

# Energy Harvesting from Millimetric ZnO Single Wire Piezo-Generators

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## ABSTRACT

This work reports on investigations into the possibility of harvesting energy from the piezoelectric response of millimetric ZnO rods to movement. SEM & PL studies of hydrothermally grown ZnO rods revealed sizes ranging from 1 - 3 mm x 100 - 400 microns and suggested that each was a wurtzite monocrystal. Studies of current & voltage responses as a function of time during bending with a probe arm gave responses coherent with those reported elsewhere in the literature for ZnO nanowires or micro-rod single wire generators. The larger scale of these rods provided some advantages over such nano- and microstructures in terms of contacting ease, signal level & robustness.

**Keywords:** ZnO, Energy Harvesting, Piezogenerator, Single Wire Generator, Hydrothermal Growth

## 1. INTRODUCTION

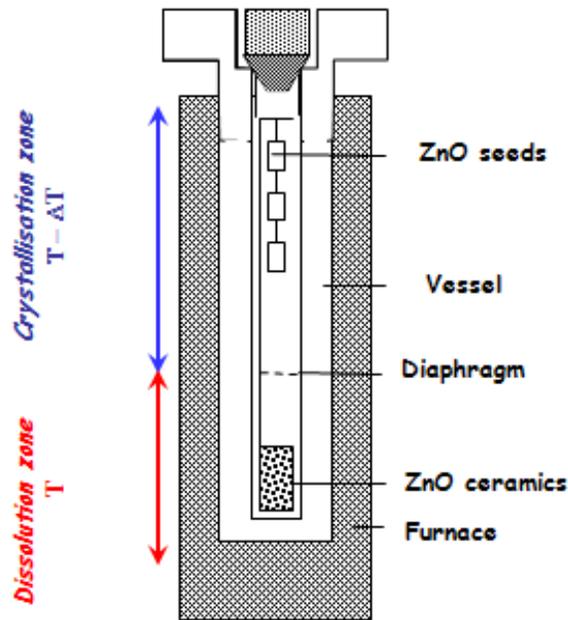
Wurtzite ZnO has one of the largest piezoelectric responses of all semiconductor materials [1]. Groundbreaking research by Wang et al. in 2006 [2] on the electrical output from ZnO nanowires (NW) when bent with an Atomic Force Microscope tip indicated that it may be possible to harvest energy from their piezoelectric response. These experiments required Schottky & Ohmic contacts at opposing ends of the NW in order to harvest the energy and gave very small signals:  $\sim 16$  pA,  $< 25$ mV [2]. In 2008 Alexe et al. [3] reported detecting a comparable “piezo” signal for non-piezo Si NWs. They also suggested that such signal dissipation was too fast to be valid ( $\tau < 1$ ps) and that the reported output voltages were too small to be rectified.

In reply to this, Wang [4] maintained that Alexe’s equipment was inadequate for accurate measurement of such small signal levels, that the low carrier concentration in his NW explained the short  $\tau$  and that it was the piezopotential that was rectified rather than the output voltage.

More recently [5-7], it was demonstrated that increased signal could be obtained using micrometer scale, laterally oriented, single wire generators (SWG). Such an approach was vaunted for simpler construction, larger output signal and more straightforward measurement. This work reports on investigations into the possibility of extending the SWG concept to millimetric ZnO rods.

## 2. EXPERIMENT

Millimetric ZnO crystals were made by hydrothermal growth in an autoclave. This technique is known to give ZnO crystals with excellent crystal quality [8].



**On the bottom:** Dissolution of the nutrient (ZnO as powder or ceramics) by the solvent KOH

**On the top:** Deposition of ZnO in solution on the seeds

**Role of  $\Delta T$ :** Transfer of matter from the top to the bottom: kinetic

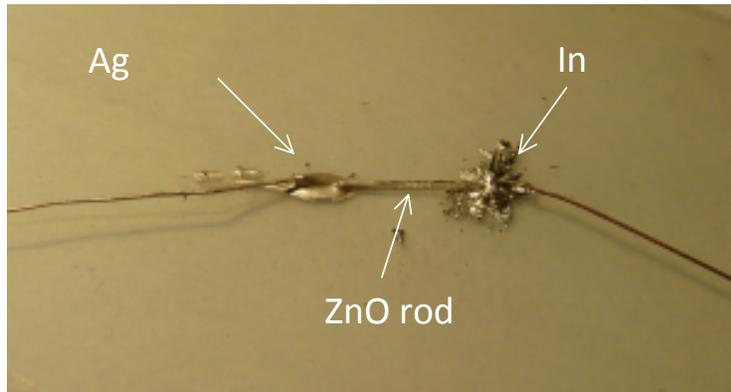
**Figure 1** Schematic diagram (with key) for the autoclave used in the hydrothermal growth.

A seed was prepared using ZnO powder which was compacted at 6000 bar (15mm) and then annealed at 300°C (3h) in O<sub>2</sub> at 65 bar. Hydrothermal growth was done in KOH (3 mol/l) at a temperature of 350 °C +/- 10°C under 1600 bar for 6.5 days.

The sample morphology was examined using a Leitz Wetzlar optical microscope with digital image acquisition and a Hitachi S4800 Field Emission Gun-Scanning Electron Microscope (FEG-SEM). Optical properties were studied via Room Temperature (RT)

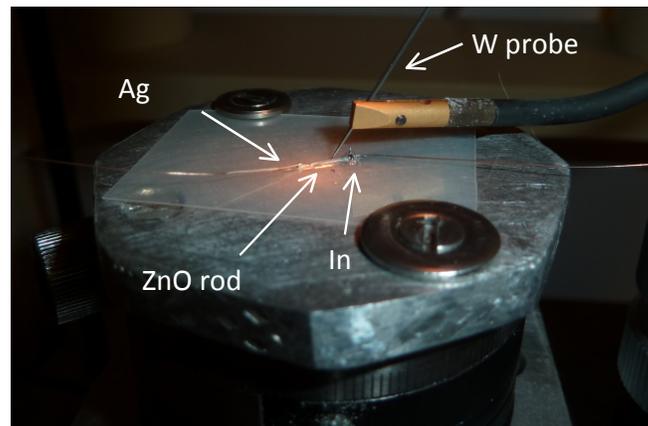
photoluminescence (PL) with a continuous-wave frequency-doubled argon ion laser (244 nm, power of 30 mW).

For the energy harvesting experiments, single ZnO rods were placed on a Teonex substrate and electrical contacts were made on opposing ends with silver paste and indium, as shown in figure 2. The intention was to obtain a Schottky contact with the Ag and an Ohmic contact with the In.



**Figure 2** Image of the contacts on the ZnO rod.

The rod was bent manually by means of a tungsten probe arm using a Karl-Suss probe station, as shown in figure 3.

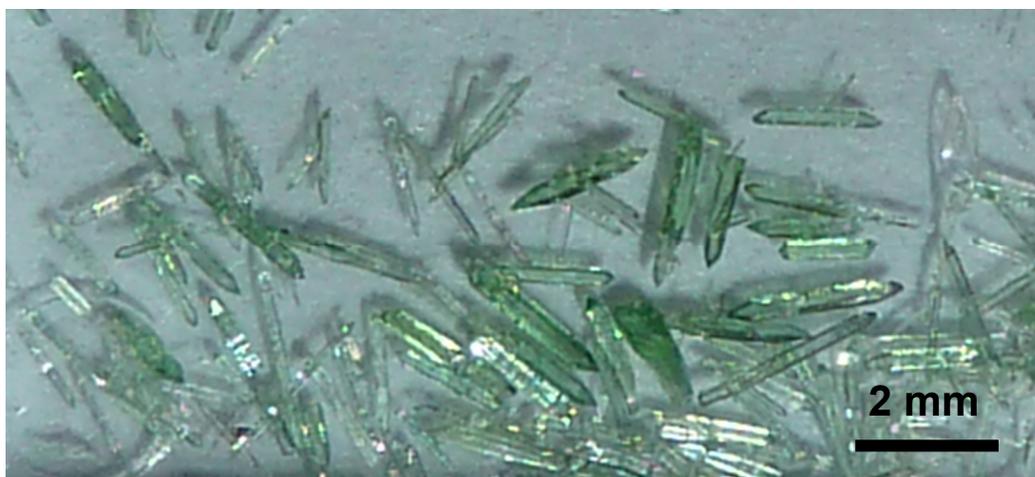


**Figure 3** Experimental set-up used for bending the ZnO rod.

Measurements of current and voltage across the rod were made as a function of time during bend/release cycles using a Keithley 2400 Source-Meter. Various control measurements were made including measuring different ZnO rods, using an inert probe arm (wooden), measuring metallic and insulating rods (Cu & wood substitutes), bending direction change and source-meter polarity reversal.

### 3. RESULTS & DISCUSSION

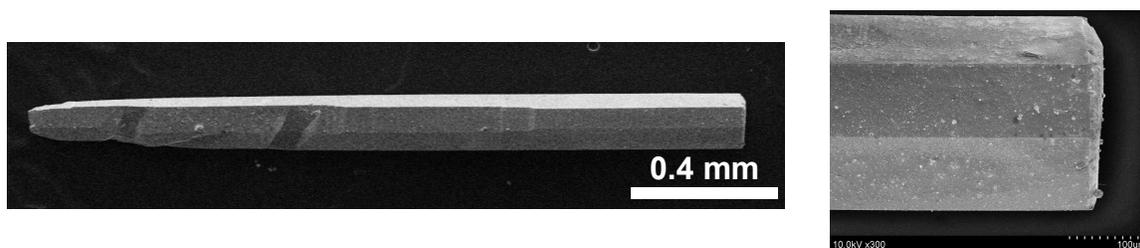
Figure 4 shows a photograph of the crystals.



**Figure 4** Photograph of the hydrothermally grown ZnO crystallites.

The crystals are of the order of 1 to 3 mm in length and 100 to 400 microns in diameter. Some of the crystals are clear and some have a greenish hue, which is commonly attributed in the literature to the presence of oxygen vacancies and/or Cu contamination and/or other sources [9].

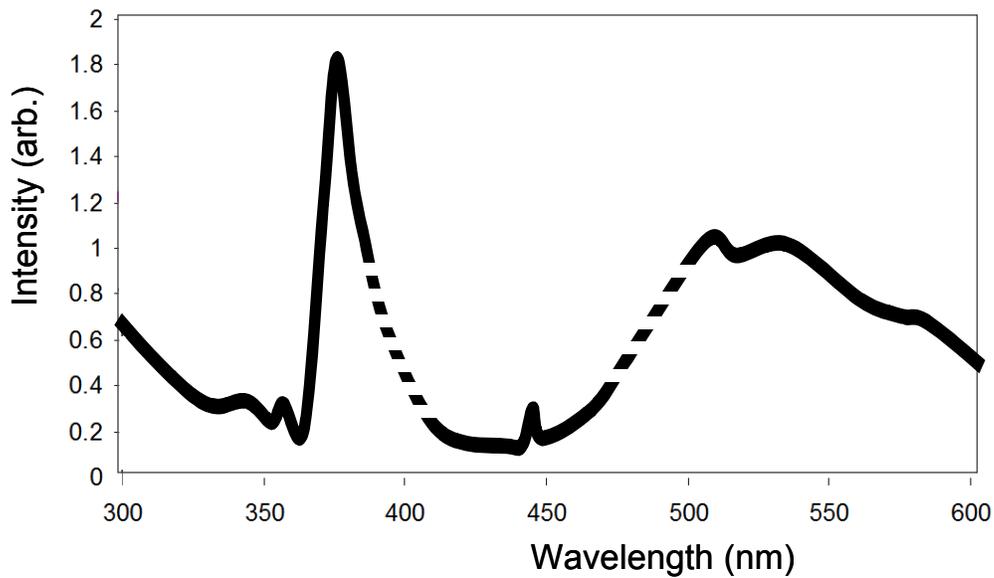
Figure 5 shows FEG-SEM images of a single rod.



**Figure 5** FEG-SEM image of one of the hydrothermally grown ZnO rods.

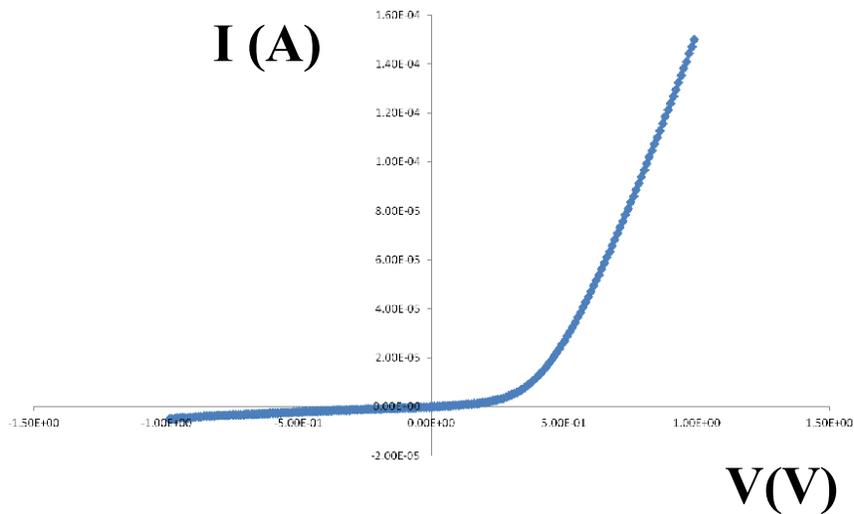
The ZnO crystal shows hexagonal faceting which extends the whole length of the rod. This suggests that the rod was mono-crystalline.

Figure 6 shows RT PL spectrum for the ZnO rods.



**Figure 6** RT PL spectrum of a hydrothermally grown ZnO rod. Dashed portions indicate uncertainty due to laser resonances.

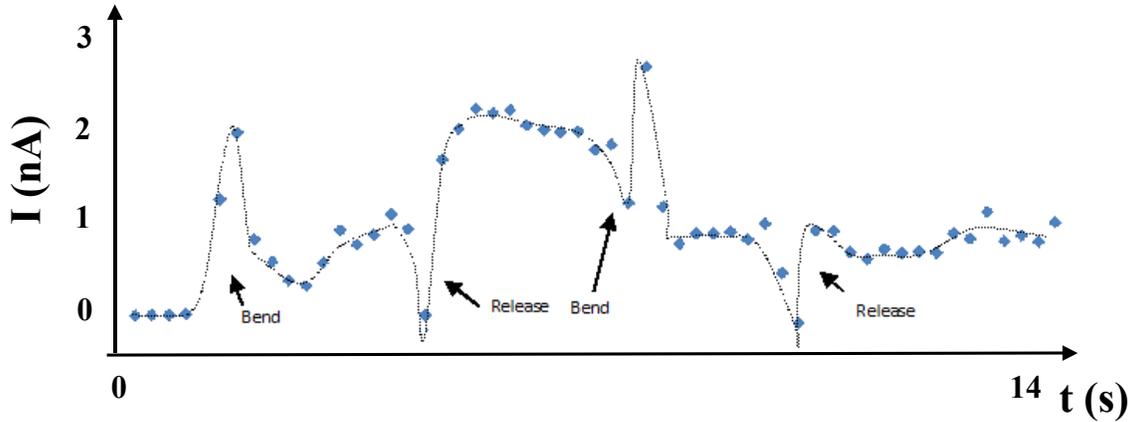
The spectrum shows a strong main peak centred at 378 nm with a FWHM of about 35 meV. This is typical for near band edge emission from wurtzite ZnO. The spectrum also shows a broad green-yellow band that is usually attributed to defect-related emission. Figure 7 shows a typical I/V characteristic for a single rod.



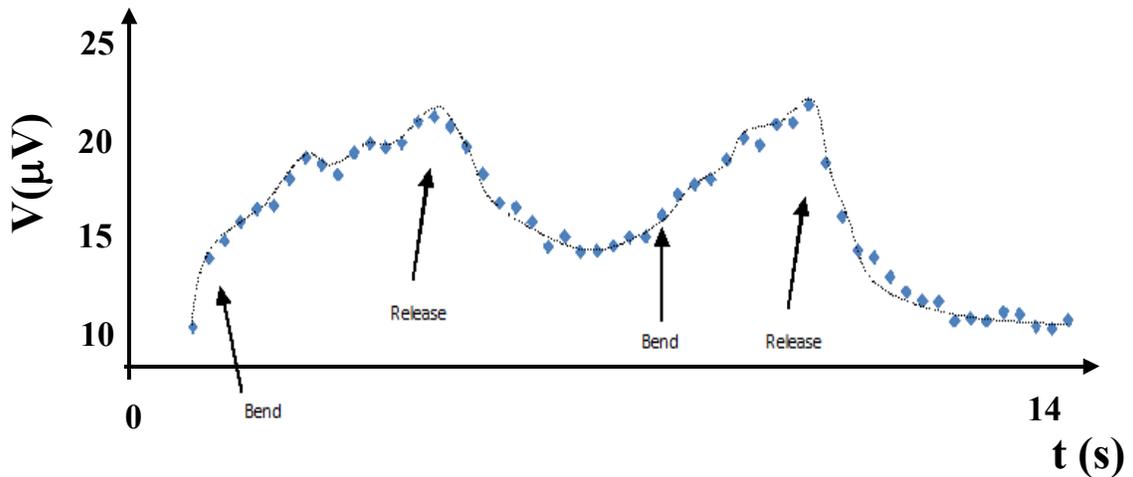
**Figure 7** I/V characteristic for a single hydrothermally grown ZnO rod.

This characteristic shows rectification (with a turn-on voltage of  $\sim 0.45\text{V}$  and a reverse leakage current of  $\sim 30\mu\text{A}$  for a reverse bias of  $0.5\text{V}$ ). Not all of the rods gave such rectifying behaviour, however, and careful study revealed that all I/V responses were effectively linear (Ohmic) for the very small signal level/range involved in these experiments.

Figures 8 and 9 show I and V as a function of time for a single ZnO rod during 2 bend/release cycles.



**Figure 8** Current as a function of time for a hydrothermal ZnO rod during 2 bend/release cycles.



**Figure 9** Voltage as a function of time for a hydrothermal ZnO rod during 2 bend/release cycles.

The current/time profile in Figure 8 shows uni-directional current spikes upon bending, which fell to zero upon release. The overall profile is reminiscent of that obtained for SWGs by Yang et al. [5].

The voltage/time profile in Figure 9 shows indications of a response to the bend/release cycling but no distinct V peaks are visible. This may be due to rather poor time resolution of the experimental set-up compared with the short response time of the piezo-potential.

#### 4. CONCLUSION

SEM & PL studies of hydrothermally grown ZnO rods revealed sizes ranging from 1 - 3  $\mu\text{m}$  x 100 – 400 microns and suggested that each was a wurtzite monocrystal. I/V characteristics for rods on Teonex with In and Ag contacts on either end only showed rectifying behaviour in some cases and were effectively linear in the small signal range of interest. Studies of current & voltage responses as a function of time during bend/release cycling with a probe arm gave responses reminiscent of those reported elsewhere in the literature for piezo-electric SWG. The larger scale of these rods provided some advantages over NW or micro-rod SWG in terms of contacting ease, signal level & robustness.

#### ACKNOWLEDGEMENTS

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