorbed on metal oxide surface and adsorption of O atom on vacant metal oxide surface has reduced number of electrons furthermore, consequently conductance would have been reduced. Sensitivity enhancemnet at higher tempertures is being one of the characteistics of oxidized ZnO nanowires. Prominent feature of the recent study is it that phenomenon has been used to generate high piezoelectric potential for self powered devices nano-scale devices.

Table 1 illustared the obtained high output piezoelectric volatge at

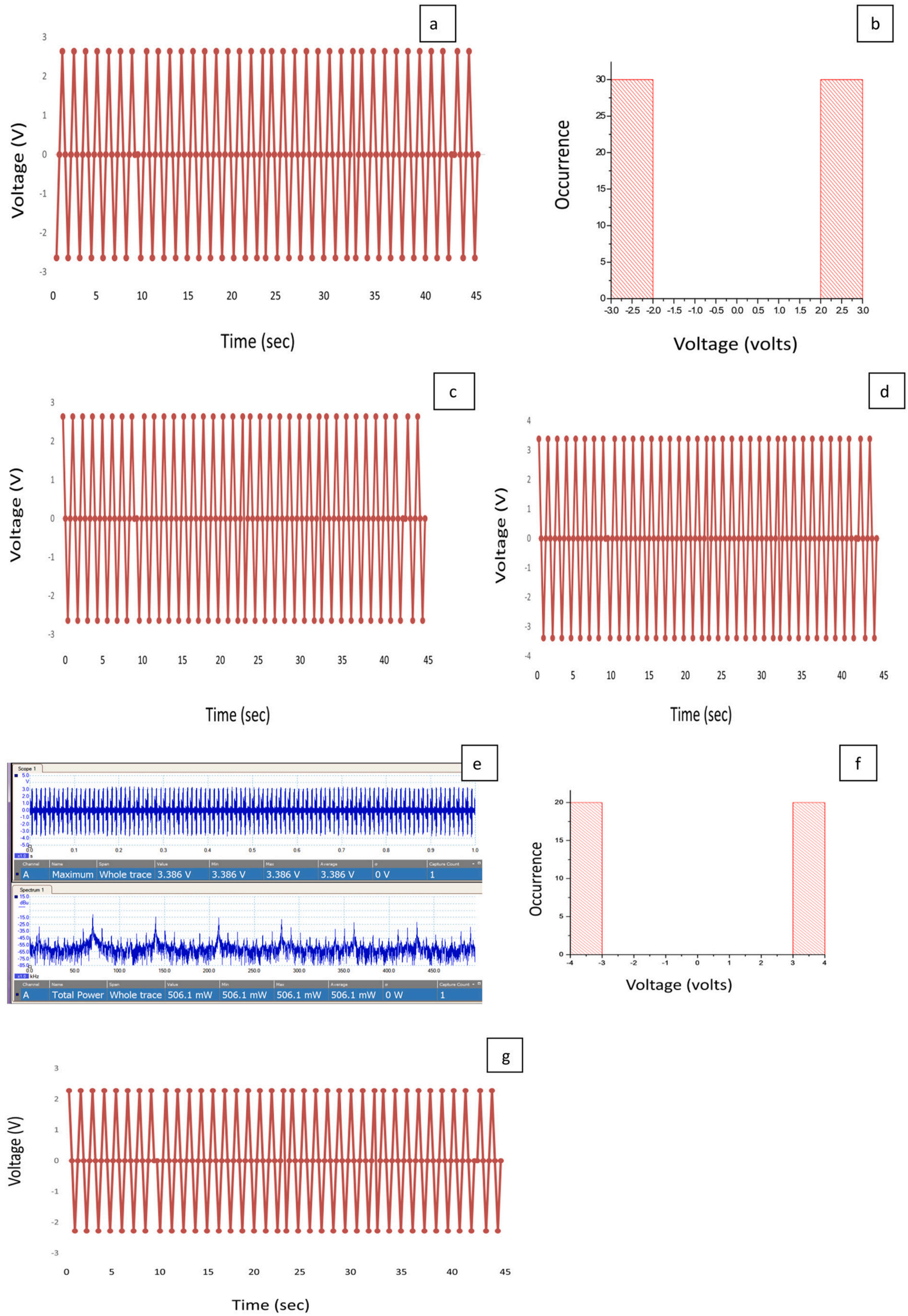


**Fig. 5.** (a) output voltage of 2.598 V obatained from ZnO nanowires modified with $O_2$ molecules at 100° C, (c)output voltage of 2.638 V at 150° C, (d) output voltage of 3.386 V at 200° C (e) output power density 506 mW/cm$^2$at 200° C, (g)output voltage of 2.283 V at 250° C (b, f) histogram showing the output voltage occurance at 100 ° and 200° C.

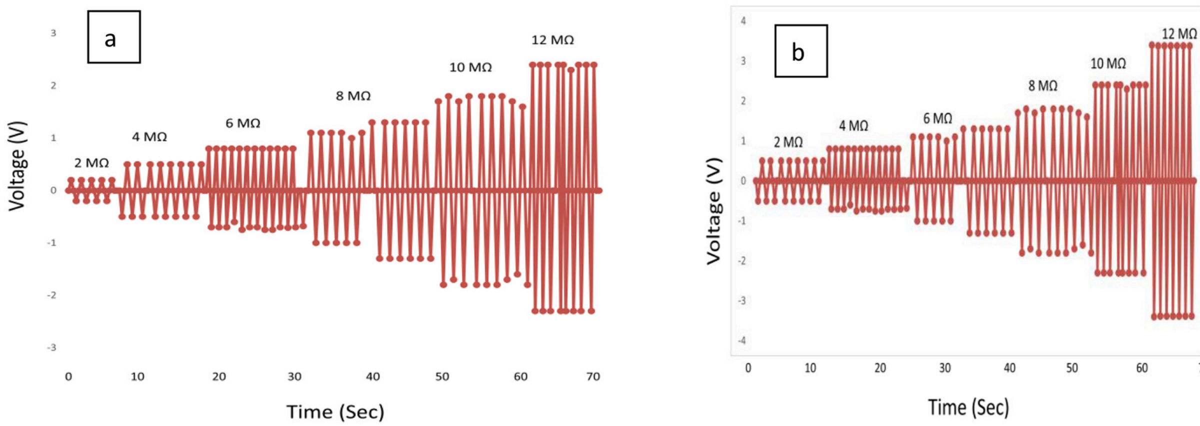


**Fig. 6.** Voltage enhancement by changing the load resistance, (a) at room temperature, (b) at 200° C.

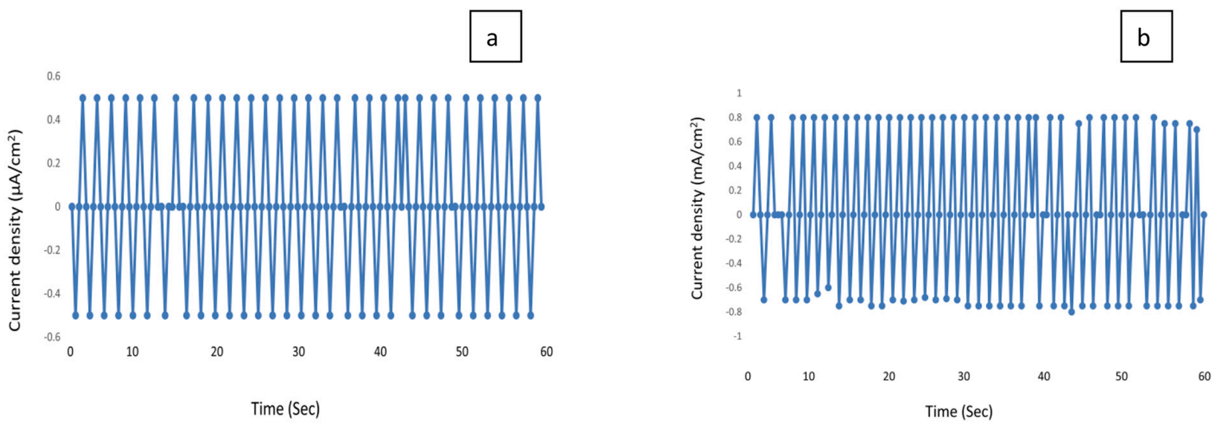


**Fig. 7.** Current generation through surface modified ZnO nanowires, (a) at room temperature, (b) at elavated temp. (200° C).

cooresponding tempearture values. It is being observed that initially, voltage has been increased by the oxidized ($O_2$, $NO_2$ and $CO_2$) ZnO nanowires and after 200° C it tends to drop for $O_2$ and $CO_2$ but for $NO_2$ voltage drop has started after 150° C but over all trend is same for all three oxidized structure. (See Table 2.)

Fig. 10 shows that during oxidation process, depletion layer is enhanced, and flow of electrons through nanowires have been reduced. Reduction in leakage current has resulted in ehnacement of piezoelectric voltage,.

Fig. 11 clearly indicated that oxdized ZnO naowires have shown gradulal increment in the voltage uptill 200° C then afterwards, ouput piezoeltric voltage has been reduced. It has been also observed that ZnO nanowies loaded with $O_2$ molecules have generated maximum peak voltage around 200° C and then output voltage has been degraded. However, ZnO naowires oxidized with $NO_2$ and $CO_2$ have generated maximum peak voltage around 150° C and 200° C respectively then volage has shown a declined trend.

We have established the optimal operating temperature for high output voltage generation via oxidized ZnO nanowires. For O, tempereautre is 200° - 210° C above it there is sudden voltage drop, similarly for $CO_2$, range is 200 °- 210° C and for $NO_2$ it has been 150°- 160 °C. Researchers have tried to achive the better sensing response at low temperatures as well but the cost of has been raised. Chen et al. has used Au funcionlised ZnO nanowires for $NO_2$ sensing but the optimal temperature range was reduced fom 250° C to 150° C. However, optimal temperature range for O and $NO_2$ varies but maximum voltage recorded by $NO_2$ oxidized ZnO nanowires is 3.307 V and for $O_2$ modified ZnO nanowires have generated maximum piezoelectric output voltage 3.386 V. Although $NO_2$ has strong oxidizing nature but at high temerature $O_2$ became more dominenet due to capturing of two electrons.

Enhanced adsorption phenomenon of $O_2$ molecules on ZnO nanowires is reported by Chen et al. [71]. Adsorption process has been enhanced by using Au functionalized ZnO nanowires but structure of ZnO nanowires has been degraded and peak intensities along (002) plane have been suppressed. $O_2$ molecules covered Au modified nanowires promoted more $NO_2$ vacancies and more adsorption of $NO_2$ molecules. However, the response of the sensor at high temperature is quite similar to the recent study. It was reported that sensing phenomenon was increased till 150° C and afterwards decreases to minimum value at 250° C. Same effect has been observed in the recent study that piezoelectric potential was enhanced till 150° C and afterwards it showed declined behavior, that is due to the desorption process taking place on ZnO nanowire surface. During the desorption process, electrons being transported back to nanowires leading rise the conduction of electrons through nanowires and appeared as reduction of piezoelectric potential at output stages. It has been observed clearly that maximum output voltage was recorded in 100° to 150° C and voltage is decreased with rise in temperature. In the recent study, pure ZnO nanowires are used to preserve piezoelectric potential developed inside nanowires due to small external pressure.

It has been observed that internal resistance of ZnO nanowires has been increased in all three cases ($NO_2$, $CO_2$ and $O_2$). Rise and decrease in piezoelectric potential with the variation of temperature is quite similar for $O_2$ and $CO_2$ but for $NO_2$ it changes. ZnO nanowires modified with $NO_2$ have shown maximum output voltage at 150° C then Voltage tends to drop. $NO_2$ is the strongest oxidizing gas among all and it gets adsorbed on the surface of ZnO surface with oxygen or without Oxygen layer [72]. Due to the reason, ZnO nanowires modified with $NO_2$ has generated high

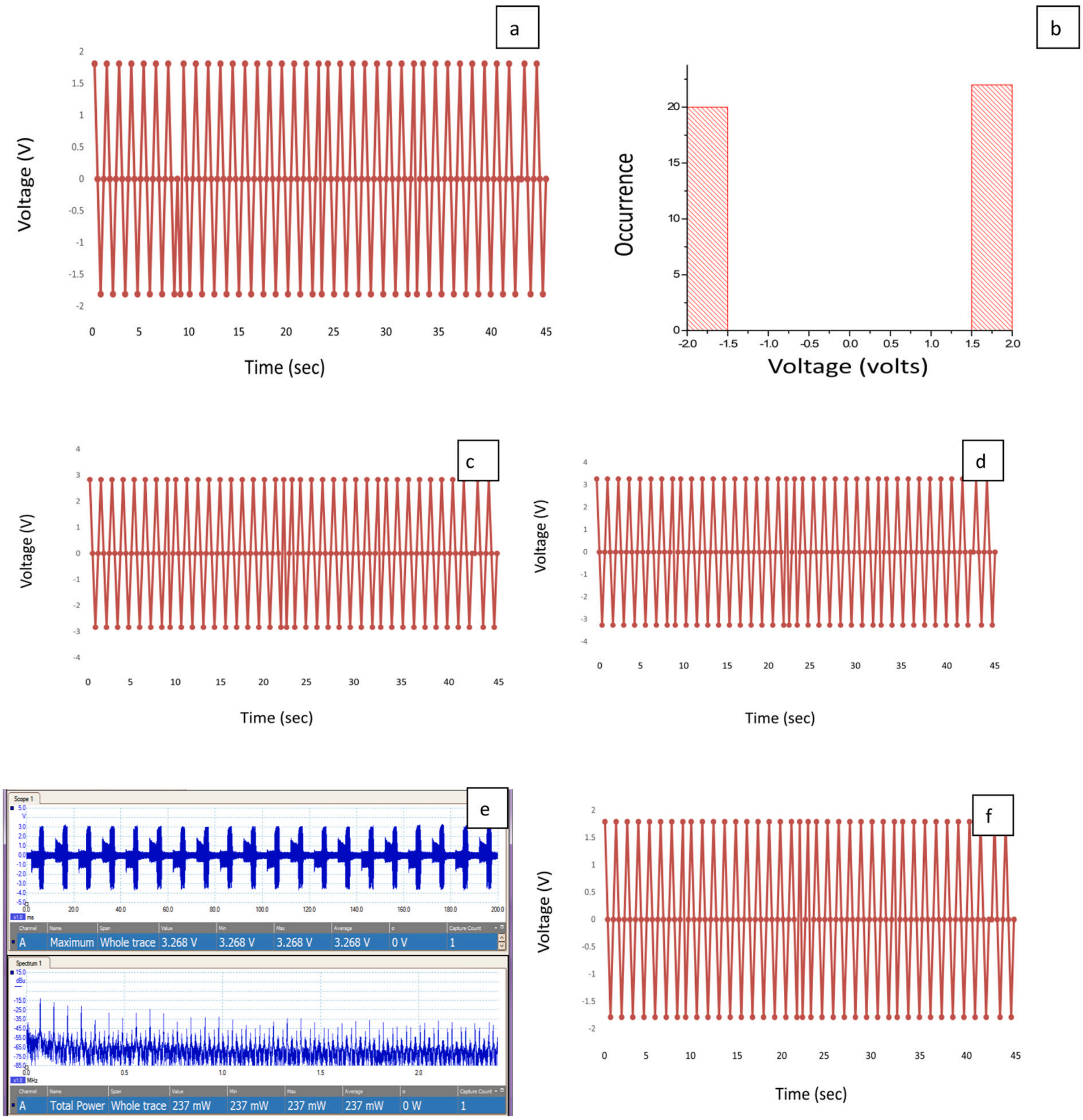


**Fig. 8.** (a) output voltage of 1.811 V obatained from ZnO nanowires modified with $CO_2$ molecules at 100$^o$ C, (c)output voltage of 2.835 V at 150$^o$ C, (d)output voltage of 3.268 V at 200$^o$ C (e) output power density 237 mW/cm$^2$at 200$^o$ C, (f) output voltage of 1.795 V at 250$^o$ C (b) histogram showing the output voltage occurance at 100 $^o$ C.

piezoelectric voltage at room temperature but due to desorption process above 150 °C, voltage has decreased quickly.

For $O_2$ and $CO_2$ the piezoelectric potential climbed up sharply till 200$^o$ C and the falls down. Phenomenon is purely due to adsorption and desorption of the gas molecules. Apart from adsorption and desorption took place on ZnO nanowire surface, scattering phenomenon is also quite crucial. At elevated temperatures, few remaining electrons within nanowires, which were not being captured by strong oxidizing gases suffered huge scattering, consequently increasing the internal resistance of nanowires.

Recent reported results are quite competitive. Earlier [38–41], we have carried out the study at room temperature and now results at high temperatures have been further improved. Considerable rise of 1.473 V has been observed at 200$^o$ C by ZnO nanowires oxidized with $CO_2$ molecules, similarly rise of 0.96 V has been observed for $O_2$ and rise of 0.34 V has been observed for $NO_2$ gas as compared to the values obtained at room temperature.

Fig. 12 clearly indicated a linear behavior. ZnO nanowires modified with $O_2$, $NO_2$ and $CO_2$ have shown considerable rise at elevated temperature. Recent results are quite competetive not only as if compared to our reported values but also for several other piezoelectic voltage generation values.

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 [73] but salient feature of the study the use of chemiresistive property of ZnO nanowires to produce high output voltage. ZnO nanowires based tiny mecanicla transducer has produced high piezoelectric voltages by using surface modification technique. Surface modification process has proved cost effective, as it did nor require any catalytic activity, expansive dopants and high vacuum and temperature conditions. As far as conventional

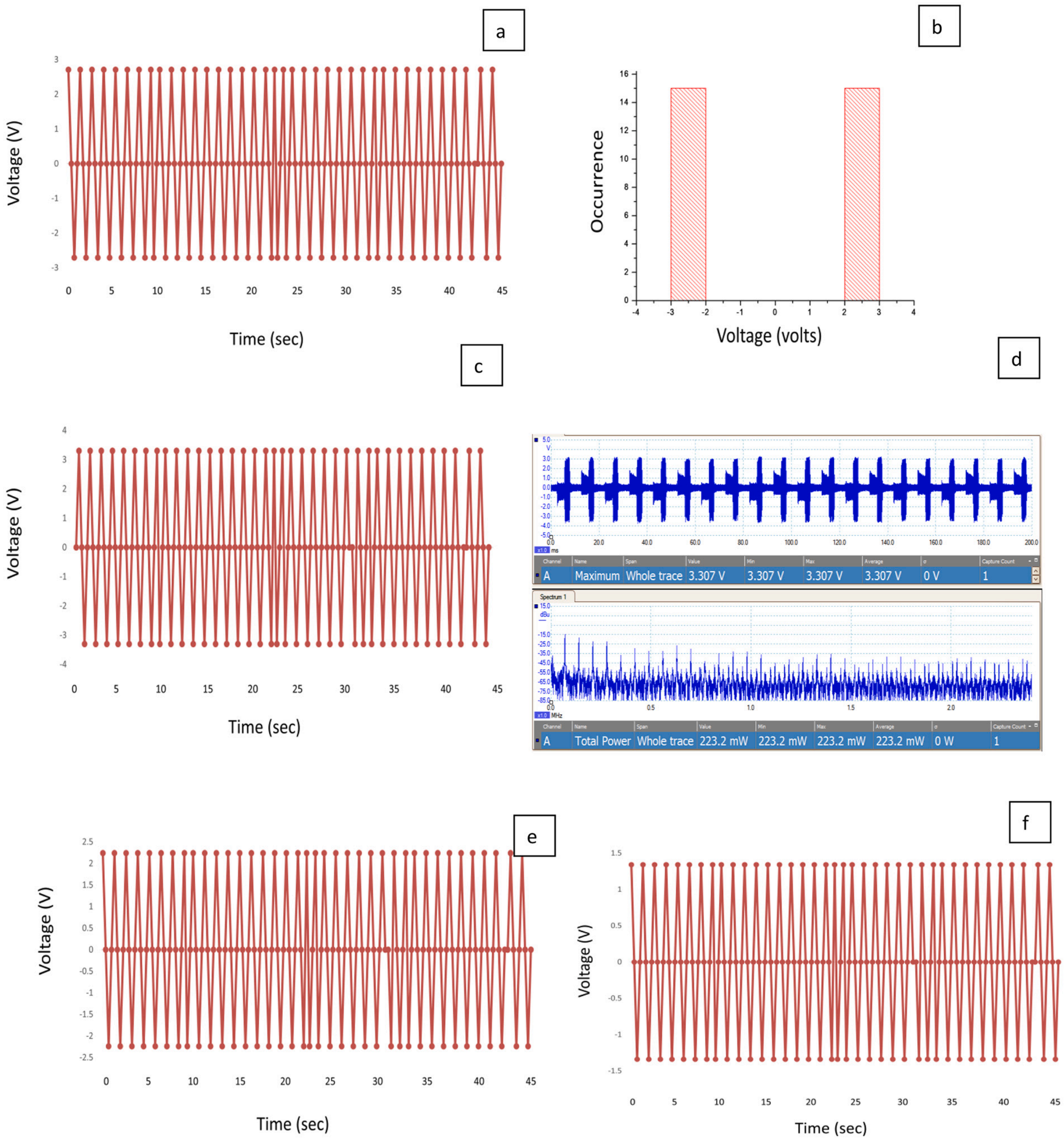


**Fig. 9.** (a) output voltage of 2.717 V obatained from ZnO nanowires modified with $NO_2$ molecules at 100° C, (c)output voltage of 3.307 V at 150° C, (e)output voltage of 2.244 V at 200° C (d) output power density 223.2 mW/cm$^2$at 150° C, (f) output voltage of 1.339 V at 250° C (b) histogram showing the output voltage occurance at 100 ° C,

**Table 1**
Comparison of output voltages, generated by ZnO nanowires modified with $O_2$, $CO_2$ and $NO_2$.

| | 100° C | 150° C | 200° C | 250° C |
|---|---|---|---|---|
| Output volatge generated by ZnO nanowires Modified with $O_2$ | 2.598 V | 2.638 V | 3.386 V | 2.283 V |
| Output volatge generated by ZnO nanowires Modified with $NO_2$ | 2.717 V | 3.307 V | 2.244 | 1.339 V |
| Output volatge generated by ZnO nanowires Modified with $CO_2$ | 1.811 V | 2.835 V | 3.268 | 1.795 V |

**Table 2**
Comparison between the voltages generated by oxidized ZnO nanowires at room temperature and at high temperature.

| | At room temperature | At high temperature |
|---|---|---|
| Voltage generated by ZnO nanowires loaded with O2 molecules | 2.44 V | 3.386 V |
| Voltage generated by ZnO nanowires loaded with CO2 molecules | 1.795 | 3.268 V |
| Voltage generated by ZnO nanowires loaded with NO2 molecules | 2.835 V | 3.307 V |

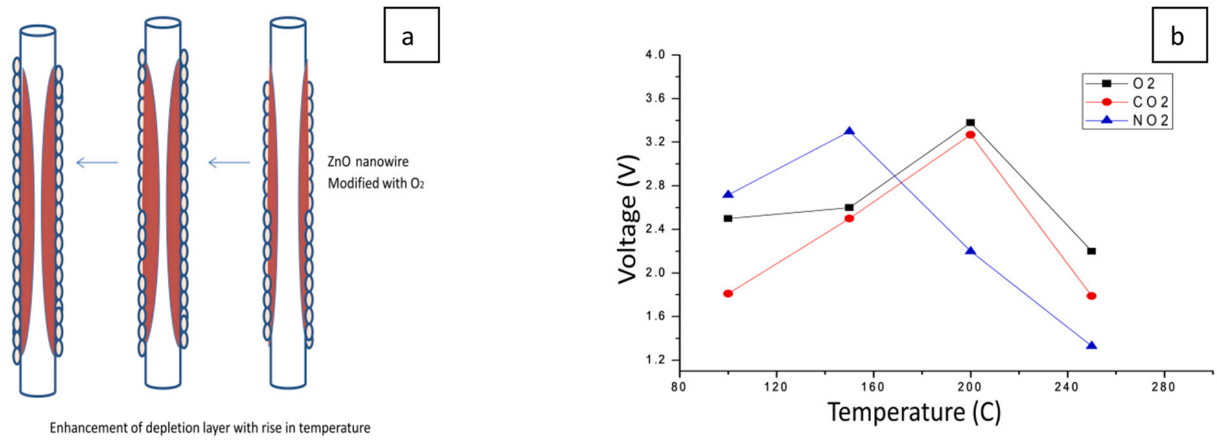


**Fig. 10.** (a) schematic diagram showing enhancemnt of depletion layer, (b) Temperature vs voltage graph of ZnO nanowires modified with $NO_2$, $CO_2$ and $O_2$.

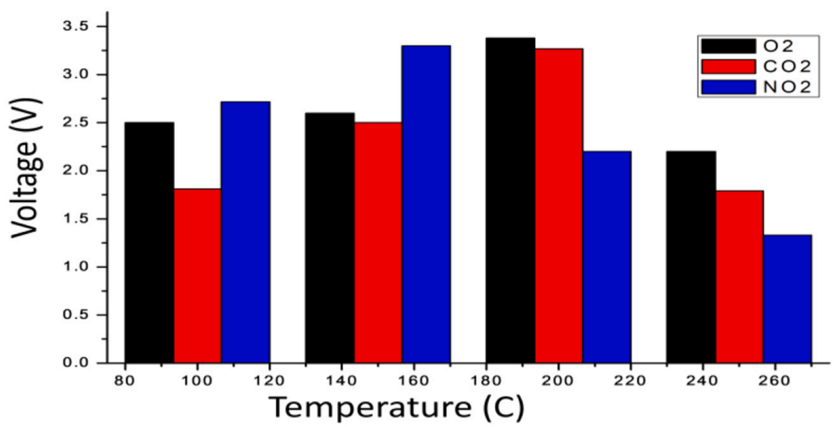


**Fig. 11.** Comparison of voltage values at different temperature range.

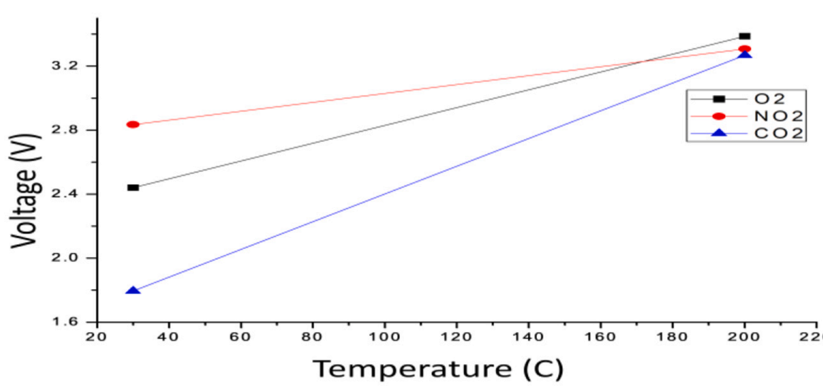


**Fig. 12.** Voltage difference between ZnO (modified) nanowires generated at room temperature and high temperature.

sensing purpose is concerned, researcher has added dopants to stabilize the REDOX mechanism [74], by doing so stability is achieved but only at room temperature but dopants have failed to keep the process stabilized at slightly higher than the room temperature."Our recent results are quite impressive that 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. For practical applications, stable and consistent output is required.

The results are quite competitive not only for certain optimal temperature range but also otherwise.

Z L Wang [75] reported number of high 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

Chemiresistive-type mechanical transducer has been developed to generate high piezoelectric voltage. We have successfully carried out thorough investigation of ZnO nanowires modified with $O_2$, $CO_2$ and $NO_2$ gas molecules at elevated temperature. Study has revealed that optimal temperature range for $O_2$ and $CO_2$ is 200-210$^o$ C and for $NO_2$ it is from 150$^o$-160$^o$ C to generate high piezoelectric voltage. Maximum output voltage of 3.386 V having power density 506.1 mW/cm$^2$ has been recorded by ZnO nanowires loaded with $O_2$ molecules, however 3.306 V having power density of 223.2 mW/cm$^2$ has been recorded for ZnO nanowires modified with $NO_2$ and 3.268 V and power density of 237 mW has been recorded for $CO_2$. Results are quite encouraging for nano-scale high output voltage devices. We propose oxidized ZnO nanowires at high temperature are ideal for self powered nano-scale devices, as they can be used as battery replacements. Small force~ 100 nN has generated high output voltage peaks. ZnO based tiny mechanical transducers hold the key for numerous nano-scale power issues.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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