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# Fabrication and Characterization of ZnO Nanowire-Based Piezoelectric Nanogenerators for Low Frequency Mechanical Energy Harvesting

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## Abstract

The present work investigates the possibility to charge a Lithium micro-battery (LiB) via direct conversion of ambient mechanical energy into electricity using piezoelectric ZnO nanowire (NW) based microgenerators (PGs). An estimate is provided for the power levels at the different stages of mechanical-to-electrical energy conversion chain, in the following areas: (1) PG output, (2) power management block and (3) LiB storage unit. Also covered in this work is the synthesis, which is a prerequisite for realising such PGs. ZnO NWs of 2 µm in length and 200 nm in diameter have been grown using a low temperature (<150 °C) hydrothermal process on 100 µm thick PET substrates (25 × 25 mm$^2$). Substrates containing bi-layer metal layers with dissimilar electro-negativities functioned as a galvanic cell in the growth nutrients, which acted as an electrolyte medium. This necessitated ZnO NWs growth on conductive surfaces, even in the absence of seed layers and/or substrate with specific lattice parameters. Finally, the assembly steps undertaken to realise the fully functional PGs are discussed, and the performances of the final PG are described thereafter. Subjecting such devices to a 10Hz sinusoidal bending force resulted in a measured PG output of ~56 mV peak to peak, on 1 MΩ resistive load.

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*Keywords:* Piezoelectric; Nanogenerators; Zinc oxide; Nanowires

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## 1. Introduction: Mechanical energy harvesting

Since the early 2000's, many new applications related to nomad electronics need "portable" electrical energy. Huge research efforts on Lithium (Li) based batteries have led to performances that made this technology the most popular for rechargeable batteries with the best energy densities. Recent efforts have also been done in order to charge them using renewable energy systems such as a photovoltaic cell. In some specific applications, the later sources of energy are not directly available. In such cases, an alternative source of energy to charge the Li battery is necessary. The mechanical ambient energy is a source of interest.

In this context, the heart of the project is to develop a prototype that integrates, on the same flexible chip, a Piezoelectric Generator (PG) that converts this ambient mechanical energy into electrical energy that can recharge a lithium battery (through a specific electrical converter). The efficiency of such a mechanical harvesting device strongly depends on the matching between: the electromechanical conversion block (the PG); the power management block; the electrical load block (a Lithium micro-battery).

### *1.1. Available mechanical sources*

In order to estimate the interest to harvest part of the "free" energy from ambient mechanical sources, some important questions must be asked, in particular on the frequency range and the amplitude of the mechanical excitation, its truly free nature, its continuous or intermittent availability, the proximity of the electrical network, the interest of wireless electronic devices... Ambient mechanical sources are encountered on vehicles (up to 300 W at 105 km/h [Singh et al. (2012)]), industrial machines, traffic ways (roads, bridges, tunnels), passage ways, wind turbines, pipelines... or on human beings (up to 1W for exhalation [Lin et al. (2013)]).

### *1.2. Lithium micro-battery*

In applications like industrial machines, trains or automotive, mechanical energy is continuously available and sufficient to power sensors, to take readings and to transmit data. But in other applications where mechanical energy is intermittent or presents insufficient levels, some form of energy storage will be necessary. Moreover, some targeted components, like the microcontroller or the RF transceiver, need a power burst up to tens of milliwatts. In addition, most electronic circuits require voltages of at last 1.8V, sometimes 3.3V or more. In order to deliver the necessary energy burst, this energy must be temporarily stored in a battery or a supercapacitor, or a low loss capacitor if the operating temperature is too high. Some commercialized Lithium microbatteries are well suited to low power applications: the 25 × 25 × 0.2 $\text{mm}^3$ EnFilm EFL700A39 (STMicroelectronics) with 0.7 mAh capacity; the 8 × 8 × 0.9 $\text{mm}^3$ EnerChip CBC050 (Cymbet Corp.) with 50 µAh capacity. Both require charge voltages around 4.2V.

### *1.3. Power management block*

The power management block - composed of a power converter and some control circuits - is designed in order to rectify the generated AC voltage; efficiently collect, store, manage and convert/regulate the harvested electrical energy into a form suitable to targeted devices (storage elements, sensors, microcontrollers, wireless transceivers); accomodate impedance requirements and output voltage limitations; manage over-voltage and under-voltage conditions that can damage energy storage devices; shift or increase the frequency bandwidth of the PG in order to better match the mechanical source frequency range.

Since 15 years, active research has been worldwide conducted to develop efficient power converters dedicated to low power energy harvesters [Liu and Vasic (2012), Guyomar and Lallart (2011), Ammar (2006)]. Moreover, a growing range of manufacturers is producing power management devices designed especially for energy harvesters: ALD (EH300) Linear Technology (LTC3588-1), Maxim IC (MAX17710), Texas Instruments, Microchip, Cymbet, AdaptivEnergy, MicroStrain. As an example, EH300 circuit - including a rectifier, a complete power converter and a storage capacitor - delivers an output voltage up to 3.6V and requires an input quiescent current of only 200nA (output in regulation, no load).

### *1.4. Piezoelectric generator*

Piezoelectric materials convert a physical pressure into the motion of electrons, and thus, the unused mechanical energy of our surroundings into electrical energy. Various technologies of piezoelectric harvesters have been tested for energy harvesting since the early 2000s [Priya et al. (2008), Defosseux et al. (2012)]: bulk PZT (Lead Zirconate Titanate), PZT fiber composites, PZT thick or thin films, PVDF films. The densities of harvested power are comprised between 1 and 10 mW/cm$^3$. Nevertheless, most of the prototypes are not integrated devices – including PG, power management block and storage element - and/or take up a volume that is too large to be compatible with embedded electronic devices.

## 2. ZnO Nanowire-Based Piezoelectric Nanogenerators

Since 2007, there is a tremendous interest for using one-dimensional (1D) piezoelectric nanostructures (GaN, PZT, BatiO$_3$, PVDF, CdS...) for mechanical energy harvesting [Nechibvute et al. (2012)]. Among several materials, ZnO NWs is one of the most promising candidates. It has high values of piezoelectric coefficients, it can be grown at low temperature on almost any substrates, and finally it is environmentally friendly (lead-free). Today, the output power density generated by the best prototypes in the literature reaches about 5 µW/cm$^2$ [Lin et al. (2013)]. In comparison, ZnO thin film cantilever PGs produce the same level of power density when they are excited at their resonance frequency. However, outside the bandwidth the conversion effectiveness is suboptimal and the output power can drop to unusable levels. Moreover, in thin film cantilever PGs, the piezoelectric thin films have strongly reduced piezoelectric coefficients due to substrate coupling. Two main structures of NW based PGs are encountered: devices with NWs orthogonal to the substrate, devices with NWs parallel to the substrate [Wang (2012)]. As the natural resonance frequency of NWs is in the hundred of MHz range [Hinchet (2014)], where no ambient source is available, the working mode of NW based PGs is non resonant.

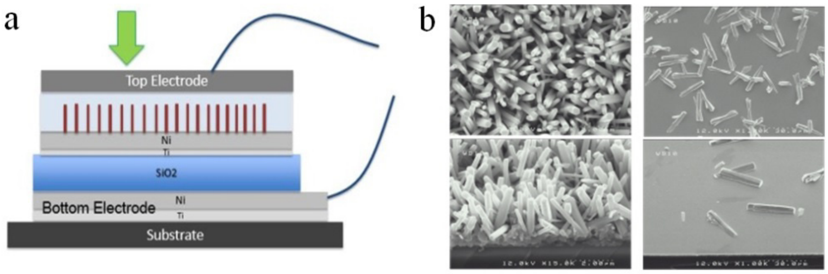

Fig. 1. (a) schematics of the ZnO nanowire-polymer composite PG ; (b) SEM images of the top and side of ZnO NWs growth using an aluminum anode (left) and the resulting growth without anode (right).

### *2.1. Manufacturing process*

The fabrication of the PG (Fig. 1a) requires several steps. PET substrate was selected because a flexible device is targeted. Each sample is 25 × 25 mm$^2$, cleaned with acetone and isopropanol. E-beam evaporation was used to deposit successively a 30 nm Titanium layer - in order to increase the adhesion on the substrate - and a 300 nm Nickel layer – the bottom electrode. The next step consists in putting an insulating layer before another metal one. This insulating layer creates a high potential barrier between the ZnO NWs and the electrode and should protect the PG from short circuiting [Lee et al. (2014)]. The SiO$_2$ layer is deposited by PECVD at 200°C. Then a 10 nm of

Titanium and 100 nm of Nickel were deposited using e-beam evaporation. This Nickel layer is required for the ZnO NWs growth, because ZnO NWs will grow on Nickel via a seedless hydrothermal synthesis [Zheng et al. (2013)]. The growth happens in a solution of HTMA (Hexamethylenetetramine) and Zinc Nitrate of equal concentration (100 mMol/L) and equal volume. Aluminium foils - laid at the edge of the substrate - are used as the sacrificing anode and ZnO growth occurs on the cathode substrate – the Nickel layer. The Nickel and Aluminium metals with dissimilar electro-negativities act as a galvanic cell in the electrolyte growth medium. This allows ZnO NWs growth even in the absence of seed layers and/or substrate with specific lattice parameters.

For the hydrothermal synthesis, the sample is placed face down in the solution in an over at 100°C for 4 hours. It is subsequently rinsed with deionized water and dried with air. A scanning electron microscope observation of the NWs - 2 µm in length and 200 nm in diameter - shows their hexagonal form, equal height, and quite aligned arrangement (Fig. 1b).

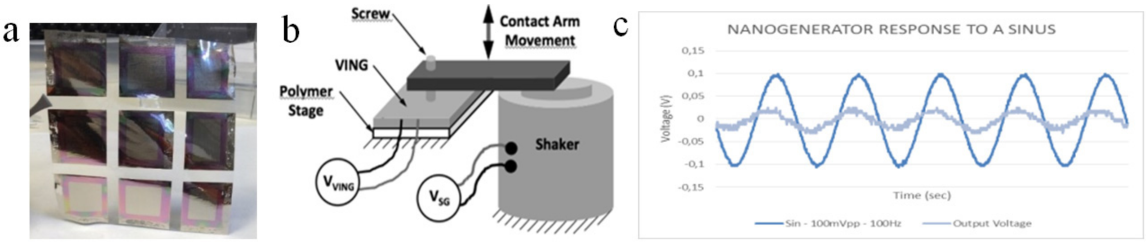

Fig. 2. (a) PET film with 9 nanowire/polymer composite PGs; (b) schematics of the test bench; (c) plot showing the signal generated by the PG with applied bending force at 100 Hz.

A thin layer of PMMA is deposited onto the NWs in order to improve their mechanical robustness and the quality of mechanical energy transfer during bending, in the harvesting operating mode. Afterwards, a metal top electrode - 10 nm of Titanium and 100 nm of Nickel - is added using e-beam evaporation. Two wires are attached to both of the PG electrodes with conductive silver paint.

For purpose of efficiency, larger PET substrate (100 × 100 mm$^2$) can be used instead of several small samples (25 × 25 mm$^2$). This large sample is divided in 9 areas using Kapton tape (5 mm) during the early manufacturing process and is cut just before the NW growth.

### *2.2. Experimental measurement*

The performance measurement set-up (Fig. 2b) was designed in order to apply a low frequency bending force in the 1 Hz-100 Hz range, like the targeted mechanical sources. The mechanical shaker is controlled by a sine signal. A screw at the tip of the lever arm was finely adjusted to be just off contact with the PG at the neutral position of the shaker. The applied signal and the resulting voltage potential produced by the PG are shown on Fig. 2c. Under a 10 Hz sinusoidal bending force, the PG produced a 56 mV peak-to-peak voltage on 1 MΩ resistive load. Identical reference samples without ZnO NWs were fabricated in parallel with the PGs. Nonetheless, the PG response is more than three times higher than the reference sample, which shows that the ZnO NWs are indeed generating voltage.

## 3. Conclusion

High density piezoelectric ZnO nanowire growth was demonstrated on metal coated PET substrates by a galvanic cell reaction-assisted hydrothermal process with an aluminium sacrificing anode. The growth method described in this work offers several advantages with regards to ZnO nanowire material for industrial scale application. For example, by forming a galvanic cell between the aluminium and a conductive cathode surface, large quantities of

ZnO nanowires can be grown without an autoclave, as in classical hydrothermal synthesis., Secondly, the potential gradient induced by the cell allows for much higher growth rates (0.5 µm/hr at 100°C). Secondly high density ZnO nanowires can be grown on specific substrate sites in the absence of seed layers and/or substrate with specific lattice parameters.

Using the as-grown ZnO nanowires, we have also demonstrated the fabrication of fully functional PGs on flexible PET plastic substrate.and preliminary results of device output performance were also presented. Subjecting such devices to a10Hz sinusoidal bending force resulted in a measured PG output of ~56 mV peak-to-peak.

In order to improve the PG output performance, further work will be focusing on: assessing the performance of PGs employing other nanowire/polymer composites (e.g. PDMS, PEDOT:PSS); Characterisation of the PGs across a wide range of mechanical input frequencies and resistive loads; Couple the PG with a power management IC device.

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