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# Fabrication and functional characterization of ZnO nanowire based piezoelectric nanogenerators

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## ABSTRACT

The present work describes the seedless approach for the growth of ZnO nanowires (NWs) on flexible polyethylene terephthalate (PET) substrates and fabrication of fully flexible ZnO NW based piezoelectric nanogenerators (NGs). The x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) confirms the high quality of grown nanomaterial. The performance of the fabricated ZnO NW based NG device is measured under a force of 5N at a frequency of 3Hz. A peak output voltage of  $\sim 950\text{mV}$  is obtained that corresponds to a power density of  $\sim 1\mu\text{W}/\text{cm}^2$ . Our results clearly demonstrate the interest of ZnO NWs for the development of autonomous micro-nano systems (MNSs).

## 1. INTRODUCTION

Over the past decade, there has been substantial increase in the interest for electrical energy harvesting from ambient energy sources (green or eco-friendly sources) for low-power applications including autonomous wireless sensors, portable electronics and biomedical implants [1]. Kinetic/mechanical energy is a power source that is ubiquitous and can be a potential solution to supply green energy for the development of autonomous systems. In this regard, a new field of research based on nanoscale piezoelectric mechanical energy harvesters, also known as nanogenerators (NGs), which exploit ambient vibrations as energy source to power the MNSs, was proposed [2]. Among the various piezoelectric nanomaterials investigated, as an active piezoelectric element in NGs, ZnO is the most extensively studied and has found practical uses for energy recovery in various device geometries. The use of ZnO nanostructures as active piezoelectric material in NGs has been largely driven by distinct advantages over the other lead-free nanomaterials, including (i) coupled piezoelectric and semiconducting properties, (ii) cost-effective synthesis methods that offer single-crystalline materials production, (iii) substrate independent synthesis method, and (iv) compatibility with living matter.

Since the first demonstration of zinc oxide NW based NGs (ZnO NW-NGs) in the scientific realm [2], they have been developed and have evolved in a variety of configurations. Broadly, they can be categorized into two class groups, namely the vertically integrated NG (VING) and the laterally integrated NG (LING) [3]. However, due to the relative ease of fabrication, the VING is by far and away the most developed and investigated device structure. In the VING structures, piezoelectric NWs such as

ZnO, are intentionally grown vertically on a target device substrate. A composite capacitor-like structure is assembled by encapsulating vertical NWs in a polymer, thus forming a hybrid organic-inorganic matrix. To ensure that the induced piezopotential is effectively coupled to an external load, a conductive metallic contact is typically deposited on the composite structure thereafter. Although ZnO NW-NGs showed promising energy harvesting performance, some of the key issues restricting the device performance are yet to be addressed such as mechanical driving mechanism, figure of merit evaluation, screening effect, type of polymer (p-type conducting or insulating) and efficient transfer of mechanical and electrical energy to and from NWs, respectively.

## 2. EXPERIMENTS

In this work, ZnO NWs were grown using hydrothermal approach. The hydrothermal growth of vertically integrated ZnO NWs were done on bare Au coated PET substrates following similar processing steps, described elsewhere [4]. The quality of the resulting ZnO NWs was studied using SEM (morphology) as well as XRD and HRTEM (crystallinity).

To fabricate VING devices, ZnO NW arrays were encased in a polymer matrix to form ZnO NW-polymer composites. For this, a thin layer of parylene C ( $\sim 300\text{nm}$ ) was deposited at room temperature. To define the active area of the VING device structure, top metal contact, Ti/Al ( $\sim 100/400\text{nm}$  thick) was deposited using physical vapor deposition (PVD). Copper wires were subsequently attached to the top and bottom conductive surfaces of the NG (by silver paste) to ensure facile probing. Finally, PDMS packaging over the entire VING structure was performed to enhance the physical robustness of the device. A schematic of the complete VING device structure is shown in Fig. 1.

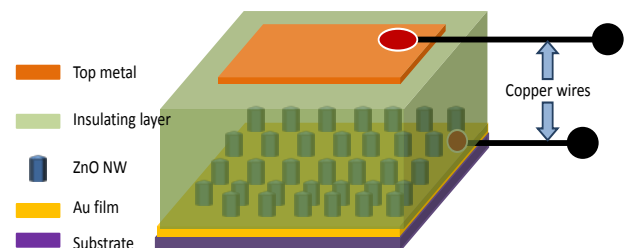
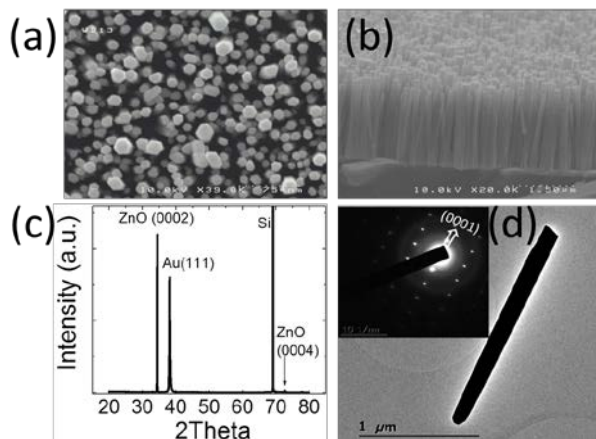


Fig. 1: Schematic of a VING device structure.

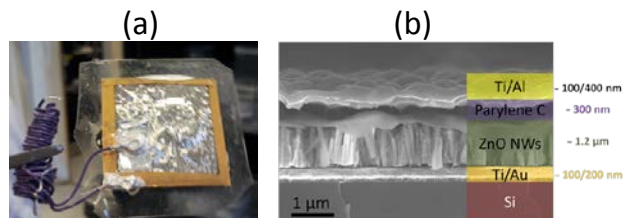
## 3. RESULTS AND DISCUSSIONS

Following the hydrothermal growth process, the ZnO NW samples were then removed from the growth chamber and were characterized systematically to observe the morphology and crystallinity of the obtained nanomaterial. For the fabrication of an efficient VING, highly orientated single-crystalline NWs are needed for integrating the output from millions of NWs. Fig. 2 shows representative SEM images, XRD and HRTEM data of as-grown ZnO NWs on Au thin-film. From Fig. 2a-b, it can be seen that highly dense ZnO NW arrays were obtained. The ZnO NWs were also observed to exhibit excellent structural orientation, perpendicular to the growth substrate. Several SEM images were assessed, revealing typical NW density, diameter and length on the different substrates to be around  $74.5 \text{ NW } \mu\text{m}^2 \pm 6.5$ ,  $115 \text{ nm} \pm 64$ ,  $0.97 \mu\text{m} \pm 0.34$ .



**Fig. 2:** The structural and morphological characterizations of ZnO NWs grown on Au thin-film: (a) top-view SEM, (b) cross-sectional SEM, (c) XRD pattern, (d) low magnification TEM image. The inset is SAED pattern showing the single crystalline nature of NW.

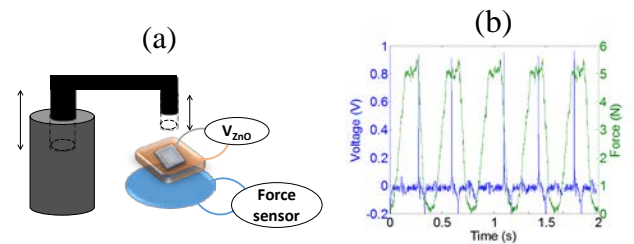
From the XRD data (Fig. 2c), two dominant peaks centered at  $2\theta$   $34.4^\circ$  and  $72.5^\circ$ , correspond to the (0002) and (0004) planes of a highly c-axis orientated wurtzite ZnO. An additional peak appearing at  $69.1^\circ$  was successfully assigned to the Si (100) growth substrate. The ZnO NW growth direction was further confirmed by HRTEM, as shown in Fig. 2d. The selected area electron diffraction (SAED) pattern shows the NW grows along the [0001] direction.



**Fig. 3:** Image of the completed VING device (a), cross-sectional SEM image of the ZnO NW-based NG (b).

Fig. 3a shows the optical micrograph of typically synthesized ZnO NWs based VING device. To have a better insight, cross-sectional SEM images were seized from the

fabricated device (Fig. 3b). It can be seen from this image that NWs are completely encapsulated by parylene C films ( $\sim 300 \text{ nm}$ ). The deposition process is very conformal with high degree of infiltration between the NWs.



**Fig. 4:** experimental setup for VING mechanical solicitation (4a), VING electrical response to an uniaxial force (4b).

The figure (4a) gives a representation of the electric performance measurement of the VING. Its output voltage is reported figure (4b). A maximum of 950mV is generated with a 5N excitation force at 3Hz. This generated voltage corresponds to a surface power density of  $\sim 1 \mu\text{W}/\text{cm}^2$ .

#### 4. CONCLUSION

The present work has successfully demonstrated the growth of single-crystalline ZnO NWs via low temperature hydrothermal process at around  $100^\circ\text{C}$  on bare Au surface. The high quality of the obtained NWs was confirmed using XRD and HRTEM characterization techniques. The fabricated NGs employed vertically oriented ZnO NW arrays on Au/PET substrates and  $\sim 300 \text{ nm}$  thick parylene C polymer matrix. The thickness of the deposited parylene C was chosen after optimization. The ZnO NW-NG device exhibited moderately high peak output voltage of  $\sim 950\text{mV}$  at a resistive load of  $1\text{M}\Omega$ , when a 5N force is applied at 3 Hz. This work may find practical applications in realization of fully autonomous MNSs.

#### 5. ACKNOWLEDGEMENTS

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