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The improved piezoelectric properties of ZnO nanorods with oxygen plasma treatment on the single layer graphene coated polymer substrate

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Abstract:

The step towards the fabrication of nanodevices with improved performance is of high demand; therefore in this study oxygen plasma treated ZnO nanorods based piezoelectric nanogenerator is developed on the single layer graphene coated PET flexible polymer substrate. ZnO nanorods on the single layer graphene are grown by hydrothermal growth method and the structural study is carried out by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The piezoelectric properties of ZnO nanorods with and without plasma treatment were investigated by atomic force microscopy (AFM). The oxygen plasma treated sample of ZnO nanorods showed significant increase in the piezoelectric potential which could be due to the decrease in the defects levels in the ZnO and also increase in the mechanical properties of ZnO nanorods. Furthermore X-ray photoelectron spectroscopy (XPS) confirms that the filling of vacancies by oxygen in the matrix of ZnO using oxygen plasma treatment has given the enhanced piezoelectric potential compared to the sample of ZnO nanorods not treated with oxygen plasma. In addition to XPS experiment, cathodoluminescence (CL) technique was used for the determination of defect level in the ZnO nanorods after the treatment of oxygen plasma and the obtained information supported the XPS data of oxygen plasma treatment sample by showing the decreased level of defect levels in the prepared sample. From the XPS and CL studies it is observed that the defect level has significant influence on the piezoelectric potential of the ZnO nanostructures.

Introduction:

Piezoelectricity involves the phenomenon of change of mechanical energy into electrical power and nowadays it has been considered the efficient methodology for the harvesting of energy to power nanoscale electronic devices from the device based on the nanoenvironment. The advantageous features of piezoelectric devices are lying in the fact of ease of generation of electrical energy through various types of existing motions such as body movement, vibration, hydraulic and wind forces; these could have resulted in the development of wireless and self-powered devices [1-8]. Zinc oxide (ZnO) is among the nanomaterials which are highly used for the engineering of piezoelectric nanodevices due to its several attractive properties including biosafe in many cases and found in a variety of the coupled piezoelectric and the semiconducting nanostructures including nanowires, nanorods, nanotubes and nanowalls [9-12]. Besides, the use of ZnO in the energy harvesting application, it is also effectively used in the optoelectronics and photo-voltaic purposes [13, 14]. Due to the piezoelectric semiconducting nature of ZnO, it can produce specific value of piezoelectric potential because of its coherent mechanical elastic property. However, ZnO is enriched with the free carriers which screen out some part of the piezoelectric potential from ZnO during the fabrication of nanodevices.

On other hand, the graphene is known as the functional material comprised on the array of carbon atoms in hexagonal honey comb like structure with tailored and unique properties such as transparent optical features, mechanical flexibility, thermal stability, and chemically stable. Moreover, the graphene sheets exhibits high mobility of $26000 \text{ cm}^2/\text{v/s}$ at room temperature [15], and high mechanical flexibility with elastic modulus of about 1TPa [16], thus it is used widely in the research areas of nanoelectronics and spintronics [17, 18]. The hybrid material of well aligned ZnO nanorods and graphene provides a novel direct current flow through electrodynamics. The thermally stable paper, cotton textile and stretchable fiber based nanogenerators reduce the unstable electrical output which is a big problem in the nanogenerators fabricated on plastic substrate because of the thermally induced stress. The nanogenerators with enhanced output power are very much applicable as a power source for the wireless sensors and microelectronics. Therefore the trend towards the utilization of flexibility to a nanogenerator is becoming more popular in order to have a real time device for the energy harvesting application with maximum output potential. Currently, ZnO nanomaterial has been used through the mechanical engineering in the development of flexible nanogenerators [19, 20]. The research community is still more focussed in the fabrication of environ-

ment friendly, cost effective, portable and efficient piezoelectric nanogenerators for the harvesting of energy from the available sources in order to bring the reduction in the demand of expensive power electronic devices. Moreover, the decrease in defect levels in ZnO nonmaterial has also considerable effect on the piezoelectric potential of fabricated device [21].

In this work, an efficient flexible nanogenerator is developed by coupling the ZnO nanorods with the graphene sheets fabricated on the PET polymer substrate. The graphene sheets on the flexible PET polymer substrate offer excellent mechanical and optical transparency for the fabrication of flexible and transparent devices with enhanced performance. ZnO nanorods were grown on the graphene sheet by hydrothermal growth method and resulting flexible nanogenerator possesses attractive features including excellent mechanical elasticity, optical transparency and simple fabrication methodology.

Experimental:

Commercially available single layer graphene coated on polyethylene terephthalate (PET) polymer was purchased from ACS Material, USA and used for the growth of ZnO nanostructures. Firstly the graphene layer coated polymer substrate was cleaned with isopropanol and the deionized water respectively. The graphene substrate was dried with the flow of nitrogen gas at room temperature. For the growth of well aligned ZnO nanorods, the zinc acetate dihydrate as a seed layer was spin coated 2-3 times at 2500 r.p.m on the graphene substrate and consequently annealed at 100°C for 10 minutes. The growth solution of equimolar (0.075) zinc nitrate hexahydrate and hexamethylenetetramine was prepared in the deionized water and the seed layer containing substrates were vertically fixed afterwards the annealing in the growth solution. The substrates containing growth solution was kept in the preheated oven at 95°C for 5-6 hours. The grown ZnO nanostructures substrates were washed with the deionized water in order to remove the unwanted residual particles from the surface of nanostructures. Scanning electron microscopy (SEM) was used for the study of morphology of ZnO nanorods. X-ray diffraction (XRD) technique was used for the investigation of crystal arrays of ZnO nanorods. High resolution transmission electron microscopic (HRTEM) experiment was carried out by using FEI Tecnai G2 TF20 UT associated with field emission gun used at 200 kV with a point resolution of 1.9Å°, equipped with energy dispersive spectrum (EDS).

Results and discussion:

Figure 1(a) shows the typical SEM image of grown ZnO nanorods on the single layer graphene coated on PET polymer substrate. It can be seen from Figure 1(a) that the ZnO nanorods are well aligned, uniform, highly dense and perpendicular to the substrate. The inset of the figure 1(a) indicates that average diameter of nanorods is around 250-300 nm. SEM image for the oxygen plasma treated sample is shown in figure 1 (b) and it confirms the damage free treatment of ZnO nanostructures. The XRD pattern of the ZnO nanorods grown on single layer graphene coated PET polymer substrate is shown in Figure 1(c). All the diffraction peaks can be indexed to the hexagonal wurtzite phase of ZnO nanorods and the obtained results are consistent with the standard JCPDS card No (36-1451). The XRD study has revealed the c-axis oriented growth pattern of ZnO nanorods with more intense (002) peak compared to other peaks. Figure 1(d) shows the HRTEM and selective area electron diffraction (SAED) images of ZnO nanorods fabricated on the single layer graphene coated PET polymer substrate. The preferred orientation of synthesized ZnO nanorod is along (0001) direction and ZnO nanorod exhibited the single crystalline array. The obtained results of TEM analysis are consistent with the SEM and XRD results.

The piezoelectricity property of ZnO nanorods is realised by performing the atomic force microscope (Digital Instruments Multimode AFM, Netherlands) and a custom-made trans impedance amplifier and stiff platinum coated probes (NT-MDT NSG01/Pt, Russian Federation) experiment. All scans were measured in contact mode with the fast scan direction perpendicular to the cantilever (0°). In the beginning the cantilever deflection signal was fixed at zero with the cantilever undeflected and measurements were performed for the set potential in the range of 1V to 5V. The observed sensitivity for the deflection signal was $100 \text{ nm/V} \pm 20\%$ and the applied vertical force was in the range of 0.6 to $3 \mu\text{N}$ using the spring constant of the tip typically of 0.6 N/m. The current–amplifier response is shown in the schematic figure 2. The cantilever was joined to the instrument ground and an isolated sample holder was employed for the measurement of piezoelectric current. However, the feedback resistor shows the gain of the trans impedance amplifier of $1 \text{ V}/\mu\text{A}$. In the whole circuit, a positive output potential describes the flow of current via tip to the ZnO nanorods sample. To avoid the stray leakage current, the sample was kept at ground potential using the feedback loop of the AD822 operational amplifier as shown in figure 2. The amplifier shows the input bias current less than 25 pA which can be ignored. The gain-bandwidth product of the AD822 is 1.8MHz which shows the effective impedance to ground of 500 Ohm at kHz with the

1M Ω feedback resistor, thus the effect of leakage current was avoided. The bias-voltage of the sample was fixed at less than 0.5 mV.

Figure 3(a) shows the three dimensional current image of the fabricated ZnO nanorods on the single layer graphene coated PET polymer substrate and the measured output potential at the time of bending of nanorods. During the scanning of tip on the well aligned ZnO nanorods through contact mode which bent the nanorods and resulting the average output potential of 80-100 mV. When the tip deflected the nanorods during this no output potential was exhibited, however the potential was measured at the maximum deflection of nanorods. When the force on the nanorods was released by the AFM tip then output potential was found to be zero. This suggests that the realization of piezoelectric potential was recorded at the end of AFM scan on the nanorods surface as shown in figure 3(b). Figure 3 (c) shows the topography image of the bending distance and the mechanism behind the generation of piezoelectric potential which is lying in the fact of displacement of the Zn²⁺ cations along with the O²⁻ anions. It is the fact that ionic charges are unable to move and recombine independently irrespective of the given out of the strain. The ZnO nanorods are asymmetric from the bottom and top contacts and are in contact with the graphene single layer coated PET polymer substrate. The mechanism of piezoelectric potential from ZnO nanorods on the flexible substrate is according to the published work [22]. It is clear from schematic diagram in figure 3(d) that at the time of applied external force, the ZnO nanorods are deformed and a piezoelectric potential is produced along the top and bottom electrodes due to short lived presence of charges. This allows the electrons to flow along the external force at the point of equilibrium. However, when the applied force is cut off then the piezoelectric nanogenerator gains its original position, thus a piezoelectric potential is diminished and the stored electrons move towards the reverse direction. The alternating current output signal might be involved from the electrical response. The AFM tip is used as the applied external force on the ZnO nanorods and the flow of charges come in account and a Schottky barrier is developed between the ZnO nanorods and the electrode. Moreover, the ZnO nanorods control the flow of charge carriers.

ZnO nanorods were treated with the O²⁻ plasma in order to reduce the defects levels in the nanorods and to observe the effect on the piezoelectric property of ZnO [21]. ZnO nanorods were treated with the oxygen plasma through the reactive ion etching (RIE) system (SAMCO, RIE-10RU). The RIE system contains the parallel plate type plasma reactor chamber was used at an RF frequency of 13.56 MHz. The oxygen plasma was produced using the applied RF power of 250 W, a gas flow of 400 sccm and a pressure of 600 Pa.

Figure 4 (a-c) shows the piezoelectric response of oxygen plasma treated ZnO nanorods and it can be inferred that the piezoelectric current is significantly increased compared to the ZnO nanorods without plasma treatment. Prior to the treatment of oxygen plasma under the bias voltage of (1mV), the average output potential was found to be 78 mV and after the treatment of oxygen plasma the piezoelectric potential came out of 122.7 mV. This increase in the piezoelectric potential can be attributed to the decrease in the defects level in the ZnO nanorods during the oxygen plasma treatment. During the oxygen plasma treatment, the generated oxygen ions and radicals diffuse into the ZnO nanorods thereby occupy the oxygen vacancies, thus the carrier concentration is also decreased. Moreover, the oxygen plasma treatment decreases the free carrier concentration in the ZnO, thus the improved piezoelectric potential is observed for oxygen plasma treated ZnO piezoelectric nanogenerator. In addition to this, the oxygen plasma treatment brings the possible filling of vacancies and therefore the elastic property of nanorod is improved which has shown the countable role in the generation of higher piezoelectric potential for the proposed nanogenerator on the flexible single layer graphene coated PET polymer substrate. Besides the plasma treatment, we also observe that the growth of nanorods and their effective working area has also influence in the generation of piezoelectric potential for ZnO based nanogenerators.

For further confirmation about the enhancement of piezoelectric potential of ZnO nanorods due to defect levels in the oxygen plasma treated sample, the X-ray photoelectron spectroscopy was carried out for the ZnO Nanorods without oxygen plasma treatment and with oxygen plasma treatment. X-ray photoelectron spectroscopy (XPS) was used for the composition analysis of ZnO nanorods grown on the monolayer of graphene coated PET polymer substrate by aqueous chemical growth method. Figure 5 (a) shows the XPS survey scan of grown ZnO nanorods and it can be inferred from the figure that sample contains only zinc, oxygen and a small quantity of carbon which is involved due to use of carbon as reference. Figure 5 (b) shows the core level XPS spectra of Zn (2p_{3/2}) of ZnO nanorods, the observed symmetric peak at 1921.4 eV that can be assigned to the formation of hexagonal ZnO nanorods [23]. Figure 5 (c) shows the XPS spectrum for O 1s and the measured peak at 530.3 eV corresponds to O²⁻ ions on the wurtzite hexagonal structure Zn²⁺ ion arrangement covered by Zn atoms which clearly confirms the full complement of neighbouring O²⁻ ions. However, appeared peak at 532.0 eV could be attributed to hydrated oxides involved from the growth solution because the binding energy for oxygen specie in OH and H₂O is in between 531.5 eV and 533 eV respectively [23-26].

In order to investigate the effect of oxygen plasma treatment on the piezoelectric properties of ZnO nanorods by using XPS technique, we observed similar results for Zn 2p_{3/2}, but different for O 1s and the chemical composition of sample is consisting on zinc, oxygen and carbon which was used as reference for the determination of Zn 2p_{3/2} and O 1s binding energies. When we compare the sample treated with oxygen plasma with the sample without treatment of oxygen plasma, it is observed that peak at 532 eV is diminished which demonstrates the filling of oxygen vacancies by oxygen during the treatment of oxygen plasma. This filling of vacancies by oxygen brought the improvement in piezoelectric properties of ZnO by providing more polarization of charges during the applied force and consequently better deflection is observed, thus enhanced piezoelectric response is obtained for oxygen plasma treated sample of ZnO nanorods.

Figure 7 shows the room temperature CL spectra of ZnO nanorods without and with plasma treatment at the accelerating voltage of 10 KV. It can be seen from the figure 7 that defect level in the plasma treated sample is decreased compare to the without plasma treated sample which indicates the filling of interstitial vacancies by either O₂ molecules or O radicals during the plasma treatment [27, 28]. This study has supported the XPS data of the oxygen plasma treated sample and confirms that the decrease in the defect levels increases the piezoelectric potential of ZnO nanostructures.

Conclusion:

In this study piezoelectric property of ZnO nanorods is realized on the single layer graphene coated PET flexible polymer substrate. Furthermore ZnO nanorods are treated with the oxygen plasma and the increase in the piezoelectric current is also observed. XPS and CL shows that the filling of vacancies in the matrix of ZnO by oxygen plasma treated sample has given the enhanced piezoelectric potential compared to the sample not treated with oxygen plasma. The enhanced piezoelectric potential of ZnO with the oxygen plasma treatment demonstrates the possible improvement in the performance of energy harvesting nanodevices based on ZnO like materials.

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Figures Caption:

Figure 1: Structural morphology of ZnO nanorods fabricated on single layer graphene coated polymer substrate. (a) As grown SEM image of the vertically aligned ZnO nanorods with high density along with inset showing the diameter of the nanorods. (b) Plasma treated SEM image of ZnO nanorods showing the damage free hexagonal wurtzite structures. (c) X-ray diffraction spectrum of ZnO nanorods. (d) High resolution transmission electron microscopy image of single ZnO nanorod.

Figure 2: Schematic diagram showing the current-amplifier response.

Figure 3: Piezoelectric power generation from as grown ZnO nanorods fabricated on single layer graphene coated PET polymer substrate. (a) Three-dimensional plot of the output voltage. (b) Typical AFM tip scanning the surface of ZnO nanorods in micrometers. (c) AFM topography image (d) Mechanism of the electrical pulse generation by ZnO nanorods.

Figure 4: Piezoelectric power generation from plasma treated ZnO nanorods. (a) Three-dimensional plot of the output voltage. (b) Typical AFM tip scanning the surface of ZnO nanorods in micrometers. (c) AFM topography image.

Figure 5: XPS analysis of ZnO nanorods without plasma treatment.

Figure 6: XPS analysis of ZnO nanorods treated with oxygen plasma treatment.

Figure 7: CL spectra of as grown ZnO nanorods and ZnO nanorods with oxygen plasma treatment.

Figure1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7: