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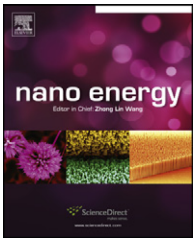

RAPID COMMUNICATION

Electricity generation based on vertically aligned $PbZr_{0.2}Ti_{0.8}O_3$ nanowire arrays

Cheng-Ying Chen[a,b], Te-Hsiang Liu[c], Yusheng Zhou[a], Yan Zhang[a], Yu-Lun Chueh[d], Ying-Hao Chu[c], Jr-Hau He[b,*], Zhong Lin Wang[a,*]

[a]*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, United States*
[b]*Department of Electrical Engineering and Graduate Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 10617, Taiwan*
[c]*Department of Materials Science and Engineering, National Chiao Tung University, HsinChu 30010, Taiwan*
[d]*Department of Materials Science and Engineering, National Tsing Hua University, HsinChu 30010, Taiwan*

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Abstract
We statistically demonstrated the electricity generation from individual vertically-aligned/epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) nanowires (NWs) using a conductive atomic force microscope (AFM). The measured outputs were analyzed in reference to the theoretically calculated piezopotential distribution in a bent NW. Our results show that the performance of the PZT NWs for electricity generation is at the same level as that of ZnO NWs although the piezocoefficient of PZT is high, due to high relative dielectric constant of PZT. Systematic investigating piezoelectricity from single PZT NWs will be useful for optimizing the performance for PZT nanogenerator applications.

Introduction

Energy-harvesting from the vibrations in ambient environment, such as body-movement, heart beating, light wind, vibration of acoustic waves and hydraulic energy, has been proposed as a potential way for powering small electronic components, including micro-electromechanical systems, nanorobots, implantable biosensors and even portable personal electronics [1-5]. For such renewable energy using nanotechnology, it is a key challenge to find the nanomaterial with effectively electromechanical coupling (*i.e.*, piezoelectric effect). Recently, ZnO has been demonstrated as one of the most promising piezoelectric materials for self-power nanodevices due to its bio-compatibility, low-temperature synthesis and ability to achieve wafer-scale uniformity [1,5,6]. In addition to ZnO, other piezoelectric nanomaterials, such as CdS nanoewires (NWs) [7], InN NWs [8] and GaN nanorods [9,10], have also attracted attention.

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*Corresponding authors.
E-mail addresses: jhhe@cc.ee.ntu.edu.tw, jhhe@ntu.edu.tw (J.-H. He), zlwang@gatech.edu (Z.L. Wang).

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As for materials with electromechanical coupling, lead zirconate titanate [$PbZr_{1-x}Ti_xO_3$ (PZT)] is a typical piezoelectric material with a larger piezoelectric constant (e_{33}=~10–15 C/m^2) [11], which is much higher than those of the piezoelectric NWs mentioned earlier. Therefore, the performance of PZT NW-based piezoelectric nanogenerators (NGs) [12,13] is expected to be much higher than that of ZnO NGs [2,5]. Similar to ZnO NW-integrated NGs [14,15], Xu et al. [12] and Chen et al. [13], respectively connected a bunch of the vertically-aligned NWs and the laterally-aligned nanofibers as the PZT-integrated NG devices for increasing the piezoelectric output. Their output voltages can be up to ~1–1.6 V, which is also comparable with those of ZnO NW-integrated NGs [14,15]. However, to maximize the NG performance of PZT NWs, it is important to systematically investigate single PZT NW NGs.

In this work, the piezoelectric measurement of single $PbZr_{0.2}Ti_{0.8}O_3$ NWs was statistically demonstrated in contact mode using a conductive atomic force microscope (AFM). The calculated piezopotential distributions in a bent PZT NW were semi-quantitatively analyzed and compared with the experimental observations. Understanding piezoelectric effect of a single NW will benefit for designing high efficient NGs.

Experimental

Epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ NW arrays (NWAs) were grown on $SrTiO_3$ (STO) (0 0 1) substrate using pulsed laser deposition with a KrF (λ=248 nm) excimer laser with a laser density of 250 mJ. A dynamic chamber pressure of 400 mTorr with O_2 and the substrate holder temperature of 750 °C were maintained during the deposition. The epitaxial PZT NWs were formed by evaporating a single quaternary $PbZr_{1-x}Ti_xO_3$ target with an atomic ratio of Pb:Zr:Ti:O equals to 1:0.2:0.8:3. The working distance between target and substrate holder was set to be 3 cm. More details of PZT NWAs growth are described elsewhere [16].

Piezoelectric measurements were performed using AFM (Molecular Force Probe MFP-3D from Asylum Research) with a conducting Pt-coated Si tip (14 μm in height with an apex angle of 70°, from Olympus) [10]. The output voltage across an outside load of resistance R_L of 500 MΩ was continuously monitored as the tip scanned over the NWs. No external voltage was applied during the experiment measurement.

Results and discussion

Fig. 1(a) and (b) shows that the top-view and cross-sectional scanning electron microscopy (SEM) images of the PZT NWAs. The vertically aligned NWAs were uniformly grown on ~100-nm-thick PZT film/STO (0 0 1) substrate. The diameter and the length of the NWs are ~50 and ~100–220 nm, respectively. The SEM observation shows the PZT NWs with smooth surfaces.

The microstructure of the NWAs was examined by X-ray diffraction (XRD), as shown in Fig. 1(c). The XRD peaks corresponding to the (0 0 1) orientation of the perovskite PZT were observed, indicating a [0 0 1] growth direction for tetragonal phase of single crystalline PZT [17]. The vertical growth and the alignment were enforced by the epitaxial growth on STO (0 0 1) substrate (Fig. 1(d)) [16], which leads to a superior alignment of PZT NWs as compared to the PZT NWs synthesized by a sol-gel method [12]. Regarding the piezoelectric polarization of the PZT NWs, previous experimental evidences revealed that the self-polarization could exist in the epitaxial PZT due to the accumulation of oxygen vacancies at the interface between epitaxial PZT films and substrates, the oxygen vacancy defect-dipole complexes throughout the fiof, and the trapping of free electrons at the interface [17–19].

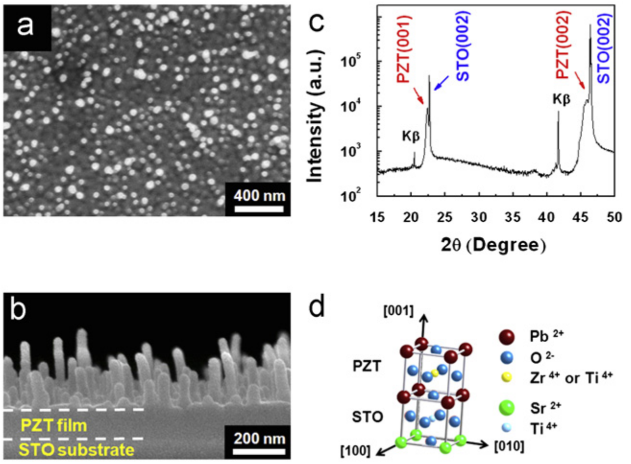

Figure 1 (a) Cross-sectional and (b) top-view SEM images of the PZT NWAs. (c) XRD patterns of the PZT NWAs on STO (0 0 1) substrate. (d) Crystalline structures and ionic arrangements of [0 0 1]-oriented tetragonal PZT on STO (0 0 1) substrate.

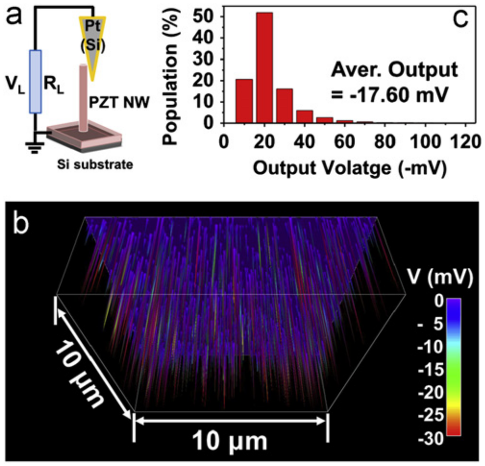

Figure 2 Piezoelectric power generation using the PZT NWs. (a) Schematic of the AFM measurement system. (b) 3D plot of the output voltage at an external load (R_L=500 MΩ) recorded when the AFM tip scanned across the NWs. (c) Statistical distribution of the piezoelectric output measured from the PZT NWs.

The piezoelectric responses of the PZT NWAs were examined in a contact mode of an AFM using a Pt-coated Si tip [2,6]. The cantilever has a spring constant of 1.55 N/m. In AFM contact mode, a constant normal force of 5 nN was maintained between the tip and the sample surface. By scanning the tip across the NW (Fig. 2(a)), output voltage was detected across an external load. No external voltage was applied during the measurement. Fig. 2(b) shows a three-dimensional (3D) plot of

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output potential generated by the PZT NWAs with a scanning area of $10\,\mu m \times 10\,\mu m$ at a scanning speed of 25.04 μm/s (corresponding to 1.0 Hz scan rate), and the color code represents the magnitude of the output potential. The statistical distribution of the measured piezoelectric output is shown in Fig. 2(c). The amount of statistical peaks is larger than 720,000 peaks, which were repeatedly measured from many different areas of $10\,\mu m \times 10\,\mu m$. Because the areas used for each measurement are different, density, morphology, tilted angle and aspect ratio of PZT NWAs would be varied slightly. Consequently, the measured piezoelectric output exhibits a statistical distribution: about 80–85% of output voltages are within the range from -2 to -30 mV. The average piezoelectric output is around -17.6 mV, which is comparable to that of our previous ZnO NGs [2,5]. However, the piezoelectric output of PZT NWs is expected to be significantly higher than that of ZnO NWs since the piezoelectric constant (e_{33}) of PZT is up to $\sim 15\,C/m^2$ [11], which is one order of magnitude higher than that of ZnO ($\sim 1.22\,C/m^2$) [6]. The unexpected phenomenon will be illustrated later by an ideal static model of piezoelectric effect with the material constants of PZT and ZnO, such as the e_{33}, the relative dielectric constant ($\kappa_\perp$).

To further confirm the origin of these piezoelectric outputs, the sample with half PZT NWAs/half PZT films, as shown in Fig. 3(a), was also examined by the AFM piezoelectricity measurement. The 3D distribution of output potential generated by the sample is shown in Fig. 3(b). The location of the peaks is correlated well with the site of the NWs, which implies that the piezopotentials are indeed induced by bending PZT NWs. The residual peaks on the film side could originate from the residual NWs on the film side.

To understand the theoretical magnitude of the electricity generation based on the PZT NWAs, the piezopotential distribution in a bent PZT NW was calculated under a lateral force (f) using the Lippman theory [6,20]. A semi-quantitative understanding can be achieved by a numerical calculation without considering the carrier concentration [6,20]. The material constants used in the calculation are: anisotropic elastic constants of PZT: C_{11}=134.8680 GPa, C_{12}=67.8883 GPa, C_{13}=68.0876 GPa, C_{33}=113.297 GPa, C_{44}=22.2222 GPa, and piezoelectric constants: e_{15}=9.77778 C/m^2, e_{31}=$-$1.81603 C/m^2, e_{33}=9.05058 C/m^2. The relative dielectric constants are $\kappa_\perp$=504.1, $\kappa_\parallel = 270$, and the density (ρ) is 7600 kg/m^3. Length and diameter of the [0 0 1]-orientated PZT NW were set to be 200 and 50 nm, respectively. The applied f was set to be 80 nN [6]. Fig. 3(c) represents the calculated side-view and top-view piezopotential distributions in the bent PZT NW pushed by an AFM tip. When the tip scans across the top of the NW and touches the NW forming an electrical circuit, the negative piezopotential (around -30 mV, as shown in the right of Fig. 3(c) drives the free electrons, resulting in a transient current in the external load. Comparing the semi-quantitatively calculated potential (Fig. 3(c) and the measured output voltage (Fig. 2(c)), the calculated potential of around -30 mV (the right of Fig. 3(c)) corresponds to the measured voltage of around -17.6 mV, revealing a reasonable agreement.

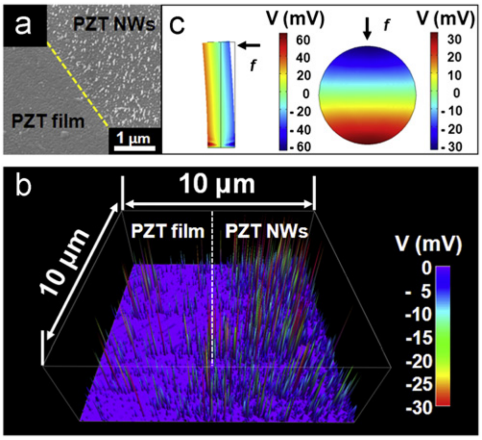

Figure 3 (a) Top-view SEM image of the sample with half PZT NWAs and half PZT films. (b) 3D plot of the output voltage of the PZT sample shown in (a). (c) Calculated piezoelectric potential distribution for a PZT NW. Left and right figures in (c) are the side- and top-view output of the piezoelectric potential in the NW, respectively.

To comprehend that the magnitude of piezoelectric output of PZT NWs is at the same level as that of ZnO NWs, we utilize the following ideal static model of piezoelectric effect. For the model without considering the conductivity, under the first-order approximation, the potential distribution along the NW induced by the piezoelectric effect relies on the length (L) and the diameter (a) of the NW, e_{33}, $\kappa_\perp$, and the maximum deflection (γ_m), using Eq. (1) as an estimation [2,10]:

$$V_S^{\pm} \approx \frac{3e_{33}}{4\kappa_0\kappa_\perp}\left(\frac{a}{L}\right)^3 \gamma_m \tag{1}$$

where κ_0 is the permittivity of vacuum and $V_S^{\pm}$ is the piezopotential, inversely proportional to $\kappa_\perp$. Accordingly, although e_{33} of PZT is one order of magnitude higher than that of ZnO, the relative dielectric constant ($\kappa_\perp$) of PZT ($\kappa_{\perp,PZT}\sim 500$) [21] is also larger than that of ZnO ($\kappa_{\perp,ZnO}\sim 8$) [6]. Assuming that the same γ_m applies to PZT and ZnO NWs with identical feature sizes, the piezopotential of PZT could be even smaller than that of ZnO. In addition, the measured piezopotential strongly depends on contact resistance between Ag pastes and thin films at the bottom of the NWs, resistance of the bottom thin film, contact resistance between the Pt tip and the NWs, limited conductivity and small capacitance of the NWs. Therefore, it would be reasonable that the measured output of our PZT NWs is similar with that of previous ZnO NGs [2,5].

In order to investigate the electricity generation details of the PZT NWs, the NG measurements were carried out by changing scan rate of the AFM. We kept AFM scanning a fin o area of $10\,\mu m \times 10\,\mu m$ and measured the average magnitude of the voltage peaks. The statistical standard deviations of the measured voltages are exhibited by the error bars, resulting from the slight variations of morphology, tilted angle and aspect ratio for the PZT NWAs. At a fim a contact force, with increasing the scan rate, their average output volatage increases slightly and almost linearly (Fig. 4). This is possibly due to a fast charging flow rate caused by a fast straining of the NWs [22]. Moreover, the quicker AFM tip scanning may lost the signal from the shorter NWs, resulting in higher average output voltage. This also is a possible reason to illustrate the relationship between the scan rate and the average output voltage. Similar result was observed in ZnO NWs as well [23].

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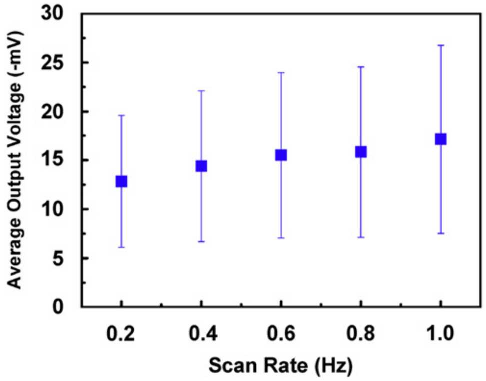

Figure 4 Statistics of piezoelectric output of the PZT NWs under different AFM scan rate in a fitat area of 10 μm × 10 μm.

Conclusion

In summary, we statistically demonstrated the electricity generation from individual vertically-aligned/epitaxial PZT NWs using a conductive AFM. The calculated piezopotential distributions in a bent PZT NW were semi-quantitatively analyzed and show a reasonable agreement with the experimental voltage outputs. Although PZT has a larger the piezoelectric constant, the NG performance of the PZT NWs is just similar with that of our pervious ZnO NWs due to its higher the relative dielectric constant. Our study provides comprehensive experimental and theoretical base for understanding the piezoelectricity from single PZT NWs, which will benefit the design and optimization of high performance nanogenerators.

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Cheng-Ying Chen received the M.S. degree in the Graduate Institute of Electrical Engineering from National Tsing Hua University, Hsinchu, Taiwan in 2005. He is a Ph.D. candidate in the Graduate Institute of Photonics and Optoelectronics at National Taiwan University and also a visiting student in the School of Materials Science and Engineering at Georgia Institute of Technology now. His research interests include carrier recombination in nanostructures, surface-related physics in nanostructures, optical anisotropy in one-dimensional nanostructures, electronic structures of nanostructures, and nanogenerator.

Te-Hsiang Liu received the B.S. degree (2009) and the M.S. degree (2011) in the Department of Materials Science and Engineering at National Chiao Tung University, Hsinchu, Taiwan. His research interests include the synthesis, characterization, and understanding of fundamental physical properties of complex oxide thin films and nanostructures.

Yusheng Zhou was enrolled into the Ph.D. program in Material Science and Engineering at Georgia Institute of Technology in 2010. His research interests include Scanning Probe Microscopy and Micro/Nano Electro-Mechanical System based on semiconducting nanomaterial for energy harvesting and sensor arrays. He received his Bachelor's degree in Applied Physics and M.S. degree in Optics from Beihang University.

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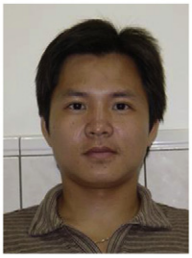
Yan Zhang received his B.S. degree (1995) and Ph.D degree (2004) in Theoretical Physics from Lanzhou University. Then, he worked as a lecturer and associate Professor (2007) of Institute of Theoretical Physics in Lanzhou University. In 2009 he worked as research scientist in the group of Professor Zhong Lin Wang at Georgia Institute of Technology. His main research interest and activities are: dynamics of time-delay systems, complex networks, self-powered nano/micro system and theoretical calculation of piezotronic.

Yu-Lun Chueh received his Ph.D degree from Department of materials science and engineering, National Tsing Hua university, Taiwan in 2006 and worked as postdoctor in electrical engineering and computer science, UC Berkeley from 2007–2009. Currently, He is assistant professor in department of materials science and engineering, National Tsing Hua university, Taiwan. He has published 85 peer-reviewed papers and 6 patents. His researches mainly concentrate on the discovery of novel nanomaterials, the fundamental understanding of the unique properties of these nanomaterials, and the assembly of these nanoscale building blocks for novel electrical, opto-electrical, biological device applications. The research directions include graphene, ReRAM, and solar cell.



Ying-Hao Chu received his PhD in Department of Materials Science and Engineering from National Tsing Hua University in 2004. He joined University of California, Berkeley in 2004 as a postdoc. His research is highly focused on complex functional oxides and nanostructures. He has extensive experience in the use of advanced characterization techniques to understand complex functional oxides and nanostructures. His papers have been published in Science(1), PNAS(1), Nature X($>$10), Physical Review series ($>$15), Nano Letters & ACS Nano (7), Advanced (Functional) Materials (8), APL/JAP ($>$30), $>$10 invited review papers etc. His goal is try to create a pathway to use topological defects for next generation electronics. Now, he is top 3 of most publication in $BiFeO_3$ and top 10 of most publication in multiferroic materials. In 2008 he joined National Chiao Tung University in Department of Materials Science and Engineering as an assistant professor.

Jr-Hau He joined Institute of Photonics and Optoelectronics, and Department of Electrical Engineering at National Taiwan University and established Green Photonics Laboratory in early 2007. He puts his efforts into the design of new nanostructured architectures for Nanophotonics and the next generation of nanodevices, including Photovoltaics, and Resistive RAM. His breakthrough researches have been highlighted by almost 30 scientific magazines such as Nature, SPIE newsroom, Chemical & Engineering News, and Nano Today. He is actively participating in the activities and services in scientific professional societies. Professor Jr-Hau He has been recognized internationally. He serves as a referee for numerous prestigious journals, and a chair, co-chair, and committee for national and international syposiums. He serves as an editorial board member of Journal of Nanoengineering and Nanomanufacturing, and International Journal of the Physical Sciences. He also serves as a guest editor for the special issue for Journal of Nanoengineering and nanomanufacturing (2011). He is a recipient of Youth Optical Engineering Medal of Taiwan Photonics Society (2011), Distinguished Young Researcher Award of the Electronic Devices and Materials Association (2011), Prof. Jiang Novel Materials Youth Prize of International Union of Pure and Applied Chemistry (IUPAC) (2011), and the Exploration Research Award of Pan Wen Yuan Foundation (2008). Details can be found at: http://cc.ee.ntu.edu.tw/~jhhe/.

Zhong Lin (ZL) Wang is the Hightower Chair in Materials Science and Engineering, Regents' Professor, Engineering Distinguished Professor and Director, Center for Nanostructure Characterization, at Georgia Tech. Dr. Wang is a foreign member of the Chinese Academy of Sciences fellow of American Physical Society, fellow of AAAS, fellow of Microscopy Society of America, and fellow of Materials Research Society. Dr. Wang has been awarded the MRS Medal in 2011 from Materials Research Society and Burton Medal from Microscopy Society of America. He has made original and innovative contributions to the synthesis, discovery, characterization, and understanding of fundamental physical properties of oxide nanobelts and nanowires, as well as applications of nanowires in energy sciences, electronics, optoelectronics, and biological science. His discovery and breakthroughs in developing nanogenerators establish the principle and technological road map for harvesting mechanical energy from environment and biological systems for powering a personal electronics. His research on self-powered nanosystems has inspired the worldwide effort in academia and industry for studying energy for micro—nano-systems, which is now a distinct disciplinary in energy research and future sensor networks. He coined and pioneered the fisys of piezo-tronics and piezo-phototronics by introducing piezoelectric potential gated charge transport process in fabricating new electronic and optoelectronic devices. This breakthrough by redesign CMOS transistor has important applications in smart MEMS/NEMS, nanorobotics, human-electronics interface, and sensors. Dr. Wang's publications have been cited for over 45,000 times. The H-index of his citations is 102. Details can be found at: http://www.nanoscience.gatech.edu.

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