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# Electrospinning route for the fabrication of $p$ - $n$ junction using nanofiber yarns

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Electrospinning is a simple, versatile, and cost effective method for generating nanoscale fibers, wires, and tubes. Nanowires and nanotubes could be important building blocks for nanoscale electronics, optoelectronics, and sensors as they can function as miniaturized devices as well as electrical interconnects. We report on a simple method to fabricate free standing ceramic nanofiber heterostructures, which exhibit rectifying behavior of a  $p$ - $n$  junction. © 2009 American Institute of Physics. [DOI: 10.1063/1.3157206]

## I. INTRODUCTION

Electrospinning has been recognized as an efficient technique for the fabrication of submicron sized fibers from a wide variety of materials including polymer, molten polymer, and polymeric precursors of ceramics.<sup>1–4</sup> When the diameters of fibrous materials are reduced from micrometers to nanometers the surface area to volume ratio becomes unusually large, so more chemically functional bonds can form and unusual mechanical properties are achieved. These outstanding properties make the nanofibers optimal candidates for many important applications. Among the electrospun nanofibers, ceramic materials are very promising for a number of applications, such as high temperature catalysis, filtration, hydrogen storage, energy conversion, electronic, optoelectronic, photonic, and sensor devices.<sup>5</sup>

It is well recognized that there are considerable difficulties in handling a single nanofiber or making well organized structures from single nanofibers. By making yarns from bundles of oriented electrospun nanofibers it is possible to obtain ordered structures large enough to handle. Since the fiber bundle or the yarn is more robust than a single nanofiber it is more convenient to transfer it onto a substrate. The electrical, physical property characterization of the nanofibers may not require special equipment.

The yarn manufacturing method<sup>6–8</sup> involves collecting the electrically charged fibers between two parallel and electrically grounded collector surfaces separated by a distance commensurate with the diameter of the loops formed by the electrically driven bending instability.<sup>9</sup> One collector shaped as a hemisphere with diameter of 8 cm is rotated around its axis at an appropriate rate to twist the nanofibers into a microyarn. The yarn is extended by translating the nonrotating rod-shaped collector in an axial direction away from the rotating collector. Properties such as yarn length, diameter, fi-

ber count, and twist per unit length are controlled by the rotation rate of the hemispherical collector and the translation rate of the rod shaped collector. Yarns of nanofibers can be produced from any polymer or polymeric precursor of ceramic solutions that can be electrospun into fibers.

We synthesized and characterized several semiconducting ceramic (ZnO, NiO) nanofiber yarns using a modified version of an electrospinning setup, which is reported elsewhere.<sup>8</sup> ZnO, a wide bandgap (3.4 eV) II-VI compound semiconductor having  $n$ -type properties, has been intensively studied due to its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors, and spin electronics.<sup>10–15</sup> ZnO is a strong candidate for semiconductor devices operating in harsh environments, such as extraterrestrial space and nuclear reactors because ZnO is more radiation resistant than either Si, SiC, GaAs, or GaN. ZnO is also very suitable for high power and high-frequency semiconductor device applications, based on its large breakdown voltage and high saturated electron drift velocity.<sup>16</sup>

NiO on the other hand is one of the relatively few metal oxides that tend to have  $p$ -type properties. It has been attracting considerable attention because of its stable and wide bandgap (3.7 eV). Nickel oxide is a very important material extensively used in catalysis, battery cathodes, gas sensors, electrochromic films, and magnetic materials.<sup>17–21</sup>

ZnO/NiO composites have been studied extensively as important soft ferrite materials, gas sensitive materials, and as semiconductors.<sup>22–27</sup> Although the most interesting property of semiconductors is the  $p$ - $n$  interface, attempts to form  $p$ - $n$  interfaces with oxide semiconductor nanofibers are rare. We demonstrate in this paper that the  $p$ - $n$  interface using oxide semiconductor nanofibers can be fabricated using electrospun nanofibers, which do not require adhesion to a solid substrate. The electrospun ZnO/NiO nanofiber heterostructures exhibit rectifying current-voltage ( $I$ - $V$ ) characteristics.

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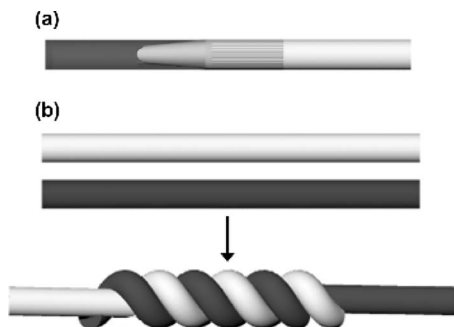


FIG. 1. Schematic diagram for the formation of (a) tapered nanofiber  $p$ - $n$  junction yarn; (b) twisted nanofiber  $p$ - $n$  junction yarn. For both junctions the white yarn is an  $n$ -type ceramic material (ZnO) while the gray yarn is a  $p$ -type ceramic material (NiO). Both types of yarns are made up of many nanofibers (not shown).

## II. EXPERIMENTAL

Zinc oxide/nickel oxide heterojunction structures were made from zinc oxide and nickel oxide nanofiber yarns in two different ways. In the first approach, as spun  $\text{Zn}(\text{CH}_3\text{COO})_2/\text{PVP}$  nanofiber yarn was made and then some portion of this yarn was masked and  $\text{Ni}(\text{CH}_3\text{COO})_2/\text{PVP}$  nanofibers were electrostatically spun around the unmasked portion of the  $\text{Zn}(\text{CH}_3\text{COO})_2/\text{PVP}$  nanofiber yarn. The twisted yarns of  $\text{Zn}(\text{CH}_3\text{COO})_2/\text{PVP}$  and  $\text{Ni}(\text{CH}_3\text{COO})_2/\text{PVP}$  nanofibers were heat treated at 873 K (at the rate of 1 K/min in ambient conditions) to obtain the twisted two-oxide ceramic nanofiber yarns. Here we refer this heterostructured yarn as tapered nanofiber  $p$ - $n$  junction yarn. In the second approach, nanofiber yarns of  $\text{Zn}(\text{CH}_3\text{COO})_2/\text{PVP}$  and  $\text{Ni}(\text{CH}_3\text{COO})_2/\text{PVP}$  were made individually and then were twisted around each other. These twisted yarns were heat treated in the same manner to obtain the ceramic heterojunction yarns. For convenience, we refer this heterostructured yarn as twisted nanofiber  $p$ - $n$  junction yarn. Figure 1 schematically illustrates the formation of  $p$ - $n$  heterojunction nanofiber yarns.

## III. CHARACTERIZATION

### A. Scanning electron microscopy

For scanning electron microscopy (SEM) (Hitachi S-2150) analysis, the nanofibers were placed on an aluminum stub with a strip of carbon tape applied to the surface to promote fiber adhesion while minimizing charging effects. The samples were silver coated (S150B Sputter Coater, Edwards) and imaged using an accelerating voltage of 20 kV. Figure 2 shows optical images of the  $p$ - $n$  heterojunction nanofiber yarns and representative SEM images of individual yarn portion. The average diameters of the yarns were 30–40  $\mu\text{m}$ . Yarn diameters were dependent on the duration of electrospinning. Zinc oxide nanofibers in the yarn had an average diameter of 60.3 nm with the standard deviation of 7.4 nm. Nickel oxide nanofibers had an average diameter of 95.2 nm and standard deviation of 4.8 nm.

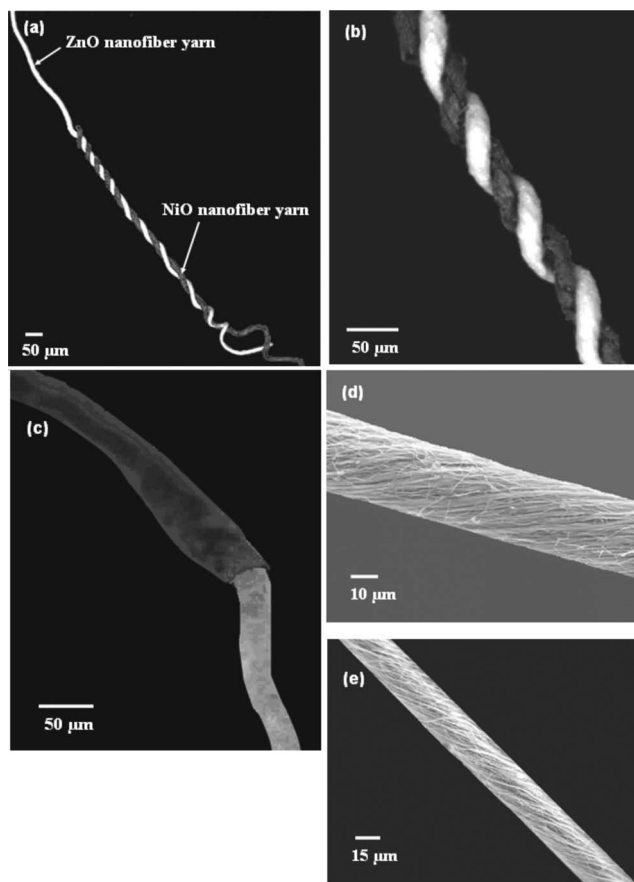


FIG. 2. [(a) and (b)] Optical microscope image of twisted  $p$ - $n$  junction NiO/ZnO nanofiber yarns annealed at 873 K. (c) Optical microscope image of tapered  $p$ - $n$  junction NiO/ZnO nanofiber yarns annealed at 873 K. (d) SEM image of NiO nanofiber yarn annealed at 873 K. (e) SEM image of ZnO nanofiber yarn annealed at 873 K.

### B. X-ray diffraction

X-ray powder diffraction patterns were obtained with a Philips diffractometer employing  $\text{Cu K}\alpha$  radiation, with  $2\theta$  in the range of  $10^\circ$ – $60^\circ$ , to examine the crystal structures of the zinc oxide/nickel oxide heterojunction nanofiber yarns. The x-ray source was operated at 40 kV and 35 mA. The diffraction profiles of zinc oxide/nickel oxide  $p$ - $n$  junction nanofiber yarns annealed at 873 K are presented in Fig. 3.

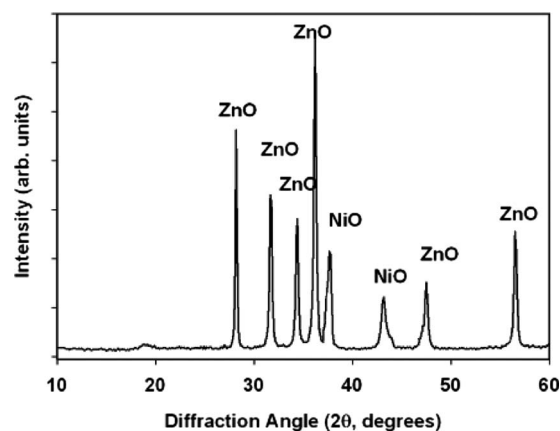


FIG. 3. XRD patterns of ZnO/NiO nanofibers annealed at 873 K.

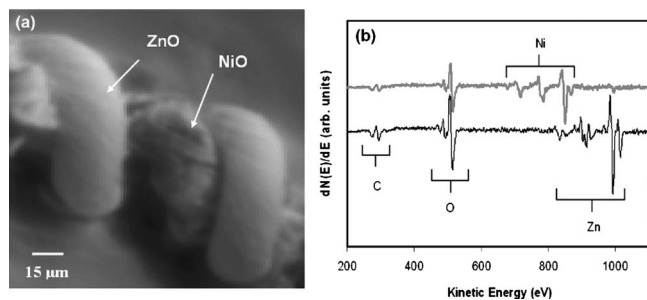


FIG. 4. (a) Secondary electron image of a twisted *p-n* junction NiO/ZnO nanofiber yarn; (b) corresponding AES summed over each region of the twisted NiO/ZnO nanofiber yarn.

The x-ray diffraction (XRD) pattern indicates that the nanofiber heterostructure is well crystallized after annealing at 873 K.

In the XRD patterns of the heterostructures, only peaks that could be assigned to ZnO and NiO were observed and there was no evidence for any different crystalline phases. The peaks can be indexed separately to the cubic nickel oxide phase at  $2\theta=37.2^\circ$  (111),  $43.2^\circ$  (200), and to the hexagonal zinc oxide phase at  $2\theta=31.79^\circ$  (100),  $34.45^\circ$  (200),  $36.28^\circ$  (101),  $47.54^\circ$  (102), and  $56.61^\circ$  (110). These reflection peak positions are also in good agreement with reported values in the literature.<sup>28,29</sup>

### C. Auger electron spectroscopy imaging

Auger electron spectroscopy (AES) measurements were performed under high vacuum conditions in a VG ESCALAB Mk II system that had been outfitted with a custom data acquisition system enabling the digital acquisition of images where each pixel has an associated Auger spectrum. The major elements detected were Zn, Ni, and O, with a minor C feature, most likely due to adventitious carbon and organic residues, as shown in Fig. 4. The two spectra shown were constructed by averaging spectra in all pixels where either the nickel or zinc signal was found to be dominant. The spectra are therefore representative of the entire sample as shown, rather than of two single points in the image. No other impurities were detectable by AES, thereby verifying the degradation and removal of the polymer precursors by annealing at 873 K. Low and controlled impurity concentrations are important if electrospun nanofibers are to be used for optoelectronic, photonic, or sensor-related device applications.

### D. Electrical properties of ZnO/NiO heterojunction nanofiber yarns

The electrical properties of the individual yarns as well as heterojunction nanofiber yarns were measured with a Keithley 2410 sourcemeter. The yarns were placed on an insulating glass slide and Ohmic contacts were made by depositing silver paste onto the two ends of the yarn. Silver wires were then connected to the electrodes of the sourcemeter for measurements. The temperature dependence of the conductivities of these individual ceramic nanofiber yarns (ZnO, NiO) is consistent with semiconducting behavior.<sup>8</sup> Seebeck

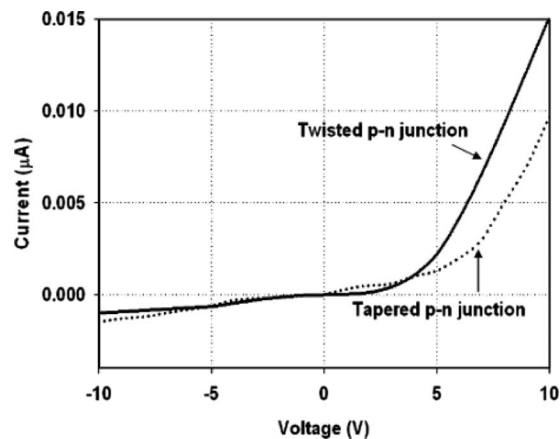


FIG. 5. *I-V* property for *p-NiO/n-ZnO* heterojunction nanofiber yarns.

coefficients of ZnO and NiO nanofibers were found to be  $-45.5$  and  $+25.5 \mu\text{V/K}$  by hot probe measurements.

The *I-V* curves for the heterojunctions without illumination of light showed clear rectifying behavior while that of individual yarn of ZnO and NiO were linear indicating Ohmic contacts. Figure 5 shows the rectifying characteristic curves of the ZnO/NiO heterojunction nanofiber yarns without light illumination. Some leakage current was observed in the reverse bias region and the turn-on voltage was  $\sim 3.0$  V.

The photo *I-V* characteristics of the twisted *p-n* junction nanofiber yarns were measured at room temperature using a black ray UV lamp (model B 100 AP, wavelength range 315–390 nm). A Mannix UV light meter (wavelength range 290–390 nm) was used to measure the intensity of light. Figure 6 shows the characteristic *I-V* curve under illumination of the UV light source with a power density of  $18 \text{ mW/cm}^2$ . Under UV illumination, the turn-on voltage is lowered and the current in both directions (reverse bias as well as forward bias) is found to increase. The observed increase in current flow is due to the generation of electron-hole pairs, created within the ZnO material from exposure to the UV photons. It should be noted that possible heating effects due to illumination by UV light was not accounted for in these measurements.

The diode matrix was fabricated using different *p-* and *n-*type semiconducting oxides with a large lattice mismatch and with polycrystalline structures. Structural imperfections

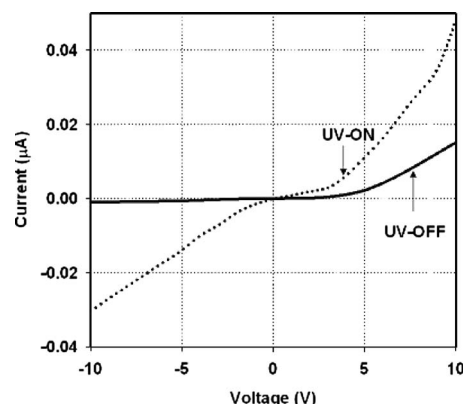


FIG. 6. Photoresponse of twisted *p-n* junction NiO/ZnO nanofiber yarns to UV excitation (wavelength range 315–390 nm) with a power density of  $18 \text{ mW/cm}^2$ .

exist at grain boundaries and the interfaces; therefore, these defects contribute to the formation of diodes with less effective rectification characteristics than in other materials systems. However, the rectifying behavior is apparent.

#### IV. CONCLUSION

Twisted yarns of several ceramic nanofibers were made using an electrospinning setup. We show that  $p$ - $n$  junctions can be formed using electrospun semiconducting nanofibers where they were not deposited on any substrate. The  $p$ - $n$  junction fabricated from  $n$ -ZnO and  $p$ -NiO nanofiber yarns showed typical rectifying current-voltage characteristics, dominated in forward bias by the flow of space-charge-limited current in the  $n$ -ZnO region. The  $p$ - $n$  junction nanofiber structure appears to be highly responsive to ultraviolet irradiation but further measurements are required to account for any heating effects.

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