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Nanoscale Piezoelectric Energy Harvesting

by Stephen J. Kilpatrick and Ashley D. Mason

ARL-TR-5229 June 2010

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ARL-TR-5229 **June 2010**

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED (From - To)**
June 2010	Progress	Summer 2009

4. TITLE AND SUBTITLE
Nanoscale Piezoelectric Energy Harvesting

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Stephen J. Kilpatrick and Ashley D. Mason

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-SER-L
2800 Powder Mill Road
Adelphi MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-5229

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The Sensors and Electron Devices Directorate (SEDD) has initiated an investigation studying nanoscale harvesting elements to expand the scope of piezoelectric research. The piezoelectric characteristics of zinc oxide (ZnO) nanowires are explored for potential use as a nanogenerator. A mechanical deformation imposed on a nanowire translates into a piezoelectric potential generated across the material. The proposed approach involves transferring grown ZnO nanowires from growth substrates to a flexible platform for mechanically deforming the wires. Due to the extremely small dimensions of the ZnO nanowires, if the mechanical deformation does not generate sufficient voltage to meet application requirements, the integration of a storage element may become necessary. We optimized the device fabrication and characterization methods to evaluate a single ZnO nanowire. The results gleaned from the initial experiments should aid the search for a viable power generation method for nanoscale devices, such as Soldier-borne and vehicle-mounted sensors.

15. SUBJECT TERMS
ZnO, zinc oxide, nanowire, piezoelectric, energy harvesting, hydrothermal

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Stephen J. Kilpatrick
Unclassified	Unclassified	Unclassified	UU	16	**19b. TELEPHONE NUMBER** (*Include area code*) (301) 394-0071

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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1. Introduction/Background

Zinc oxide (ZnO) has previously attracted a lot of attention because of its large bandgap, good transparency, high electron mobility, biosafety, and other desirable characteristics. ZnO has since found potential applications in optoelectronics, thin-film transistors, sensors, and energy harvesting applications (*1*). The ability to repeatedly create nanostructured ZnO also makes it an attractive candidate for future electronic nanodevices. The energy harvesting applications of ZnO nanowires are of particular interest to the U.S. Army as a potential means to reduce the quantity of batteries that need to be carried by the American Soldier. Previous work by Wang et al. from the Georgia Institute of Technology demonstrated that small amounts of energy can be harvested from bending ZnO nanowires (*2*). ZnO is piezoelectric, an inherent material property in which a mechanical stress results in the generation of an electric potential across the material. Due to the infancy of ZnO nanowires as an energy harvesting system, many challenges must be overcome and many questions still need to be answered.

The charge-distribution created in a bent wire is a complicated model dependent on the strain gradients (*3*). Depending on the type of bending and the device being created, different models have been proposed. When a single nanowire, or an array of nanowires, is bent with an atomic force microscopy (AFM) tip, previous research suggested that the charge-distribution runs along the diameter of the nanowire (analogous to piezoelectric films) (*2*, *4*). However, when flexing a single microwire, the same research suggested that the charge-distribution in that case runs along the length rather than the diameter (*5*).

Alternative models have been presented that assess the systems used in previous work, theorize ideal placement of electrodes, and propose new device designs and measurement systems (*6*, *7*). The work on devices inspired by the piezoelectric effect exhibited by ZnO is still dominated by one primary research group, and not many instances of independent confirmation of successful energy harvesting systems have been documented (*8*). Additional studies are required to determine the viability of such devices and evaluating their success in potential markets is still necessary.

2. Experiment

2.1 Nanowire Growth

ZnO nanowires were grown on silicon (Si) substrates with ZnO seed layers using two different methods: (1) vapor-solid growth using ZnO and graphite precursors and (2) hydrothermal growth using zinc nitrate ($Zn(NO_3)_2$) and hexamethylene tetramine (HMT).

2.1.1 Vapor-solid Growth

Vapor-solid nanowires (NWs) were grown using a tube furnace with ZnO and graphite precursors. The ratio of the precursors was 1:1. The ZnO and graphite were ground and mixed together before being placed into the furnace. The temperature of the furnace at the location of the precursor mixture was ~915 °C. The substrate was placed downstream, where the temperature was ~760 °C. The pressure in the tube was then reduced to 1 torr. Nitrogen was flowed through the tube at a rate of 150 sccm, and 1 to 3 sccm of oxygen was injected near the substrate to aid in NW nucleation. The growth time was 30 min, after which the furnace was turned off and the tube was allowed to cool to room temperature.

2.1.2 Hydrothermal Growth

Hydrothermal ZnO NWs were grown in solution using $Zn(NO_3)_2$ and HMT at 80 °C. The solution was heated using a hot plate and mixed continuously using a magnetic stir bar at 60 rpm. The growth substrate was taped with two pieces of Kapton tape to the backside of a Petri dish, which was then floated on top of the solution. During growth, the solution was covered with parafilm to minimize evaporation. Although the hydrothermal method is performed at low temperature, facilitating the use of various substrates, growth can take up to 24 h.

The purpose of using two different growth methods was to examine the differences in resulting morphologies and the respective effects on the piezopotential generated by one NW. The experimental setups are shown in figure 1 with the associated results shown in figure 2. Further investigation of precursors used for the solution growth method is ongoing to obtain longer wires. Development of this growth process will aid in other areas where lower processing temperatures are necessary.

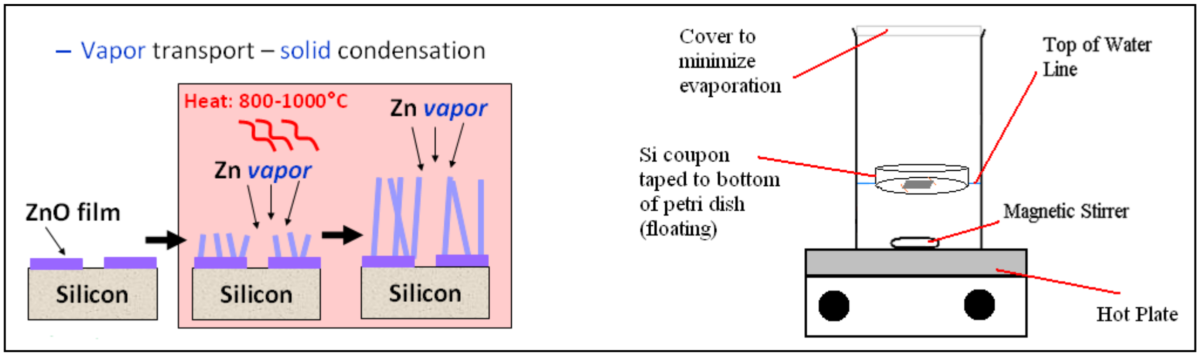

Figure 1. Experiment setup diagrams for vapor-solid and hydrothermal NW growth.

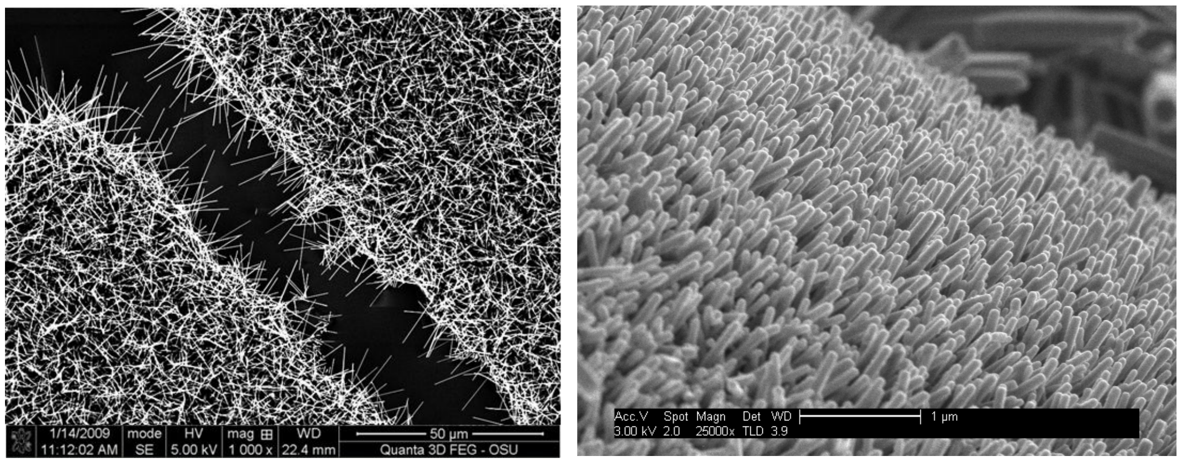

Figure 2. Images of nanowires grown using vapor-solid (left) and hydrothermal (right) methods.

Note: The difference is shown in scale bars.

2.2 Overview

A general list of tasks was created to outline the steps necessary to design and implement a single-nanowire device. An appropriate, non-charging substrate is necessary for identifying the NW's position in a scanning electron microscope (SEM) before e-beam lithography. Due to poor visibility of the NWs through the photoresist, the pattern was made using reference coordinates taken from an image of the NW before the photoresist was deposited.

The chosen substrate was patterned with a large-scale mask to reduce the amount of time necessary to finish the e-beam write to the NW. The NWs were to be transferred between two separate lithography steps. A system for bending and measuring the piezoelectric potential was designed for use after contacting the NW. Preliminary tests were performed using existing equipment: a probe station and a Keithley 4200 Semiconductor Characterization System. As needed, alterations were made to reduce ambient noise or interference. If a higher frequency actuation is needed, the voice coil and associated controller (at Oregon State University) can be modified to bend the NW.

2.3 Initial Tests

After NW growth, a test of the mechanical transfer process was performed to move the vertically aligned NWs to a new substrate where the NWs were laid horizontally on the substrate (figure 3). Images were taken using a SEM to see if pressing the two substrates together and lightly rubbing them was enough to transfer wires from one substrate to another. Figure 4 shows that NWs could be successfully transferred to a silicon substrate with native oxide, and that a single nanowire could be isolated.

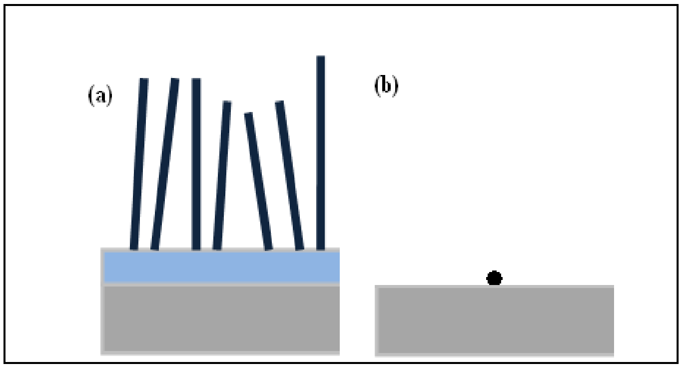

Figure 3. Cross-sectional views of (a) growth substrate showing the silicon sample (grey), ZnO seed (blue), and nanowire growth; and (b) the transferred wire on substrate.

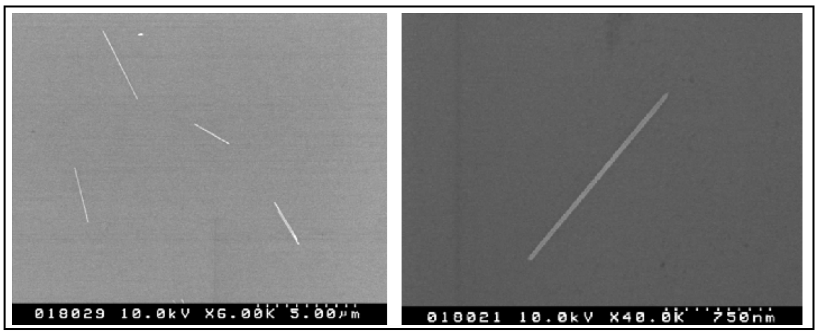

Figure 4. SEM images showing transfer of NWs from the growth substrate to the secondary substrate and isolation of a single ZnO NW.

When choosing a substrate, there are a few considerations which limit the viable options. Potential transfer substrates should be flexible enough to bend without damaging the substrate or the measurement apparatus, but robust enough to withstand the device fabrication processing. Preliminary bending tests were performed using a probe station. Alternatively, a carrier wafer could be used as long as the flexible substrate could be removed and handled without damaging the device. As mentioned previously, the contacts to the wire are written using e-beam lithography. The substrate must not undergo excessive charging in the environmental SEM (ESEM), so that the coordinates taken from images prior to photoresist (PR) placement are reliable.

Various substrates were examined as candidates. Table 1 summarizes the experiments and results obtained when trying to complete processing up through the first metallization and NW transfer. Figure 5 shows the Kapton tape double-layer on an Si carrier. Figure 6 illustrates the problems with the Kapton tape and gold (Au). Figure 7 shows the SiO_2 flaking off of the stainless steel (SS) substrate.

Table 1. A summary of the various substrate candidates and their results.

Substrate Description	Summary of Results
Kapton tape on SS	There were adhesion problems with platinum on Kapton tape. During lithography, the Kapton started to peel off of the SS substrate. A metal etch was unsuccessful because of adhesion problems. We tried to sonicate the excess metal that was left and all metal was removed.
Kapton tape double-layer on Si carrier (see figure 5)	This sample was created as a double-layer Kapton tape sample that could be removed from the Si wafer once processing was complete. Problems with the adhesion of the platinum on Kapton ruled out this substrate option as well.
Aluminum oxide (Al_2O_3) on aluminum	The thermal Al_2O_3 layer could not be grown thick enough on aluminum in the Blue M oven.
Kapton	The Kapton has to be coated to reduce charging in the ESEM. We tried an Au coating because oxygen plasma needed for removing carbon could change the electrical properties of the wires. We tested the ability for Kapton to withstand potassium iodide (Au etch). The Kapton survived the necessary etch times. We tried coating and etching of ZnO wires on a Si substrate in parallel with trying to determine how much Au was needed to reduce charging. The Kapton could not be coated with Au well enough to reduce charging in the ESEM in high vacuum mode, which was needed for e-beam writing. Also, on the Si samples, when the Au was removed, the NWs were removed as well (see figure 6).
Silicon dioxide (SiO_2) on SS	First, the Unaxis VLR 700 deposition tool was used to deposit SiO_2 on the SS. The SiO_2 flaked off of the substrate (see figure 7). After some discussion, we discovered that the recipe on the Plasma Therm 790 was better developed. We completed a successful deposition. We successfully imaged the NWs as well.

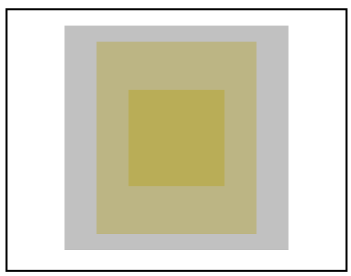

Figure 5. The center square is adhesive side up, which is held in place on the Si wafer by the face-down Kapton tape.

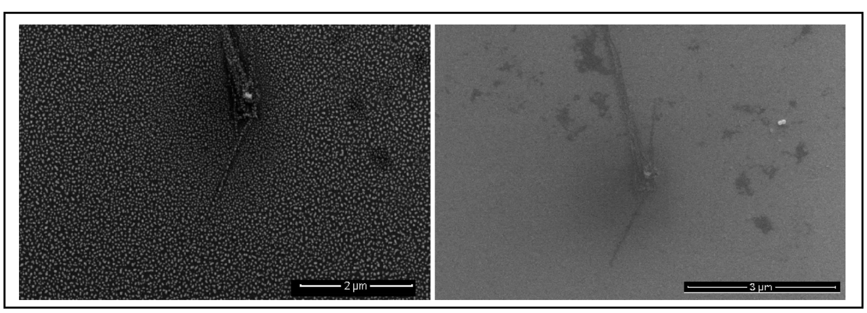

Figure 6. The etch on Si showing that when the Au is completely removed, the NWs are removed with the Au.

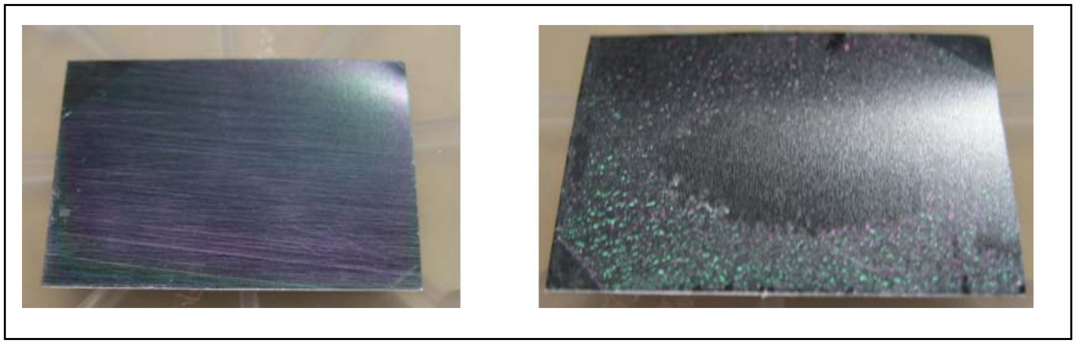

Figure 7. SiO_2 on SS showing the flakes that resulted from using the Unaxis tool.

3. Results and Discussion

A non-charging substrate was discovered that could be integrated into a NW bending system through systematic trials. NW transfer to the flexible substrate became more difficult with the integration of the large-size contacts. Figure 8 shows the resulting transfers, where wires would gather around the Au contacts or not transfer as desired. For future devices, only one set of large-size contacts (two per sample previously) will be patterned to leave space available for direct transfer of wires to the SiO_2/SS sample.

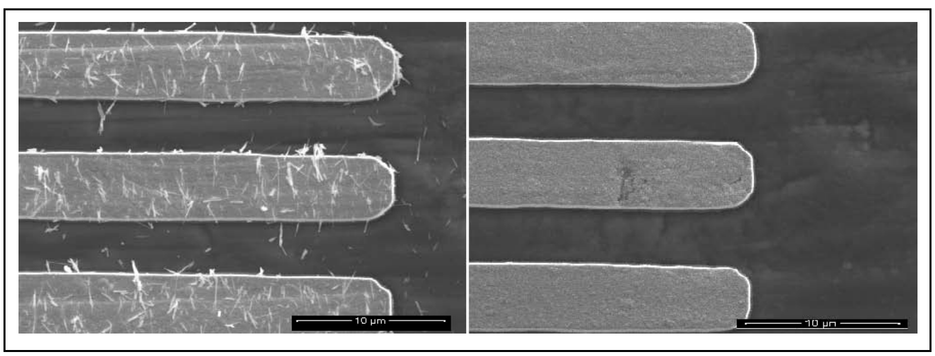

Figure 8. The influence of large-sized Au contacts on the ZnO NW transfer.

Initial measurements using the probe station and Keithley 4200 showed that ambient noise was greater than the piezoelectric measurements from actuation. Preliminary testing was performed on samples that had NWs connecting the large-scale contacts rather than an e-beam patterned connection to a single wire. The mechanical actuation of the sample was performed by mounting a sample to a larger stage and applying pressure with a probe tip on one side of the substrate.

4. Summary and Conclusions

The results gleaned from experiments over a two-month period showed a necessity for minor revisions to the previously used processing technique. We will continue this work at Oregon State University with an investigation of modified hydrothermal growth methods. Using a microwave as a heating mechanism to decrease growth time has been suggested by Unalan et al. (*9*). We will design experiments around determining the best growth parameters for obtaining NWs that are long enough (~1 μm) to pattern with e-beam lithography.

To facilitate easier alignment of a single NW, we will perform electrophoresis studies. Additionally, the project could be extended to actuate multiple, horizontally aligned NWs at once to potentially increase the usable piezoelectric potential. Measurement and actuation systems at Oregon State University will be developed in parallel.

Continuing partnerships with ON Semiconductor and Hewlett-Packard will help ease the load of SEM analysis, which needs to be performed to examine the growth, transfer, and alignment of the ZnO NWs. A research grade microwave, with integrated temperature control, is available for demo from CEM Corporation. Plans to compare the piezoelectric output from ZnO NWs grown using different methods are in progress as well.

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