Energy harvesting for implantable nanodevices using piezoelectric zinc oxide nanowire arrays

<u>Pranav Soman</u>, Daniel Eils, Max Darnell, Marc David Feldman and Shaochen Chen Department of Mechanical Engineering, University of Texas, Austin

Statement of Purpose: Implanted nanoscale devices such as a bio-sensor or a drug delivery system would require a coupled power source for their independent, sustainable and continuous operation. Piezoelectric ZnO nanowires (NWs) are great candidates for providing power to drive such nanodevices. Vibrations or motions inside the body can be used to create and accumulate piezoelectric charges in arrays of ZnO NWs and delivered to an implantable device. Wang et al. demonstrated that biomechanical energy, such as the body motion of a live hamster can be converted into electricity using zinc oxide microwires(1). The original papers in this area used vertically aligned arrays of NWs, but problems of wear and fatigue seemed imminent. Problems also arise in effectively exciting even a small fraction of the NWs in a given area. Vertically grown wires are also difficult to pattern in an array on a flexible substrate. On the other hand, a horizontal configuration of NWs is a much more robust design. Horizontal alignment allows for electrodes to be patterned over the ends of the nanowires, effectively employing each nanowire.

In this work, we have patterned an array of horizontally grown zinc oxide nanowires on ZnO substrate. We have also found that it is feasible to grow NWs with extremely high aspect ratio using this method. High aspect ratio provides more charge per unit area and therefore is the key to the development of this technology. In this study, ZnO NWs were shown to have acceptable cellular biocompatibility and biodegradability. Such biocompatible arrays printed onto flexible PDMS substrates can deliver the necessary electrically power for in-vivo nano/micron scale drug sensing/delivery systems.

Methods: Zinc Oxide NWs were grown using a modification of a method described elsewhere (2). A single crystal ZnO [2110] wafer (MTI, California, US) was cleaned using acetone, ethanol and de-ionized water. A 100 nm thick layer of PMMA (polymethyl methacrylate, A2, MICROCHEM) was spun on the wafer and baked on a hotplate at 180°C for 2 min. Electron Beam Lithography (EBL) was used to write a dot pattern on the wafer. Dosages and spacing between dots were optimized to get consistent results and these parameters were used for subsequent experiments. After electron beam exposure, the substrate was developed in a mixture of 1:1 (in volume) ratio of IPA (isopropyl alcohol) and MIBK (Methyl isobutyl ketone) for 30sec and washed with IPA for 30sec. The wafer was floated face-down on the hydrothermal growth solution (2.5 mmol/L 1:1 ratio of zinc nitrate and HMTA (hexamethylenetetramine) at 90°C for 2.5 hrs. LEO 1530 scanning electron microscope was used to characterize the pattern.

Results: Because of the matching planes of the nanowires and the single-crystal ZnO substrate, the growth kinetics

favor nanowire growth parallel to the surface. The ZnO NWs are uniform in length and width (Fig.1). In our case, we patterned an area of 500 x $500\mu^2$. The patterned horizontally aligned ZnO NW arrays can be scaled up for any practical applications. There is some lateral expansion of ZnO NWs after they grow out of the photoresist openings, however the dimensions can be controlled by the EBL dosage which controls the dimension of the dot patterns.

We also tested the cellular biocompatibility (NIH 3T3 fibroblasts) of various concentrations of ZnO NWs grown on PDMS substrates. Preliminary results show no significant difference in viability of fibroblasts on ZnO NW array as compared to control substrates. Biodegradability evaluations of ZnO NWs are invaluable for in vivo biosensing applications since ZnO NWs can dissolve into ions and can be completely absorbed by the body. Our study found that ZnO NWs did not show any signs of degradation in Dulbecco's Modified Eagle's Medium (Mediatech, Inc., Herndon, VA) mixed with 10% bovine calf serum for 24hrs. At 3 days however, SEM images showed visible etching of the NWs. (Data not shown).



Figure 1. SEM image of an array of horizontally grown ZnO nanowires. (Length $- 6\mu m$; Diameter - 300nm)

Conclusions:

Arrays of ZnO NW were grown epitaxially on single crystal ZnO (2110) by hydrothermal decomposition at 90°C and E-beam lithography. EBL dosage and spacing was optimized to get consistent array of NWs. Current work is focused on (1) optimization of aspect ratio and (2) patterning electrodes for every nanowire to work in parallel to increase the cumulative current output. Such NW arrays can be expanded to a larger scale making it applicable in supplying power to nanoscale drug delivery devices.

References:

R. Yang, Y.Qin, C. Li, G. Zhu and Z.L. Wang, *Nano Lett.*, 2009, 9 (3), 1201-1205

S. Xu, Y. Ding, Y. Wei, H. Fang, Y. Shen, A. K. Sood, D.L. Polla, and Z.L. Wang, *J. Am. Chem. Soc.*, 131 (2009), pp. 6670-6671