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Ferroelectric Nanorods: Control and Application to Piezoelectric Energy Harvesting

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ABSTRACT

Piezoelectric energy harvesters (PEHs) are expected to power trillions of miniaturized sensors as vibration in the environment is ubiquitous. Among a wide range of materials showing piezoelectricity, ferroelectric materials are of particular interest because of their superior piezoelectric response. A typical design used to enhance the output power of PEHs employs a cantilever based on ferroelectric films at the resonant frequency of the vibrations. However, this design requires a cantilever with relatively large dimensions to meet the typical vibration frequency. In addition, the intensity and frequencies of the vibration is susceptible to environmental changes, which makes it difficult to maximize the efficiency of the PEHs. In this article, we introduce our recent approach that employs ferroelectric nanorods, instead of films, to minimize the size of PEHs while maintaining efficiency; 1) the ferroelectric domain of the nanorods was controlled to maximize the piezoelectric response, and 2) the PEHs using ferroelectric nanorods were theoretically analyzed and the large figure of merits (FOMs) of nanorods were experimentally demonstrated.

INTRODUCTION

Technologies based on the Internet of Things (IoT) have been rapidly developed for various purposes; for instance, for enhancing the safety of infrastructures, reducing energy consumption, and making our daily lives more convenient. [1] It used to be difficult to achieve technologically since IoT involves trillions of microscale or nanoscale sensors, and devices operating in more remote areas require higher costs of maintenance. However, energy harvesters, which are promising power sources that can use ambient mechanical, thermal or optical energy, will be a competitive candidate for powering the IoT sensors, with the merits of long-term endurance, high integration and negligible pollution. [2]

Among all kinds of energy harvesters, piezoelectric energy harvesters (PEHs) have been intensively investigated and applied due to their high conversion efficiency from mechanical energy to electric power. Seen from the available energy E_a of a piezoelectric unit applied with uniaxial stress T shown in Eq. (1) [3], the figure of merit (FOM) d^2/ε, T, and volume U are found to be the influential factors to E_a, as well as to the output power of PEHs.

$$E_a = \frac{1}{2}CV^2 = \frac{1}{2}\frac{d^2}{\varepsilon}T^2U = \frac{1}{2}\cdot \mathrm{FOM}\cdot T^2U, \qquad (1)$$

where C represents the capacitance, ε the dielectric constant, d the piezoelectric constant of the piezoelectric materials, and V is the electric potential. Therefore, piezoelectric materials with not only large d but also small ε are expected to be used for PEHs. Furthermore, since the piezoelectric and dielectric constant are strongly correlated with each other, there is no straightforward strategy to create materials with a large FOM.

Apart from the improvement of the piezoelectric properties, the output power of PEHs can be increased by optimizing the configuration of devices to achieve large induced strain. A typical strategy uses cantilever-based PEHs that work at the resonant frequency. However, it

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requires a cantilever with relatively large dimensions to meet the ambient vibration frequency that is lower than 300 Hz, especially in the case where the traditional design of ceramic layers with metal or silicon substrates is used. In order to minimize the size of PEHs while keeping the resonance, more flexible PEH devices using piezoelectric polymers such as polyvinylidene fluoride (PVDF) and polymer-based piezoelectric composites adhered to polymer substrates have been studied. [4, 5] Although a number of interesting and valuable results have been reported [6, 7], achieving a large piezoelectric response remains challenging. In addition, the intensity and frequencies of the vibration are susceptible to environmental changes, which makes it hard to maximize the efficiency of the cantilever-based PEHs.

Another strategy is directly magnifying the applied stress regardless of the resonance. For example, a PEH consisting of aligned nanorods driven by the force that is normal to the substrate can be a prospective candidate. In this article, we introduce our recent approach that employs ferroelectric nanorods to minimize the size of PEHs while maintaining efficiency; 1) the ferroelectric domain of the nanorods was controlled to maximize the piezoelectric response, and 2) the PEHs using ferroelectric nanorods were theoretically analyzed and the large FOMs of nanorods were experimentally demonstrated.

CONTROL OF FERROELECTRIC DOMAINS IN Pb(Zr, Ti)O_3 (PZT) NANORODS

Domains of ferroelectric materials significantly affect their piezoelectric properties. In the case of PZT, which is one of the most representative ferroelectric materials, the (100)/(001)-oriented tetragonal phase has two types of domains; *a*- and *c*-domains. The former has the spontaneous polarization parallel to the substrate, and the latter has that perpendicular to the substrate. When the external force is applied along the direction perpendicular to the substrate, only the *c*-domain shows the piezoelectric response along the same direction. Therefore, for such a condition, the larger *c*-domain volume fraction there is, the larger piezoelectric properties it exhibits. [8] It has been widely known that the domain volume fraction of ferroelectric films can be easily controlled by the mechanical stress from the substrate. [9, 10] However, since the nanorods are almost free from the substrate, there was no straightforward strategy to control it. Nevertheless, there was an interesting and pioneering work showing that the shape of single crystal $BaTiO_3$ nanocolumns can affect their domain structure. [11] We focused on such a phenomenon and systematically investigated the influence of the size and electrostatic boundary conditions on the domain structure using PZT nanorods. [12-14] For this experiment, the nanorods were

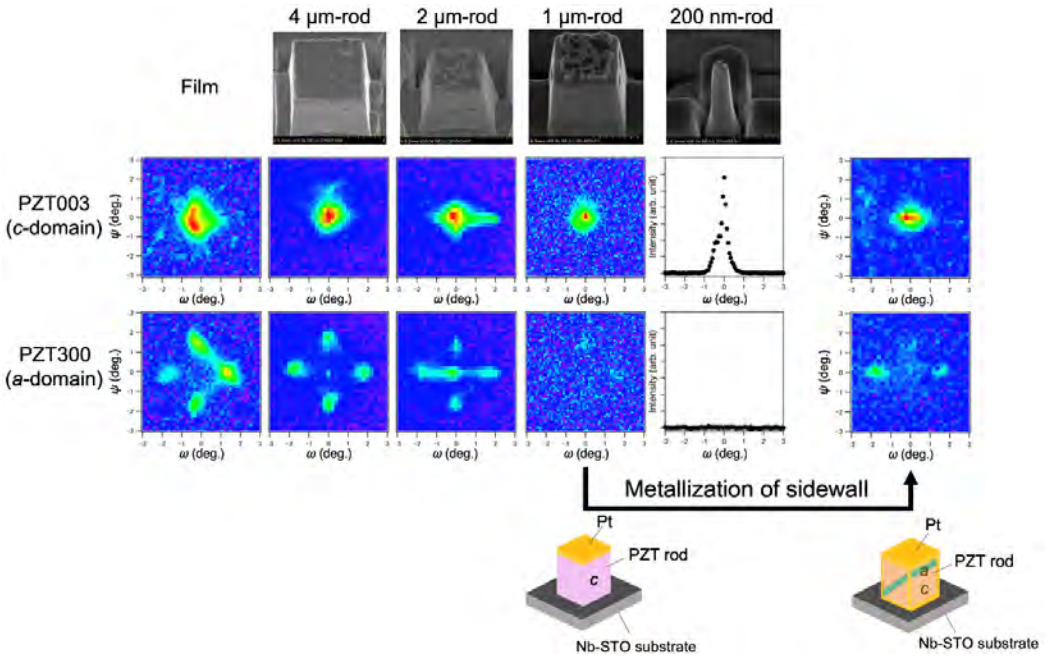

Fig. 1: Synchrotron XRD ψ-ω maps for PZT 003 (*c*-domain) and 300 (*a*-domain) of the film and nanorods of widths 4 μm, 2 μm and 1 μm (left), and ω-scans at $\psi = 0°$ for the nanorod with a 200 nm width (middle). The ψ-ω maps for the nanorod with a 1 μm width after the metallization of sidewall are also shown (right). [12, 14]

fabricated by etching (100)/(001)-epitaxial PZT films on substrates, using a focused ion beam (FIB). After the FIB process, the nanorods were annealed to recover from the process damage and to stabilize the domain structure at the given shape. For the characterization of domain structure, synchrotron X-ray diffraction (XRD) was used. An X-ray beam was focused onto the fabricated single PZT nanorod to detect the diffraction intensity from the *a*- and *c*-domains. Figure 1 shows the synchrotron XRD ψ-ω maps for a- and *c*-domains of a PZT film and nanorods on Nb-doped $SrTiO_3$ (Nb-STO) substrates. It can be clearly seen in the figure that the *a*-domain fraction decreases with decreasing the nanorod width, and the *c*-domain becomes dominant for the narrowest nanorod. Furthermore, by coating the sidewall of nanorods with Pt, the *a*-domain fraction increases.

These behaviors can be explained by the imperfect charge screening on the sidewall of the nanorods. The bound charges of polarization can never be perfectly screened because of the finite screening length. Without perfect charge screening, a depolarizing field arises due to the polarization discontinuity at the surface. When the width of nanorods decreases, the depolarizing field perpendicular to the rod increases while the depolarizing field parallel to the rod is unchanged. Therefore, the *a*-domain having polarization perpendicular to the rod becomes unstable as compared with the *c*-domain having polarization parallel to the rod. If the sidewall of nanorods is metalized, the depolarizing field perpendicular to the rod weakens; thus, the *a*-domain fraction increases. As shown in Fig. 2, a width less than 1000 nm gives the perfect *c*-domain. The spatially separated nanorod arrays with an average diameter of 166 nm, fabricated by pulsed laser deposition (PLD) at an elevated oxygen pressure [14, 15], indeed showed the perfect *c*-domain. Therefore, the fabrication of spatially separated narrow nanorod arrays is beneficial for maximizing the piezoelectric response.

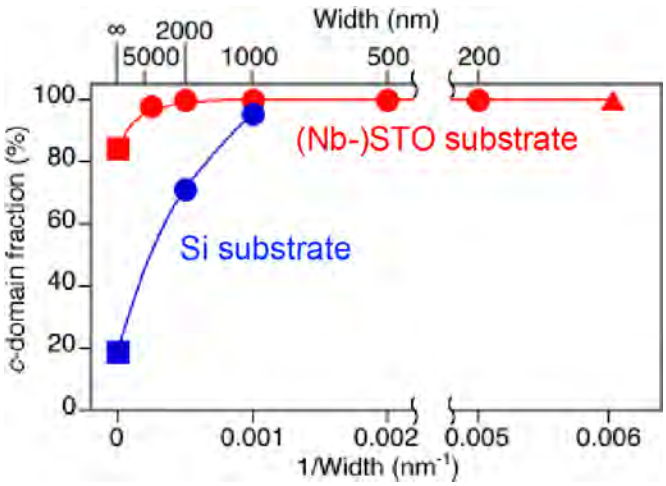

Fig. 2: *c*-domain fractions of PZT films (■) and nanorods (● and ▲) on (Nb-)STO and Si substrates. ● and ▲ denote the nanorods fabricated by FIB and PLD at an elevated oxygen pressure, respectively. [14]

THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF PEHS USING PZT NANORODS

Here, we consider a simple case of a PEH with an aligned nanorod array powering a resistant device. Sinusoidal vibration force $F = F_m \sin(2\pi ft)$ is applied normally to the substrate, i.e., in the axial direction of the nanorods. For the given amplitude F_m, the applied stress varies with the contact area A between the piezoelectric materials and the vibration source, giving $T_m = F_m/A$. Thus, the maximum output power of the nanorod-based PEH deduced from Ohm's law is expressed as [16]

$$P_{\max} = \frac{V_m^2}{4X_C} = \frac{\pi f d_{33}^2 F_m^2}{2\varepsilon A^2} U, \qquad (2)$$

where V_m represents the amplitude of the generated voltage, and X_c the impedance of the piezoelectric materials. The same model was also introduced into the finite-element simulation software, COMSOL Multiphysics 5.3a, for a more precise calculation.

Figure 3 illustrates the effect of the contact area of the nanorods. Here A_0 denotes the contact area of a dense film. It was found that the power increases with the decrease of the contact area of the nanorod array, namely, the increase of the volume of the gaps in between the nanorods. We strongly expect that the output power can be one or two orders of magnitude higher than that of a film if the contact area becomes small enough (within the fracture limit). The improvement of the output power can also be attributed to an effective FOM of the nanorod arrays. The effective FOM is expressed with $d^2/\varepsilon_{\text{eff}}$, where ε_{eff}, i.e., the effective dielectric constant, is the composite dielectric constant of nanorods and gaps. As the volume fraction of the gaps increases, the effective FOM is enhanced, owing to the decrease of ε_{eff}.

Several limitations are associated with the application of nanorod arrays. On one hand, induced stress is limited by the mechanical strength of the piezoelectric material.

On the other hand, vibrations cannot perfectly apply the normal force to the substrate without causing low-frequency lateral oscillations. Such oscillations would induce shear stress, which could suppress the performance of the nanorods. Another thing that needs to be mentioned is that the vibration in practical devices always accompanies mechanical and piezoelectric damping, though it is a minor factor on limiting the power at off-resonant frequencies.

Nevertheless, nanorod-based PEHs show great potential to power microsensors. Simulations on a typical cantilever-based PEH, using the same materials and substrates with a nanorod-based PEH, show a dramatic fall of the output power when shortening the length of the beam down to the micro scale. It is due to the strong correlation between the dimensions and the natural frequency of the device. Since achieving such a microscale cantilever-based PEH with a low resonant frequency will be costly, nanorod-based PEHs have the potential to become a prospective alternative for IoT applications.

The enhanced output performance of the nanorod arrays shown in Fig. 3 is also supported by the experimental characterization of PZT nanorods grown on STO substrates by PLD. Before growing PZT nanorods, $SrRuO_3$ bottom electrode layers were deposited. After the fabrication of PZT nanorods, Pt top electrodes were deposited using electron-beam evaporation. A PZT film of the same chemical composition was also prepared for comparison. The performance of the film-based and nanorod-based

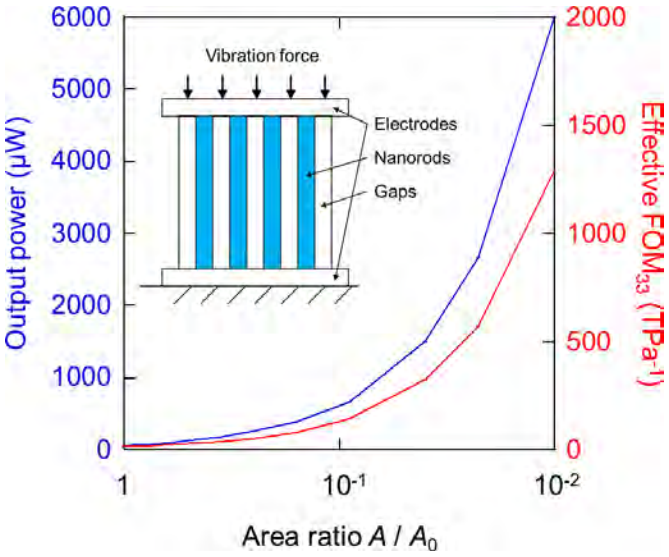

Fig. 3: Dependence of output power and effective FOM on the area ratio of the PZT nanorods.

PEHs is shown in Fig. 4. Limited by the accuracy of the measurements, direct piezoelectric constants of both films and nanorods are around 50 pC/N on average and no more than 75 pC/N. However, it is clearly seen that the effective dielectric constant of the nanorods is lower than that of the films because of the contribution of the gaps to the effective dielectric constant. According to Eq. (1) and the data shown in Fig. 4(a), the available energy density was estimated by applying 100 N/cm^2. As Fig. 4(b) illustrates, the nanorods exhibit stronger output capabilities due to the lowered effective dielectric constant.

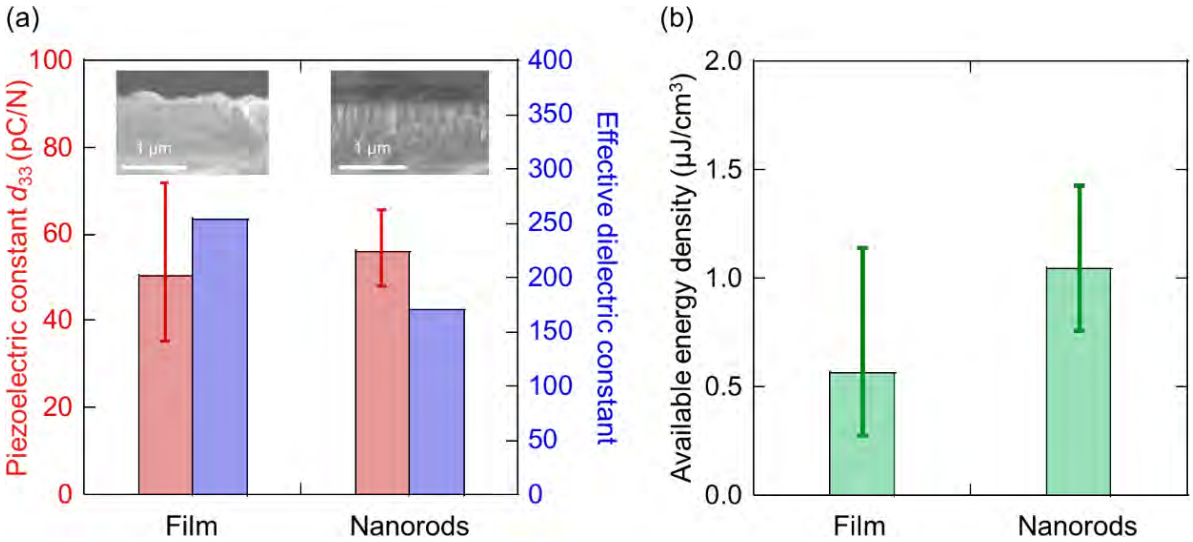

Fig. 4: Performance of the PZT film-based and nanorod-based PEHs. (a) Measured direct piezoelectric constant and effective dielectric constant. (b) The maximum available energy density estimated when applying 100 N/cm^2.

Figure 5 plots effective FOMs for three sets of PZT nanorods and films. Each set uses a different composition and crystal orientation of PZT, whose details will be described elsewhere. Typical ranges for PZT, (K, Na)NbO_3 (KNN) and PVDF reported in literature are also shown. [16] As can be seen, the effective FOMs remarkably increases by fabricating the nanorods. Although they do not exceed the maximum value of typical range for PZT, they can be further increased by the optimization of composition and orientation, and the reduction of density of nanorods. It is worth mentioning that our approach using nanorods can also be applied to other materials such as lead-free ferroelectrics, which are expected to replace PZT due to environmental issues.

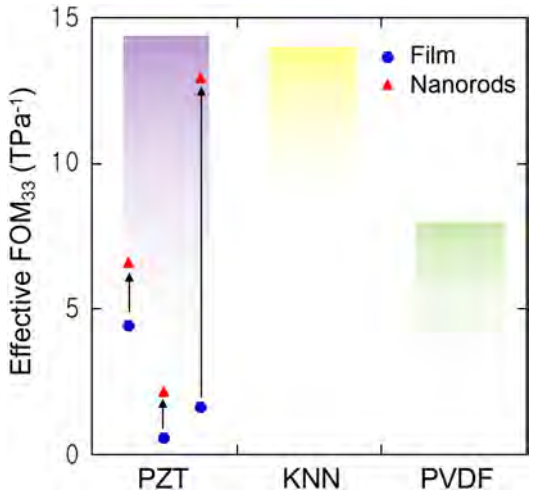

Fig. 5: Effective FOMs of PZT films and nanorods in the present study. ectangular areas show the typical ranges reported in literatures. [16]

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