Nitride Nanowires: From Rigid to Flexible Piezo-generators

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Abstract. Here we employ self-assembled Mg-doped GaN nanowires (NWs) grown by plasma assisted molecular beam epitaxy on Si(111) substrates to fabricate piezogenerators. We first discuss the fabrication and testing of rigid nanowire-based generators and then a flexible generator prototype is shown.

1. Introduction
The development of autonomous electronic equipment requires efficient and portable power supplies. Besides the solar energy, another renewable resource for small-scale energy harvesting is the mechanical vibrations. Thanks to their superior mechanical properties and high piezoelectric coefficient with respect to their bulk materials [1,2], piezoelectric semiconductor nanowires (NWs), in particular GaN NWs, have emerged as promising piezo-materials alternative to conventional piezoceramics to fabricate novel ultra-compact power sources.

2. GaN nanowires and their piezoelectric properties

2.1. Growth of GaN nanowires
Self-assembled GaN NWs were grown by Plasma-Assisted Molecular Beam Epitaxy (PA-MBE) on a thin n-doped AlN buffer layer [3] deposited on n-type doped Si(111) substrate (the NW morphology is illustrated in Figure 1). The growth was performed at 760°C, under N-rich conditions. NWs have a cylindrical shape with a hexagonal cross section delimited by \{10-10\} planes [4]. They are characterized by a height and diameter of the order of 1 µm ± 120 nm and 45 nm ± 20 nm respectively and by a density of the order of 10^9 NWs/cm².

2.2. Piezoelectric potential of individual GaN nanowires
The piezoelectric properties of single GaN NWs were investigated by atomic force microscopy (AFM) equipped with an adapted home-made Resiscope module [5]. By scanning over the array of vertical NWs, the conductive AFM tip bends the NWs and at the same time records the output voltage piezo-generated by the nanostructures in response to their deformation [6,7]. Figure 2 shows a 3D
representation of the output voltage generated by GaN NWs and collected by the AFM for normal constant force of 149 nN. The average and maximum outputs are respectively 228±120 mV and 350 mV.

**Figure 1.** Tilted (a) and cross section (b) SEM images of Mg-doped GaN NWs grown by PA-MBE on a Si(111) substrate. Inset of (a) displays a high magnification image showing NWs with a diameter as low as 50 nm.

**Figure 2.** 3D representation of output voltage generated by GaN NW array under the constant bending force (149 nN) of the AFM tip.

3. Fabrication and characterization of rigid piezogenerators

![Process steps](image)

**Figure 3.** Process steps to realize rigid piezogenerator device from self-assembled NWs.

3.1 Fabrication of rigid piezogenerators

To fabricate rigid devices, the as grown NW arrays are encapsulated into spin-on glass (HSQ), which is annealed at 400 °C. Then the NW tops are uncovered by doing reactive ion etching and the Schottky contact is deposited, though a shadow-mask, on the NW top side. Finally, an ohmic contact is directly deposited on the substrate (Figure 3).

3.2 Characterization of rigid piezogenerators

The device (Figure 4(a)) is tested by using a cyclic flexion strain setup showed in Figure 5(a). The measured device is fixed at two extremities, and is deformed by the applied force in the middle. Due to the difference of thickness between the substrate (350 µm) and the active layer (1 µm), and thanks to the strong mechanical adherence of the HSQ matrix to the NWs, the lateral bending of the device can induce a stretching of the matrix, thus a thinning of the active layer as a consequence of the volume conservation. This matrix deformation is transmitted to the embedded GaN NWs leading to their homogeneous compression, as illustrated on Figure 5(b).
Figure 6 presents the output voltage generated and synchronized with the magnitude of the force applied to bend the device. We can observe that the generation follows the applied deformation. The solicitation is conducted at low frequency, 3 Hz and 6 Hz separately. By considering the measuring circuit and the device shape, we estimate an average output power density of 6.35 mW/cm$^3$, and a maximum output power density of about 12.7 mW/cm$^3$ [8].

**Figure 5.** (a) Schematic of the setup used to characterize the GaN NW-based piezo-generator; The lateral bending of the generator induces a thinning and thus a compression of the active layer as illustrated in (b).

**Figure 6.** Output voltages generated by the piezo-generator as a function of its deformation for a bending cycle rate of 3 Hz (left) and 6 Hz (right).

4. Flexible piezogenerator
The flexibility enables the integration of devices on different objects with arbitrary shape and offers prospects for medical applications. To achieve flexible nanowire generators while keeping the advantages of vertical control-by-design NW arrays, we develop a fabrication method based on PDMS NW encapsulation, membrane lift-off and transfer to a flexible substrate.

First, we embedded the root part of the NWs in a very thin layer of photoresist. Then, diluted PDMS is spin-coated on the NWs to fully encapsulate the NWs array. By doing reactive ion etching, we uncover the top part of the NWs from PDMS layer with a free part length of about 100 nm. Then, a Schottky contact is deposited to fully cover the summits of the NWs, followed by another thick layer of PDMS in order to thicken the structure and facilitate its manipulation. After a short annealing and a submersion of the whole sample in acetone, we use a razor blade to peel the sandwich structure off the substrate and fix the membrane up-side down on another rigid substrate. Making sure that the entire membrane is generally flat over the substrate, we deposit ohmic contact on the NW base part. Finally, the membrane is again flipped and fixed on a flexible substrate. It is easy to get rid of the PDMS thick layer on the other side by simple mechanic lift-off after the sticking step. In this way, we can obtain a vertical-NWs-in-PDMS membrane with metallic contacts on both top and bottom sides of the layer.
(Figure 7). A SEM tilted image of this membrane is shown in Figure 8 and Figure 9 presents an optical image of the final device. The characterization of these flexible piezo-generators is in progress.

Figure 7. Process flow of the nanowires lift-off and the realization of flexible device

5. Conclusion
Here we demonstrate the fabrication of rigid and flexible piezo-generators integrating vertical array of GaN NWs. The measured results of rigid device set the new state of the art of piezogenerators based on GaN NWs. The generation of the flexible device is promising and is currently under measurement.

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