Topical Review

From single III-nitride nanowires to piezoelectric generators: New route for powering nomad electronics

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Abstract

Ambient energy harvesting using piezoelectric nanomaterials is today considered as a promising way to supply microelectronic devices. Since the first demonstration of electrical energy generation from piezoelectric semiconductor nanowires in 2006, the piezoelectric response of 1D-nanostructures and the development of nanowire-based piezogenerators have become a hot topic in nanoscience. After several years of intense research on ZnO nanowires, III-nitride nanomaterials have started to be explored thanks to their high piezoelectric coefficients and their strong piezogeneration response. This review describes the present status of the field of piezoelectric energy generation with nitride nanowires. After presenting the main motivation and a general overview of the domain, a short description of the main properties of III-nitride nanomaterials is given. Then we review the piezoelectric responses of III-N nanowires and the specificities of the piezogeneration mechanism in these nanostructures. Finally, the design and performance of the macroscopic piezogenerators based on nitride nanowire arrays are described, showing the promise of III-nitride nanowires for ultra-compact and efficient piezoelectric generators.

Keywords: GaN nanowires, piezoelectric properties, energy harvesting, nanogenerators, piezogenerators

(Some figures may appear in colour only in the online journal)

1. Introduction

Portable electronic equipment such as biomedical devices, portable multimedia, distributed sensor networks or mobile communication are omnipresent in our daily life and the question concerning their autonomy is a key societal challenge. Electronic devices have known tremendous progress in recent decades with the development of systems at micrometer and even nanometer scale. Device miniaturization, in particular, results in the reduction of their energy consumption to milliWatt and even microWatt. Despite the recent progress in the development of batteries with high-energy density (Miller and Simon 2008, Armand et al 2009) as well
as of nanobatteries, these sources are not ideally suited to supply electronic microdevices since they present limitations such as complex integration, limited capacity and considerable cost. In this context, new competitive ultra-compact and integrable electrical sources should be developed generating sufficient power to supply the microdevices without increasing the microsystem size and adding weight.

Energy harvesting, i.e. conversion of the ambient energy found in the vicinity of the device into usable electrical energy, appears as the most promising way for powering wireless microdevices. Among the alternative sustainable energy resources, mechanical deformations and vibrations present the advantages of being ubiquitously available at all times and more accessible than solar and thermal energies. The vibration energy may have various origins such as body movements, sound vibrations, hydraulic movements, wind, friction, etc. The harvesting of this energy through the use of piezoelectric materials has, in recent years, received much attention due to the ability of these materials to convert mechanical deformation directly into electrical energy.

Piezoelectric energy harvesting is not a new concept. It has been practised for decades at the macroscopic scale and commercialized. The most common application of piezoelectric materials is the fabrication of sensors and actuators. However, their use as electrical generators remains, until now, rather limited (the best-known applications are the quartz used in watches or the electric cigarette lighter). Indeed, the power output from conventional bulk piezoelectric ceramics is low. In addition, bulk materials are not well suited to energy-harvesting applications since they are massive, not easily integrable and their sensitivity to ambient mechanical vibrations is very weak. To increase the sensitivity to the applied force and thus the conversion efficiency, micro-structured piezo-composite materials such as for example 1–3 connected ceramic-polymer composites have been developed (Chan et al. 2005). However, the fiber diameter in these materials (tens to hundreds of microns) remained rather big. With the development of nanotechnologies, it has been shown that further downscaling of the fiber dimensions, i.e. their replacement by nanowires (NWs), can significantly enhance the conversion efficiency.

Semiconductor NWs presenting piezoelectric properties have recently emerged as excellent candidates to fabricate novel ultra-compact and efficient piezoelectric generators. Due to their specific structural properties, these 1D-nanostructures can enhance the piezoelectric properties of the material compared to its bulk or 2D form. In particular, the NWs present superior mechanical properties. Due to the structural perfection of NWs, resulting in the absence of defects, such as dislocations, they can be subject to large elastic deformation without plastic deformation or fracture (Yang et al. 2010). They are also characterized by higher flexibility, higher robustness and higher resistance to fatigue, which extend the operational lifetime of the piezogenerator. The NWs can be bended under an extremely small applied force due to the small diameter and the large aspect ratio characterizing these 1D-nanostructures. Hence, it is possible to generate a significant strain in the NWs under pico/nano-Newton applied forces (Zhou et al. 2013). Finally, as illustrated in table 1, quasi-1D geometry results in an enhancement of the piezoelectric coefficients in comparison with their bulk counterparts, due to surface effects (Zhao et al. 2004, Agrawal and Espinosa 2011, Minary-Jolandan et al. 2012).

The first electricity generation from the mechanical deformation of ZnO NWs has been demonstrated by the group of Prof. Wang from the Georgia Institute of Technology in the USA (Wang and Song 2006). Since this first demonstration, several 1D-nanostructures including nanostructured conventional piezoceramics have been studied, such as CdS (Lin et al. 2008), CdSe (Zhou et al. 2012), PZT (Chen et al. 2012), BaTiO3 (Wang et al. 2010), etc. Despite their strong piezoelectric response (Bernardini et al. 1997), III-nitride nanostructures have been studied far less than ZnO. These materials, crystallizing in wurztite phase with hexagonal structure, are characterized by a strong internal electric field, which results from the combination of the spontaneous and piezoelectric polarizations. The first electric generation resulting from the deformation of a GaN nanorod was evidenced in 2007 by Su et al. (Su et al. 2007). The investigation of the piezoelectric properties of GaN NWs was then continued by different groups (Xu et al. 2010, Huang et al. 2010b, Xu et al. 2011, Gogneau et al. 2014). Nitride NW materials other than GaN were investigated, namely AlN, AlGaN (Wang et al. 2010b) and InN (Huang et al. 2010, Xu et al. 2012). To date, the best mechanical-electrical conversion from NWs in terms of the output voltage has been obtained with GaN and InN NWs, with a maximum generated voltage per NW of about 440 mV (Gogneau et al. 2014) and 1 V (Huang et al. 2010), respectively. These output voltages measured from single piezoelectric III-N NWs are larger than those for other piezoelectric semiconductors, and in particular ZnO NWs, which is today the most widely used material in nanostructure-based piezogeneration and whose output voltages do not exceed 45 mV (Gao et al. 2007) and 80 mV (Lu et al. 2009), respectively, for n-doped and p-doped materials.

It should be noted that semiconductor NWs such as ZnO or nitrides differ from conventional piezoceramics by the presence of free charges (controlled by doping), which impact the piezoconversion. From the theoretical viewpoint, the finite element method is usually used to analyze the piezoconversion with semiconductor NWs and in particular to predict the electric potential resulting from their deformation (see for example (Hinchet et al. 2014)).

The studies of the piezoelectric properties of individual semiconductor NWs have naturally lead to the development of macroscopic NW-based piezogenerators. To avoid confusion existing in the literature, in this review we define a

| Table 1. Piezo coefficient $d_{33}$ (pm V$^{-1}$) for low-dimensional and bulk GaN and ZnO. |
|-----------------|-----------------|-----------------|
| Material       | Low-dimensional | Bulk            |
| ZnO            | 14.3–26.7 (Zhao et al. 2004) | 9.93 (Zhao et al. 2004) |
| GaN            | 12.4 (Minary-Jolandan et al. 2012) | 2.8–3.7 (Guy et al. 1999) |
‘nanogenerator’ as a single NW producing electricity via a piezo effect, while we call a ‘nanowire-based piezogenerator’ a macroscopic device based on a NW array. The first prototype of an integrated piezogenerator realized by Prof. Wang’s group was based on a single layer of ZnO NWs and exhibited an operational power output of approximately 2.5 nW cm$^{-2}$ (Wang et al. 2007). Subsequent realizations have significantly improved the performance of the ZnO-based piezogenerators. Three different configurations have been introduced: the lateral NW integrated nanogenerator (LING) (Xu et al. 2010), the nanocomposite electrical generator (NEG) (Momemi et al. 2010) and the vertical NW integrated nanogenerator (VING) (Xu et al. 2008). Interest in the use of flexible substrates to fabricate NW piezogenerators was first evidenced by a new prototype based on cyclic stretching/releasing of a single piezoelectric wire packaged on a flexible substrate. Such a nanogenerator configuration producing an AC output voltage of around 50 mV has been reported as being very attractive for harvesting biomechanical energy (Yang et al. 2009). The advantage of this flexible support has been combined with the VING configuration in order to increase the generator performance. An output power density in the order of several hundreds of mW cm$^{-3}$ was reported (Zhou et al. 2013a).

A fundamental difference should be noted between NW piezogenerators and piezoelectric micro electromechanical systems (MEMS). MEMS operate in a resonant mode (with a typical resonance frequency in the MHz range), which is not efficient for energy harvesting from ambient vibration sources, which are either non-periodic or have a low frequency (typically below 200 Hz). In contrast, the enhanced flexibility of NWs enables the operation of NW generators in a quasi-static regime, so that the amount of converted energy is determined not by the operating frequency, but by the number of active NWs (Ardila et al. 2012).

From ZnO NW-based piezogenerator prototypes, self-powered nano-systems without an external battery have been demonstrated, including pH, UV (Xu et al. 2010), chemical (Li et al. 2010) and biological sensors (Lee et al. 2011), commercial or nanostructured light-emitting diodes (LEDs) (Zhu et al. 2010, Chen et al. 2012b), liquid-crystal-display (CCD) screens (Hu et al. 2011) or wireless radio frequency data transmitters (Hu et al. 2011b). Finally, piezogenerators based on ZnO NWs have been applied to self-powered nanodevices for in vivo biomedical applications by harvesting biochemical energy (Pan et al. 2010) or a combination of biomechanical and biochemical energy (Hansen et al. 2010, Pan et al. 2011, Lee et al. 2014).

Although ZnO NWs remain, today, the dominant material investigated for the development of NW piezogenerators, the field has been extended to other materials such as PVDF (Chang et al. 2010) or PZT nanofibers (Chen et al. 2010). Concerning III-nitride nanostructures, to the best of our knowledge, only a few macroscopic piezogenerators based on nitride NWs have been reported in the literature. The first prototype consists of multiple layers of dispersed NWs embedded in polymethyl methacrylate (PMMA) (Lin et al. 2011), while the second is based on vertically aligned InN NWs (Liu et al. 2016), with both generators exhibiting an output power density of ~0.3 mW cm$^{-3}$ and ~0.15 mW cm$^{-3}$, respectively (calculated from the published data). Finally, the third piezogenerator integrating a vertical array of GaN NWs was reported to generate a power density in the order of 12.7 mW cm$^{-3}$ (Jamond et al. 2016), which approaches the best values reported for ZnO NW-based piezogenerators (Zhu et al. 2012). Piezoelectric properties of nitride NWs have also been used for applications other than energy harvesting. For example, high sensitivity pressure sensors based on GaN NWs have been reported (Zhou et al. 2013, Salomon et al. 2014). In general, the interplay between the semiconducting and piezoelectric properties in nanostructures today receives increasing attention since it offers new, interesting functionalities (Wen et al. 2015).

It should be noted that there is no consensus in the literature on how to evaluate the generated power of a NW-based generator in a normative way. The electrical performance is either given in absolute values or is normalized with respect to the generator volume or surface area. Different electrical load circuits are used, so that comparison between different reports is not straightforward. In this review, when the generated power is not given, we try to estimate it from the parameters provided in the publications, where possible.

Numerous realizations show the capability of NW piezogenerators to produce electrical power in the $\mu$W—mW range. Their use for energy harvesting thus appears as a very promising concept for realizing self-powered microelectronics. However, the optimization of the mechanical-electrical conversion of individual NWs and of the macroscopic generator architecture are crucial issues for the development of efficient devices. In this review, we address the status of these two technological challenges, restricting ourselves to the specific case of III-nitride NWs. After a short description of the main properties of III-nitride nanomaterials for piezogeneration in section 1, the piezoelectric responses of III-N NWs and the analyses of the piezogeneration mechanism are presented in section 2. Section 3 is dedicated to the overview of the existing piezogenerators based on nitride NW arrays.

2. III-Nitride NWs

III-nitride NWs have been intensively studied from the early 2000s. The strong interest in these nanomaterials has been mainly stimulated by their numerous optoelectronic applications, in particular for light emission. Nitride NWs can be elaborated by different growth techniques, of which the most widespread ones are chemical vapor deposition (CVD), molecular beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE). III-N NWs grown by MBE are particularly interesting for piezogeneration, since this technique allows for ultimate control over the NW properties such as their size, aspect ratio, doping level, etc (Bertness et al. 2007, Songmuang et al. 2007, Tchernycheva et al. 2007). In addition, NWs with diameters as small as 20 nm can be achieved, as illustrated in figure 1.

III-nitride NWs crystallize in wurtzite structure, where the cations and anions form a tetrahedral coordination. The III-N
materials are characterized by the absence of inversion symmetry, which confers on them two important characteristics. The first is the presence of polar surfaces with metal-terminated (0001) and N-terminated (000-1) orientation (figure 2). These two faces are not equivalent and present different properties, such as different surface morphologies, optical and kinetic properties (Feenstra et al 2002, Huang et al 2002, Jang et al 2002). The second characteristic is the existence of an internal polarization along the \( z \)-axis. This consists of the sum of the spontaneous polarization \( P_{SP} \) and piezoelectric polarization \( P_{PS} \). When the hexagonal structure is at equilibrium, i.e. not subjected to an external deformation, the centroids of the positive and negative charges do not coincide. This results in the formation of a set of dipoles oriented along the same direction, leading to the appearance of a macroscopic polarization in the material, the so-called spontaneous polarization, \( P_{SP} \) is aligned with the \( z \)-axis and oriented from N to Ga atoms. Thus \( P_{SP} \) is parallel to the (000-1) growth direction and anti-parallel to the (0001) growth direction, as illustrated in figure 2. The piezoelectric polarization results from the relative displacement of the Ga cations with respect to the N anions along the deformation direction when a stress is applied to the material. Its orientation along the \( z \)-axis is driven both by the \( P_{PS} \) orientation and the strain created inside the materials. Hence, under axial compression, \( P_{PS} \) is oriented anti-parallel to the \( P_{PS} \), while it is parallel to the \( P_{PS} \), under axial stretching.

3. Piezoelectric properties of III-N NWs

The performance of a piezoelectric energy-harvesting system primarily depends on the piezoelectric properties of the material used to fabricate the generators. For this reason, it is of great importance to quantify the mechanical-electrical conversion efficiency and the achievable output power of the NWs as a function of their structural and electric characteristics.

One of the most common methods to measure the piezoelectric effect in NWs consists of a lateral bending of the nanostructure, while simultaneously measuring the generated electric potential resulting from the NW deformation. The atomic force microscope (AFM) equipped with an electrical module is a powerful tool for measuring the piezoelectric properties of 1D-nanostructures. In fact, this nondestructive characterization technique combines the scanning and deflection measurement capabilities with a nanometer-scale resolution and the real-time electrical measurements under the usual AFM scanning conditions.

The general principle of measurements is as follows: The conductive AFM tip is brought into contact with the surface of the GaN NWs under a controlled and constant normal force. During the imaging, the tip induces a local bending of the NWs. In response to this deflection and due to the piezoelectric effect, the NWs generate a voltage which is detected through the conductive AFM tip. Throughout measurements, both the topographic and the electrical signals (output current or output voltage) are recorded continuously and simultaneously. In this specific instrumental configuration, the external electrical system is connected via an ohmic contact formed between the NWs and the substrate, and a Schottky contact formed between the NW top and the AFM tip, which ensures the charge recuperation for piezogeneration (Liu et al 2008). No external voltage is applied and the voltage waveform generated by the NW is observed across a load resistance \( R_L \).

Two different configurations are usually used to perform these measurements: The first is the scanning configuration (figure 3(a)). In this configuration, the AFM probe scans laterally a vertical array of NWs. The NWs are subjected to an external lateral force resulting from the convolution of the constant normal force and the lateral force resulting from the tip/sample relative displacement. Nanostructures are bended under this external force and an electric field is created inside the nanostructure through the piezoelectric effect. Depending on the distribution of potential within the bended NW and the position of the conductive tip on its surface, the Schottky junction formed between the metal tip and the semiconductor NW can be reversely-biased or forward-biased. In this configuration, by soliciting successively each NW over the entire surface scanned by the AFM tip, it is possible to map simultaneously the topography and voltage/current peaks.

The second configuration is the perpendicular bending configuration (figure 3(b)). In this specific instrumental configuration, the sample is vertically mounted so that the conductive AFM tip applies a local force perpendicular to the free-standing NW at a selected force location. This method allows a direct bending of individual NWs and provides a more precise control of the applied force and its point of application. However, because the conductive AFM tip is only in contact with the stretched side of the bended NW, the Schottky diode has to be forward-biased, which implies that for this technique to be effective, a given distribution of the...
piezoelectric potential within the nanostructure is needed (which in turn depends on the specific characteristics of the nanostructure such as doping and polarity, as detailed in section 3.2).

3.1. Piezogeneration analysis of individual III-N NWs

The first demonstration of the generation of electrical energy from the mechanical deformation of 1D III-nitride nanostructures was done by Su in 2007, by bending GaN nanorods with an AFM in the scanning configuration (Su et al. 2007). An output current with a magnitude of \( \sim 0.03 \, \text{nA} \) was measured as illustrated on figure 4(a). The increase in the output current magnitude with the scanning speed has also been evidenced. The authors assigned this effect to the transfer of kinetic energy resulting from the displacement of the nanorods induced by the scanning of the AFM tip to the elastic energy of the bended nanorods (Su et al. 2007).

In contrast to ZnO NWs, which have engendered wide enthusiasm for the piezogeneration application, nitride nanostructures have been studied far less, despite these promising early results. It was probably related to the need for more sophisticated elaboration tools for nitride NW synthesis. It was not until 2010 that nitride nanostructures started to be actively studied as potentially interesting candidates for the development of piezoelectric generators. The group of Prof. Wang, who introduced the concept of a single ZnO NW-based nanogenerator (Wang and Song 2006), has measured the piezoelectric response of the nitride binary nanostructures, GaN, AlN and InN and of the ternary alloy AlGaN (figures 4(b)–(e)).

Wang and co-workers (Wang et al. 2010b) have evidenced the detection of sharp output voltages for all the nitride nanostructures, except for AlN nanococones. Hence, outputs of about 4, 7 and 60 mV, respectively, for AlGaN, GaN and InN nanococones have been measured using the AFM technique in a scanning configuration. The authors attributed this dispersion in the observed output voltages for the different analyzed nanomaterials to the difference in their conductivity, mainly related to the carrier density. Following their consideration, the AlN nanostructures produced no output signal due to their very high resistivity, while the InN nanocones, due to their high conductivity, generated the largest output voltage. The promise of GaN and InN nanostructures...
for piezogeneration has been confirmed with the measurement of output voltages reaching 300 mV (Chen et al 2012) and 1 V (Huang et al 2010) per single GaN and InN NWs, respectively (figure 5). This output voltage achieved for InN remains, to date, the highest value for any type of piezoelectric semiconductor NW.

To better understand the piezoelectric response of III-nitride nanostructures, the group of Montès has investigated the
output voltage generated by intrinsic GaN and GaN/AlN/GaN heterostructured NWs grown by plasma-assisted MBE (Xu et al 2011). The AFM technique in the perpendicular bending configuration was employed. The authors have observed that for both types of NWs, the electrical potential increases as a function of the applied force, as illustrated in figure 6(a). The impact of the rate with which the NW is deformed has also been investigated (figure 6(b)), highlighting a good stability and a high reproducibility of the piezo-generated potential.

The perpendicular bending configuration of the AFM technique offers a very good control over the force and the position where this force is applied to the nanostructure. By
intrinsic GaN NWs generated a potential in the order of 17 mV, AlN NWs (conditions comparing the two sets of samples under the same experimental Figure 7. (a) Output voltage generation as a function of the NW deflection for an intrinsic GaN NW (red) and a GaN/AlN NW (blue). (b) Relation between the NW deflection and the measured electrical generation for an intrinsic GaN NW (red) and a GaN/AlN NW (blue). (Reproduced with permission from (Xu et al 2011), copyright IOP Publishing.)

comparing the two sets of samples under the same experimental conditions \( F_{\text{Applied}} = 250 \text{nN} \), the authors observed that the intrinsic GaN NWs generated a potential in the order of 17 mV, while this potential reached 200 mV for heterostructured GaN/AlN NWs (Figure 7(a)). In addition, to evidence the impact of the NW structure, the authors experimentally analyzed the relation between the NW deflection and the measured electrical generation (Figure 7(b)). The deflection-generation curve can be described as being composed of three parts. In the cut-off region, i.e. at the beginning of the manipulation, although the deflection is already non-zero, the created piezoelectric potential is too small to allow charges to cross the Schottky barrier, and thus no output signal is detected. In the quasi-linear region, the NW deflection induces a sufficient potential to open the Schottky barrier. The output voltages can thus be measured in this regime and are found to increase linearly with the NW deflection. Finally, in the saturation region, the NW deflection becomes very large. The internal piezoelectric potential cannot increase further due to the saturation of the rotation of electric dipoles (Donald 2007), and thus the electrical output saturates.

Piezoelectric conversion mechanisms of III-nitride NWs were further analyzed by Gogneau et al (Gogneau et al 2014). The authors investigated the output voltage generation of a vertical array of intrinsic n-doped GaN NWs as a function of the applied force by using AFM equipped with a Resiscope module in the scanning configuration (Schneegans et al 2011). With this technique, the authors acquired large measurement statistics, with the output signal distribution reflecting the dimension dispersion of the NWs. However, because of the convolution of the normal force and the lateral force due to the scanning movement of the tip (as illustrated in Figure 3(a)), the nanostructures are subjected to a higher degree of deformation than when they are stressed by a normal force (perpendicular bending configuration of Figure 3(b)). Under these conditions, the quantitative analysis of the piezogeneration efficiency of the NWs is technically very complex due to a very strong NW deformation bringing them directly into the saturation regime. In order to reduce the NW bending and thus to achieve more reliable electrical measurements, the NWs were mechanically consolidated by embedding their base part into a PMMA layer (more details can be found in (Gogneau et al 2014)). Figure 8 presents the 3D output voltage maps of a partially encapsulated GaN NW array recorded at different constant normal tip forces. As Xu et al observed on single NWs in a quasi-linear region (Xu et al 2011), Gogneau et al showed a statistical enhancement (i.e. enhancement of the maximal value and of the average value) of the signal generated by the ensemble of GaN NWs with increasing the applied force. Two phenomena were put forward to explain this behavior. The first followed the consideration of Xu et al (Xu et al 2011) on the potential versus NW deflection relation. As the NW deflection increases, the resulting internal piezoelectric potential increases, in agreement with theoretical predictions (Gao and Wang 2007). The second phenomenon put forward by Gogneau et al considered the harvesting of the generated energy. The increase of the force applied by the conductive AFM tip leads to a larger surface of the Schottky contact and thus to the improvement of the metal-semiconductor contact stability (Perea-Garcia et al 2007). This improved contact allowed then a better harvesting efficiency.

From these measurements performed on a large array of GaN NWs, a statistical analysis of the piezoconversion capacity of the nanostructures was given. An average output voltages of \(-74 \text{ mV}\) and a maximal value of \(-443 \text{ mV}\) per NW were obtained. This latter value largely exceeds the maximum
voltage generated by single ZnO NWs (45 mV (Gao et al 2007) and 80 mV (Lu et al 2009) for n-doped and p-doped ZnO NWs, respectively) and represents the highest output voltage reported for GaN NWs. It is noteworthy, that in contrast to Xu et al (Xu et al 2011), the electric signal for the largest force measured by Gogneau et al did not reach saturation. This means that the generated output voltage can potentially exceed $-443 \text{ mV}$ with the increase in the NW deflection.

Several other groups have presented AFM characterizations of single piezoelectric properties of nitride NWs, demonstrating their promise as nanogenerators (Huang et al 2010, Wang et al 2010b, Xu et al 2011, Gogneau et al 2014). On the basis of these AFM characterizations performed on free-standing nitride NWs, power densities reaching several hundreds of mW cm$^{-2}$ (Su et al 2007, Xu et al 2011, Chen et al 2012b, Gogneau et al 2014) were estimated. These estimations are usually done for an ideal case under a hypothesis that all NWs show the same piezoelectric behavior (by taking the highest measured output and multiplying by the NW density). Although this way of calculating the output power surely leads to an overestimation, it still demonstrates the potential of GaN NWs to generate high output energy. Therefore, III-N NWs can be used as an active material in ultra-compact and integrable renewable energy sources for sustainable, independent and maintenance-free operation of microdevices.

3.2. Mechanical-electrical conversion mechanisms in III-N NWs

The enhancement of the mechanical to electrical energy conversion necessary for developing optimized NW-based piezogenerators requires a fundamental understanding of the piezoelectric mechanisms taking place inside the nanostructures. Again, the AFM in scanning mode is well suited to analyze the mechanical-electrical conversion mechanisms in individual NWs. Since this nanometer-scale-resolved technique allows simultaneous recording of topographic and electrical signals, it is possible to directly correlate the morphology of a given bent NW with its generated voltage peak. This correspondence was established in (Su et al 2007, Gogneau et al 2014b) highlighting that the piezogeneration of nanostructures is always observed when the AFM tip gets into contact with the stretched side of the n-doped GaN nanostructures, i.e. when the tip gets into contact with the NW and the deflection starts (figure 9).

The opposite behavior was observed for n-doped ZnO NWs: in this case, the output signal is generated when the tip is in contact with the compressed side of the NW (Wang 2008, Lin et al 2009). To understand this difference, the piezoelectric properties of the nanomaterials and their doping and polarity characteristics have to be considered. In both cases, the NWs are n-type doped. This electrical characteristic is confirmed by the negative output signals measured by AFM (Lin et al 2009). The GaN nanostructures are also characterized by being terminated by N-polar surface (N-polarity) as has been demonstrated by KOH etching (Su et al 2007, Largeau et al 2012). These two specificities are of great importance, since they determine the behavior of the Schottky diode formed at the interface between the bended GaN NW and the conductive electrode (AFM tip).

When the GaN nanostructure is laterally bended by the AFM tip in scanning configuration, an asymmetric strain is...
created across the NW. The inner side of the 1D-object is compressed leading to a negative strain, while the outer side is stretched leading to a positive strain, as illustrated in figure 10(a). As a consequence of this strain field, a PZ appears inside the nanostructure. Under compression, the PZ is oriented anti-parallel to the PS (oriented parallel to the growth direction since the nanostructure is N-polar terminated) and thus oriented opposite to the growth direction, while under stretching, the PZ is parallel to the PS and aligned with the growth direction. Due to the specific orientation of the PZ in the N-polar GaN NWs, the piezoelectric potential distribution in the wire evolves between $V_S^+$ at the compressed facet and $V_S^-$ at the stretched facet (figure 10(b)). From this potential distribution through the NW volume, two different situations occur at the Schottky contact (figure 10(c)). When the AFM tip starts to deflect the n-doped GaN nanostructure, the contact between the tip and the stretched side is a positively biased Schottky diode ($\Delta V = V_m - V_S^- > 0$, where $V_m$ is the potential of the metal tip, close to zero under standard conditions). Since the majority of carriers are electrons, charges flow across the interface driven by the piezoelectric potential, resulting in an external output voltage detected across the load resistance. By contrast, when the conductive tip reaches the compressed side of the nanostructure, the Schottky diode is reversely-biased ($\Delta V = V_m - V_S^+ < 0$) and the charge flow across the interface is blocked, explaining the absence of output voltage.

By comparison, the n-type doped ZnO NWs are characterized by metal polarity, i.e. the NWs are terminated by Zn atoms (Wang et al 2003, Wang 2007b). This metal polarity of the ZnO NWs orients the SP anti-parallel to the growth direction. The PZ in metal-polar structures is thus oriented in the opposite direction in comparison with the anion-polarity structures (N-terminated GaN). Consequently, the electric potential through the metal-polar ZnO NWs evolves between $-V_S^+$ at the compressed side and $+V_S^+$ at the stretched side. This difference in crystal polarity inducing a difference in potential distribution explains the different generation behavior between n-doped ZnO and n-doped GaN NWs.

By considering this mechanism, the piezogeneration of p-doped N-polar GaN NWs should be detected on the compressed side of the NWs. In order to verify this point, Gogneau et al have grown and characterized by AFM in scanning mode an array of N-polar Mg-doped GaN NWs (Jamond et al 2016). Indeed, the generation was observed only when the AFM tip was in contact with the compressed side of the NW due to the opposite behavior of the Schottky diode and the sign of the output voltages was changed to positive, as expected for a p-doped structure. This is illustrated in figure 11.

The results described in this section demonstrate that the piezogeneration mechanism crucially depends on the polarity and doping characteristics of the nanostructures, which is of crucial importance to design optimized piezoelectric generators and maximize their conversion efficiency.
4. Piezoelectric generators based on III-N NWs

Investigations of the piezoelectric energy harvesting by III-nitride individual nanostructures have prepared the development of macroscopic NW-based piezoelectric generators. Today, in spite of the numerous and very promising results obtained on single nanostructures, to the best of our knowledge, only three macroscopic (i.e. with hundreds of micrometers to centimeter dimensions) piezogenerators integrating arrays of III-nitride NWs have been reported in the literature.

The first prototype was proposed by Prof. Wang and coworkers in 2011 (Lin et al. 2011). It consists of multiple layers of dispersed GaN NWs embedded in PMMA, and sandwiched by two metal electrodes of Cr/Au, the ensemble of the device being supported by a film of Kapton, as illustrated in figure 12(a). To mechanically solicit this generator, the device has been attached to a flexible polystyrene substrate, to which an external force has been applied to bend the generator. Output voltages and output currents up to 1.2 V and 0.16 μA cm⁻² have been measured (figure 12(b)). By considering the dimensions of the devices, namely an effective size of 5 × 5 mm for a thickness of approximately 6.4 μm, a power density of 0.16 mW cm⁻³ can be estimated.

The second prototype published very recently (Liu et al. 2016) integrates either vertically aligned p-doped InN NWs or intrinsic InN NWs. The nanostructures are embedded into PMMA and the Schottky contact necessary to detect the piezoelectric signal is formed between the InN NWs and the MoO₃/Au electrode (figure 13(a)). The piezogenerator devices have been tested under external dynamic strain by anchoring the substrate on a fixed stopper, leaving the top electrode facing outward. By moving up and down the system, a periodic strain was applied. The response of the device to the mechanical solicitation appears in the form of voltage (current) spikes, as shown in figure 13(b). Open-circuit voltage and short-circuit current of ~55 mV and ~211 nA for a p-type piezogenerator and of ~85 mV and 80 nA for an intrinsic-type piezogenerator have been measured for the same experimental solicitations. The power production of the p-type piezogenerator was found to be 70% more than the power production of the intrinsic generator, reflecting better piezoelectric energy conversion efficiency for p-type doped NWs.

A third piezogenerator prototype (Jamond et al. 2016) is based on a vertical array of dense GaN NWs. A similar vertical design was proposed by the group of Montes in 2012 (Montes et al. 2012). However, the device characterization...
details have not been published. In the work of Jamond et al, the device consists of an array of p-doped GaN NWs several square millimeters in size embedded into spin-on glass with a Schottky contact for rectification and collection of the piezo-generated carriers (figure 14(a)). For p-doped GaN NWs having nitrogen polarity, the top Schottky contact collects the carriers under compressive strain. In order to homogeneously strain the active spin-on glass layer, the generator is clamped by inducing a vertical movement of its central part (figure 14(b)). Due to the difference in thickness between the substrate (350 μm) and the active layer (~1 μm), the lateral bending of the device induces stretching of the spin-on glass matrix and, as a consequence of the volume conservation, a thinning of the active layer. The spin-on glass deformation is transmitted to the embedded GaN NWs leading to their homogeneous compression (figure 14(b)). In response to a periodic stressing, the device generates a voltage signal synchronized with the magnitude of the applied force (figure 14(c)). The piezogenerator exhibits a saturated maximal output voltage of about 200 mV, resulting in a maximum output power density of about 12.7 mW cm⁻³. This value decides the new state-of-the-art for piezogenerators integrating arrays of GaN NWs and more generally nitride NWs, and offers promising prospects for the use of GaN NWs for high-efficiency ultra-compact energy harvesters.

5. Conclusion and perspectives

Piezogenerators based on nitride NWs show promising performance with generated power densities that are already interesting for real-world applications (e.g. supplying of remote wireless transceivers, etc). However, the performance of macroscopic devices is still far from the estimations done by extrapolating the best value measured for single NWs to...
the NW array. It is, therefore, clear that the optimization of the NW properties and in particular a better wire-to-wire homogeneity would allow us to enhance the generator performance. NW arrays grown by selective-area epitaxy can respond to this need. The impact of different NW characteristics (alloy composition, structure, dimensions, density and conductivity) on the piezoelectric conversion also needs to be explored.

Semiconductor NWs open the possibility for new designs and new functionalities beyond simple size reduction. Axial or radial heterostructures that can be incorporated into NWs can be used to engineer strain in the active region to further enhance the energy generation. Indeed, when a NW heterostructure contains materials with different lattice constants with layer thicknesses below the critical thickness for relaxation, an elastic strain is created inside the NW modifying the built-in electric fields and the piezoresponse. One example of the usefulness of this strategy is given by the analogy that can be drawn with existing piezo-actuators using prestrained materials to achieve symmetrical voltage response and to improve linearity. Besides, barriers of a higher bandgap material (Xu et al. 2011) can be used to localize the free carriers and thus to engineer the internal impedance of the NWs.

Along these lines, it is very likely that future research and development of NW-based piezogenerators will bring these devices to maturity and to the world of real widespread applications as miniature portable energy sources.

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