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Facile growth of high aspect ratio c-axis GaN nanowires and their application as flexible p-n NiO/GaN piezoelectric nanogenerators

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ABSTRACT

Piezoelectric nanogenerators (PNGs) have attracted great interest as energy sources to power-up smart clothing, micro/nano systems, and portable electronic gadgets. Due to non-centrosymmetric crystal structure, bio-compatibility, and mechanical robustness of GaN, it is a promising candidate to fabricate PNGs. In this study, c-axis GaN nanowires were grown by MOCVD, then were embedded inside polydimethylsiloxane and flipped on to the flexible substrate, followed by the deposition of p-type NiO to form heterojunction. The fabrication of GaN nanowires based heterojunction PNG on flexible substrate is the first report to the best of our knowledge. The piezoelectric properties of PNGs were investigated as a function of the GaN nanowire length. A maximum piezoelectric output potential of 20.8 V and current of 253 nA were measured. The stability of the device was also evaluated and found stable even after 20,000 cycles. This high piezoelectric output was attributed to the suppression of free carrier screening and junction screening. Moreover, the underlying reasons for the high stability are the malleability of the device and high aspect ratio of the GaN nanowires. The design and stability of our device make it a promising candidate for applications in self-powered systems for environment monitoring and low power electronics.

1. Introduction

Faced with the depletion of fossil fuels in the near future and the increasing demand for energy, there is an urgent need for scavenging new energy sources from the environment [1–8]. Even though several natural energy resources such as solar, wind, and hydro power are abundant in the environment, but they cannot be efficiently exploited due to environmental factors. Piezoelectric generators (PGs) that convert applied mechanical stress in specific solids into electrical charges are considered to be among the most promising energy harvesters for microsystems [9–11]. Sources of mechanical energy are abundant in our surrounding environment [12], which include fluid flow [13], vehicle movement [14,15], vibrations [16,17], human walking [18], heartbeat [19], breathing [20], and muscles movement [21]. The electrical energy generated by PGs can be utilized to power-up systems with power consumption in the range of micro to milliwatts such as wearable/portable electronic gadgets, remote sensors, implantable biosensors, wireless transmitters, and microelectromechanical systems.

A prerequisite for the occurrence of piezoelectricity in a semiconductor material is a non-centrosymmetric crystal structure under stress. In a typical non-centrosymmetric crystal structure, the material under stress experiences a shift in the centers of both cations and anions to form a dipole. The superposition of these electric dipoles results in a piezoelectric potential. Among the various piezoelectric materials, ZnO, $BaTiO_3$, and GaN have been widely studied due to their high piezoelectric coefficients [22–25]. Among these, GaN is particularly suitable due to its mechanical robustness, bio-compatibility, and the availability of well-developed industrial scale growth processes. Several designs for the fabrication of GaN-based piezoelectric nanogenerators (PNGs) with various morphologies such as thin film or 1D nanostructures have been reported [26–28]. Both 1D nanostructures and thin films have their merits and demerits; for example, the growth of thin films is relatively easy at higher temperatures, which means that it is very difficult to grow them on flexible substrates. Despite being difficult to grow, 1D nanostructures are being

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extensively studied in view of their advantages in the design of compact and efficient PNGs. The 1D structure results in enhanced piezoelectric properties of the material as compared to its bulk counterpart, and quasi-1D nanostructures also have enhanced d_{33} piezoelectric coefficients [29]. A variety of geometric structures such as nanorods [30], nanowires [31], nanotubes [32], triangular belts [33], nanoparticles [34], nanosheets [35], nanocomposites [36], and nanofibers [37] have been investigated to generate piezoelectricity. Among the above mentioned 1D nanostructures, nanowires are the most promising candidates for piezoelectric generation due to their superior mechanical properties, structural perfection due to the absence of defects such as dislocations, better strain confinement, and deformation up to a high elastic limit without plastic deformation [38]. Moreover, the high flexibility and high fatigue resistance can also improve the operational lifetime in nanowire-based PNGs [39,40]. Due to their compliance to small loads, mechanical energy can be converted efficiently in these structures, which means that a significant strain can be achieved under a very small applied force. Yun et al. fabricated nanowire- and nanotube-based PNGs using $LiNbO_3$ [41]. The piezoelectric output potential and current of the nanowire-based PNGs were found to be approximately two times higher than those observed in the nanotube-based PNGs. Zhu et al. fabricated a PNG using vertically aligned ZnO nanowires where a peak output voltage (open circuit) and current (short circuit) of 58 V and 134 μA were measured, respectively, leading to a maximum power density of 0.78 W/cm^3 [42]. Moreover, due to the higher aspect ratio and reduced stiffness under mechanical stress as compared to bulk materials, a higher piezoelectric output can be harvested using nanowires based PNGs [43].

In order to harvest the piezoelectric output from nanowires, Wang et al. used the Schottky contact configuration of an atomic force resiscope [44]. An alternative approach to harvest a superior piezoelectric output from nanowires is to form a matrix with nanowires [37,45]. Moreover, a thin film matrix can be used to form a homo or hetero junction p-n diode, which results in a dramatic improvement in piezoelectric output [46–48]. Thus, a rectifying contact such as Schottky junction, homojunction, or heterojunction p-n diode plays a vital role in efficiently harvesting the piezoelectric output. In the case of junction-based PNGs, the piezoelectric output is harvested in the reverse bias configuration. The Schottky junction exhibits a higher leakage current due to the presence of intrinsic defects at the metal-semiconductor interface. Moreover, the barrier height is also greatly influenced by the stress applied to Schottky junction-based PNGs [49]. In the case of homojunction GaN PNGs, there exist limitations of Mg doping in GaN, leads to a lower resistivity of the film and a higher leakage current for the reverse-biased p-n homojunction PNGs; this phenomenon is known as junction screening. In contrast, forming a heterojunction can be an appropriate choice to obtain a high-resistivity p type GaN-based material. The first GaN-based heterojunction piezoelectric generator with a very high piezoelectric potential of 26 V was reported by our group [46]. Moreover, GaN thin film based heterojunction PNG fabricated on flexible substrate demonstrated an output of 30 V [50].

In this work, the heterojunction was formed by depositing a highly resistive p-type NiO thin film on the GaN nanowire matrix with the aim of harvesting a very high piezoelectric output for GaN nanowire-based PNG fabricated on flexible substrate. Vertical c-axis GaN nanowires embedded in polydimethylsiloxane (PDMS) matrix were transferred onto a polyethylene terephthalate (PET) substrate, after which, p-type NiO was deposited to form a p-n heterojunction PNG. The piezoelectric output was measured by using both finger force and cyclic stretching–releasing agitation driven by a linear motor with frequencies up to 7 Hz. A very high piezoelectric output of 20.8 V and 253 nA was measured. The scientific principle behind the enhanced piezoelectric output which has been attributed to the suppression of junction screening, has been briefly discussed. Finally, the stability of the PNG was evaluated by performing a stability test for 20,000 cycles using cyclic stretching–releasing agitation.

2. Experimental procedure

Due to its non-centrosymmetric wurtzite crystal structure, monocrystals grown along the c-axis demonstrate piezoelectric bias under stress. The process flow for the fabrication of scalable-transparent-flexible (STF) PNG is shown in Fig. 1. To grow c-axis GaN nanowires, a c-axis GaN thin film was grown on a c-axis sapphire substrate using metal organic chemical vapor deposition (MOCVD). The nanowires were grown in the presence of a catalyst by the vapor-liquid-solid (VLS) technique. Gold was chosen as the catalyst and a 1 nm-thick thin film of gold was deposited by an electron beam evaporation system under high vacuum. Since gold has a very high melting temperature, we used In-Ga-Au alloy as the catalyst. Ultra-thin films of indium and gallium were deposited on the samples in the MOCVD reactor at 550 °C and 650 °C, respectively. The metal alloy has a melting temperature of 780 °C and agglomeration was carried out at 850 °C for 600 s in H_2 environment. The precursors for GaN, which were trimethyl gallium (TMGa) and ammonia for gallium and nitrogen, respectively, were introduced into the MOCVD reactor after agglomeration of the catalyst. The respective flow rates of TMGa and NH_3 were 26 μmol min^{-1} and 3.1 mmol min^{-1}. After the growth of c-axis GaN nanowires, the PDMS thin film was spin-coated on the nanowires with a spinning speed of 7000 rpm for 300 s to form the matrix of PDMS-GaN nanowires; the thickness of the PDMS layers was higher than the length of the nanowires to cover the tips of the wires. After hardening PDMS at 150 °C for 600 s, the matrix was flipped and transferred on indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrate using doctor blading. To form a p-n heterojunction, a 300 nm-thick p-type NiO thin film was deposited on the top side of the transferred matrix using RF magnetron sputtering; thus, the NiO thin film was in direct contact with GaN nanowires. NiO was deposited at room temperature under Ar flow (20 sccm) with 400 W RF power. Sputtering conditions were similar to those in our previous reports and the resulting NiO exhibited the same crystal quality and electrical properties [47,51]. A thin layer of PDMS was deposited again to make the structure mechanically more stable, after which, ITO was deposited to make the final/top contact on the STF PNG.

The STF-PNG was characterized using different techniques at the various stages of its fabrication. The morphology of the nanowires was confirmed using analytical high-resolution scanning electron microscopy (Hitachi SU-70; the growth direction (along c-axis) was confirmed from both high resolution transmission electron microscopy images and SAED patterns obtained using a field emission electron microscope (JEM-2100F, JEOL)). The transparency of STF-PNG was evaluated by measuring the transmittance at the end of the different fabrication steps, using a UV–Vis spectrophotometer (Lambda 950 spectrometer, Perkin-Elmer). The piezoelectric performance of STF-PNG was measured by a high-speed current-voltage measurement unit (PARSTAT 3000/Potentiostat/Galvanostat/ELS analyzer, Princeton Applied Research), while the device was actuated using finger force and cyclic stretching–releasing agitation.

3. Results and discussion

3.1. Growth and transfer

The wurtzite crystal structure shows non-centrosymmetry