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Electricity generation based on vertically aligned PbZr$_{0.2}$Ti$_{0.8}$O$_3$ nanowire arrays

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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 nanowires (NWs) [7], InN NWs [8] and GaN nanorods [9,10], have also attracted attention.
As for materials with electromechanical coupling, lead zirconate titanate \([\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3} (\text{PZT})]\) is a typical piezoelectric material with a larger piezoelectric constant \((e_{33}=-10-15 \ \text{C/m}^2)\) [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 \(-1-1.6 \ \text{V}\), 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 \(\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\) 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 \(\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\) NW arrays (NWAs) were grown on \(\text{SrTiO}_3\) (STO) substrate using pulsed laser deposition with a KrF \((\lambda=248 \ \text{nm})\) excimer laser with a laser density of 250 mJ. A dynamic chamber pressure of 400 mTorr with \(\text{O}_2\) and the substrate holder temperature of 750 °C were maintained during the deposition. The epitaxial PZT NWs were formed by evaporating a single quaternary \(\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3\) target with an atomic ratio of \(\text{Pb}:\text{Zr}:\text{Ti}:\text{O} = 1:0.2:0.8:3\). 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 \((14 \ \mu\text{m} \ \text{in height with an apex angle of 70°}\) from Olympus) [10]. The output voltage across an outside load of resistance \(R_L\) of 500 MΩ was continuously monitored as the tip scanned across 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 NWs were uniformly grown on \(\text{SrTiO}_3\) (STO) substrate using pulsed laser deposition with a KrF \((\lambda=248 \ \text{nm})\) excimer laser with a laser density of 250 mJ. A dynamic chamber pressure of 400 mTorr with \(\text{O}_2\) and the substrate holder temperature of 750 °C were maintained during the deposition. The epitaxial PZT NWs were formed by evaporating a single quaternary \(\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3\) target with an atomic ratio of \(\text{Pb}:\text{Zr}:\text{Ti}:\text{O} = 1:0.2:0.8:3\). The working distance between target and substrate holder was set to be 3 cm. More details of PZT NWAs growth are described elsewhere [16].

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**Piezoelectric power generation using the PZT NWs.** Fig. 2(a) Schematic of the AFM measurement system. (b) 3D plot of the output voltage at an external load \((R_L=500 \ \text{MΩ})\) recorded when the AFM tip scanned across the NWs. (c) Statistical distribution of the piezoelectric output measured from the PZT NWs. 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 film, and the trapping of free electrons at the interface [17-19].

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 μm x 10 μm 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 μm x 10 μm. 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/m² [11], which is one order of magnitude higher than that of ZnO (~1.22 C/m²) [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 ($\varepsilon_r$), and the maximum deflection ($\gamma_m$).

To further confirm the origin of these piezoelectric outputs, the sample with half PZT NW/half PZT films, as shown in Fig. 3(a), was also examined by the AFM piezoelectric 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, $C_{12} = 67.8833$ GPa, $C_{13} = 68.0876$ GPa, $C_{33} = 113.297$ GPa, $C_{44} = 22.2222$ GPa, and piezoelectric constants: $e_{33} = 9.77778$ C/m², $e_{31} = -1.81603$ C/m², $e_{32} = 9.05058$ C/m². The relative dielectric constants are $\varepsilon_r = 504.1$, $\varepsilon_i = 270$, and the density ($\rho$) is 7600 kg/m³. Length and diameter of the [0 0 1]-oriented 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(e)), 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.

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, $e_{33}$, $\varepsilon_r$, and the maximum deflection ($\gamma_m$), using Eq. (1) as an estimation [2,10]:

$$V_z^\perp \approx \frac{3e_{33}}{4\varepsilon_0 \gamma_m} \frac{a^3}{L} \gamma_m \tag{1}$$

where $\varepsilon_0$ is the permittivity of vacuum and $V_z^\perp$ is the piezopotential, inversely proportional to $\gamma_m$. Accordingly, although $e_{33}$ of PZT is one order of magnitude higher than that of ZnO, the relative dielectric constant ($\varepsilon_r$) of PZT ($\varepsilon_r$) is also larger than that of ZnO ($\varepsilon_r$) [6]. Assuming that the same $\gamma_m$ 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 fixed area of 10 μm x 10 μm 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 fixed scan rate, their average output voltage increases slightly and almost linearly (Fig. 4). It 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].
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 piezoelectric constant, the NG performance of the PZT NWs is just similar with that of our previous 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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