Supporting Information for:

Piezoelectric Nanoribbons Printed onto Rubber for Flexible Energy Conversion

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For characterizing the fundamental piezoelectric performance of the PZT film as well as the PZT nanoribbons, the piezoelectric charge constants *d* were measured. This value represents the polarization generated per unit of mechanical stress applied to a piezoelectric material, or, conversely, the mechanical strain experienced per unit of electric field applied. The piezoelectric charge coefficient is a tensor, with components d_{ij}, where i indicates the direction of polarization generated in the material when the electric field is zero (or the direction of the applied field strength), and j is the direction of the applied stress (or the induced strain).

I. d_{31} Measurement

The most practical of the piezoelectric constants is d_{31}, the transverse operation mode. To determine d_{31} of the PZT thin film, we utilized the "wafer flexure" approach. Figure S1 illustrates the basic configuration of the experiment, consisting of a uniform pressure rig (diameter = 39 mm, depth = 22 mm). A 2'' PZT/Pt/MgO wafer with Au/Cr top electrode is sandwiched between the top and bottom halves of the rig to form a closed chamber system. To form the 2'' wafer with bottom and top electrode, 80 nm Pt bottom contact electrode was deposited via e-beam evaporation and then post annealed at 600 ºC for 1 hour, prior to PZT thin film deposition. Au (120 nm) / Cr (30 nm) top contact electrodes with an area ~2 mm^2 were deposited at the wafer center using e-beam evaporation. The PZT thin film was synthesized using the sputtering procedure described in the manuscript.

A pipette bulb connected to the rig was used to apply an oscillating planar stress, which subjects the wafer to controlled bending. Assuming the bending of the film is slight, small deflection plate theory may be used to determine the principal stresses, which can be determined by direct calculation from the read-out of a pressure transducer (Omega PX209, 30 psi full

scale). Generated charge is collected from the top electrode on the PZT film and converted to an RMS voltage via a charge integrator circuit.

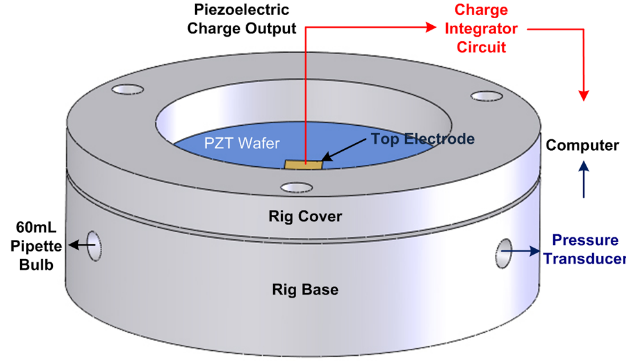

Figure S1. Measurement apparatus used for d_{31} measurement. The induced charge was measured via a charge integrator circuit between the contact electrodes, while the pressure is measured with a pressure transducer.

The principal stresses near the center of the wafer were calculated from the pressure readings via classical mechanical plate theory according to:

$$\sigma_1 + \sigma_2 = \left(\frac{E_{PZT}}{E_{MgO}}\right)\left(\frac{1-\nu_{MgO}^2}{1-\nu_{PZT}}\right)\left(\frac{3Pa^2}{4t^2}\right) \quad (1)$$

Where σ_1 and σ_2 are the radial and tangential principal stresses applied to the film, E is Young's modulus (E_{MgO} = 249 GPa, E_{PZT} = 101 GPa), ν is Poisson's ratio (ν_{MgO} = 0.18, ν_{PZT} = 0.3), P is the uniform pressure as measured by the transducer, t = 0.5 mm is the thickness of the wafer, and a = 19 mm is the inner radius of the pressure rig. The piezoelectric coefficient is finally calculated according to the following, where D_3 is the induced dielectric displacement:

$$d_{31} = \frac{D_3}{\sigma_1 + \sigma_2} \quad (2)$$

II. d_{33} Measurement

To determine the piezoelectric coefficient d_{33}, piezoresponse force microscopy (PFM) was used, in which an AC bias voltage was applied with amplitude U_f (V). The sample displacement or tip vibration is measured as the piezoresponse amplitude P_f (pm), which is the product of the vertical deflection signal V_f (V) and sensitivity δ (pm/V). The slope of piezoresponse vs. applied AC voltage is calculated as the effective piezoelectric coefficient d_{eff}..

$$d_{eff} = \frac{P_f}{U_f} = \frac{V_f * \delta}{U_f} \quad (3)$$

Because the electric field under the tip is not uniform, the effective piezoelectric coefficient d_{eff} is not necessarily the same as true piezoelectric coefficient of the film d_{33}. Kalinin *et al* (see reference 35 in the main text) provides a theoretical explanation of the tip-surface interaction. Generally, a blunt tip and an intermediate force are required to ensure that the measured signal is electromechanical response dominated.

As a control for our experimental conditions, a PPLN crystal standard sample was measured with a tip of radius 50 nm and an applied force of 2000 nN (Fig. S2). The measured curve is linear and corresponds to an effective piezoelectric coefficient d_{eff} = 7.7 pm/V, which is in good agreement with the known d_{33} value of PPLN (7.5 pm/V). These results confirm operation in the strong-indentation limit for the thin film PZT samples on the MgO host substrate.

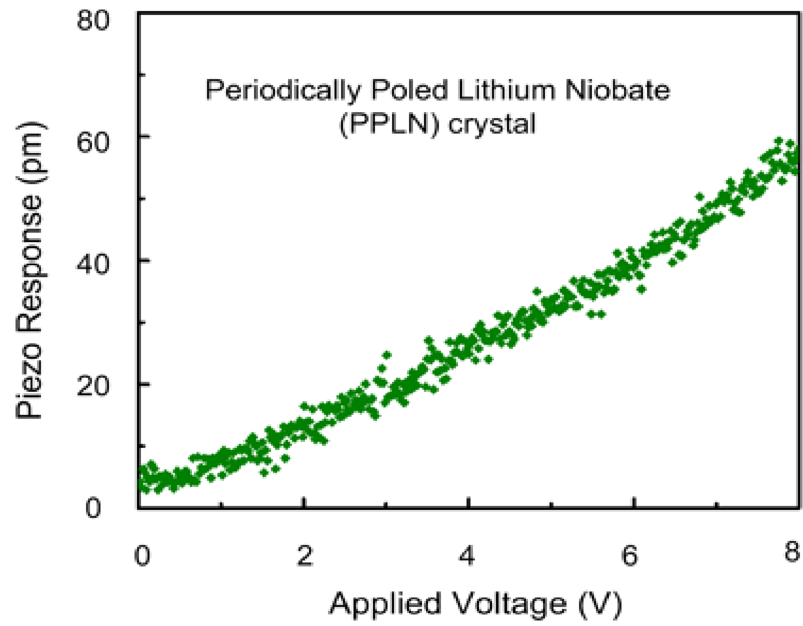

Figure S2. PFM measurement on a standard PPLN sample. The slope of the linear piezoresponse vs. applied voltage was calculated as d_{eff}.