Piezoelectric and Pyroelectric Energy Harvesting from Lithium Niobate Films

G Clementi, S Margueron, M A Suarez, T Baron, B Dulmet and A Bartasyte
Femto-ST Institute, Université de Bourgogne Franche-Comté, 26 rue de l’Epitaphe, 2500 Besançon, France

Abstract. Single-crystalline LiNbO$_3$ films were studied as a pyro- and piezoelectric transducer for energy harvesting applications. Two types of devices: piezoelectric cantilever (PiEH) and pyroelectric chip (ThEH) were microfabricated. Different types of characterization were done, starting from a comparison of finite element method (FEM) simulated eigen-frequencies of cantilever beam and optical vibrometer measurements. According to electrical characterization, resonance frequencies of two cantilevers with different thickness were 1.26 kHz and 485 Hz with generated spontaneous power of 14 $\mu$W and 4 $\mu$W at 275-300 $\Omega$, respectively. Finally thermal characterization of pyroelectric samples showed voltage amplitudes ranging from 1 to 2.5 mV in the temperature range of 50-200 °C.

1. Introduction
At present, many different ferroelectric (PbZr$_{1-x}$Ti$_x$O$_3$ (PZT), BaTiO$_3$ (BTO), K$_{1-x}$Na$_x$NbO$_3$ (KNN), etc.) and non-ferroelectric (AlN, ZnO) piezoelectric materials in the form of films, nanostructures and ceramic/crystals bonded on wafers are explored for the fabrication of piezoelectric vibrational energy harvesters (PiViEHs) [1]. Obtaining high power output from piezoelectric harvesters in many applications requires a high electromechanical coupling, $K^2$; hence this resulted in the preference and common use of bulk PZT in piezoelectric harvesters. However, in future, PZT maybe has to be replaced by lead-free materials, even for thin films. Non-ferroelectric piezoelectrics such as ZnO & AlN and their derivatives, have much lower $K^2$ than PZT, but offer the compatibility with the conventional integrated circuit technology. Ferroelectric material, such as LiNbO$_3$ (LN) [2] presents FoM similar to that of PZT [3]. Moreover, LN presents extremely high Curie temperature thus, it is compatible with high-temperature applications of transducers (up to 1000 °C) [4] and EHs (at least up to 500 °C, further experiments are needed to find the temperature limit) [5]. This makes LN particularly attractive for the EHs applications where the working temperature is elevated (in oil, exhaust pipe, close to motor temperature can reach 600 °C), as PZT, BTO and KNN loss their piezoelectric properties at these temperatures. LN presents quite high pyroelectric figure of merit (FoM) [6]. Lithium niobate has been extensively studied in acoustics and optics field [7] and it is produced industrially in the form of single crystals (wafers with diameters up to 6 inches are available). However, the application of LN in PiViEHs is still very little studied and considerable efforts have to be done towards LN thin film integration to the conventional processing of MEMS [7].
In this paper, we introduce single-crystalline LN films as a piezo- and pyro-electric transducer for Piezoelectric and Thermal Energy Harvesters (PiEH and ThEH).

2. Experimental details
Initially, a silicon substrate with 500 μm thickness was gold bonded to a Y-36° lithium niobate wafer 50 μm thick. LiNbO₃ surface was polished until 30 μm thickness, then the samples were cleaned with acetone, ethanol and deionized water. Al electrodes with thickness of 200 nm were structured on the LN surface by using UV lithography, evaporation deposition technique and lift-off process (figure 1a).

Finally after dicing and cleaning, photoresist was coated on the bottom side of the samples, in order to remove selectively part of the silicon substrate through reactive ion etching (figure 1b). The final result were several cantilevers with different thicknesses, but same tip mass size. Figure 1c shows two different samples fabricated: piezoelectric cantilever and pyroelectric chip.

The characterization of the piezoelectric cantilever and pyroelectric chip were carried out, separately. An optical vibrometer (Polytec MSA-500) was tracking the position of the tip of the cantilevered beam to investigate the displacement and frequency response. The results were then compared to FEM simulations. Then the piezoelectric cantilevers were clamped to a structure fixed on a shaker. The amplitude of the vibration excitation given to the system was varying between 1-2 V. An electrical circuit with several loads was connected to the cantilever under scrutiny. A laptop controlling the vibrating system through a National Instruments card was scanning the frequency range of interest, and setting the frequency resolution for the measurements.

The pyroelectric samples were positioned over a micro-furnace that was heating the bottom part of the sample. The charges were collected on the top and bottom electrode with different probes. The electrodes had different shapes, to investigate geometrical effects on the voltage measured. We could also change the dwell velocity, threshold temperature and number of heating cycles. Typically the samples were heated with a ramp of 5 °C and then the temperature would stay constant for 20 seconds. Several sets of measurements were conducted starting from temperature of 50 °C until the maximum temperature of 200 °C.

3. Results
The characterization was carried out on cantilevers with two different thickness as a function of different loads to investigate the amplitude of the voltage and the spontaneous power generated. The first sample characterized had a substrate thickness of 500 μm (PiEH-1). With an optical vibrometer were measured two resonances, at $\nu_1=1.26$ kHz and $\nu_2=7.9$ kHz, representing the first and second eigen-frequencies of the beam, respectively. The FEM simulated values, $\nu_{s1}=1.34$ kHz and $\nu_{s2}=8.2$ kHz, were in good agreement to the measured ones, confirming our model (figure 2a). The peak, observed at low frequency, is due to mechanical resonance of the system and the sample holder. The second device characterized had a substrate thickness of 250 μm (PiEH-2). The first frequency detected was $\nu_1=485$ Hz, while the second one at $\nu_2=3.9$ kHz (figure 2b). As expected, the less stiff cantilever had a value of bending resonance inferior to the previous one. The simulated values were $\nu_{s1}=500$ kHz and $\nu_{s2}=4.2$ kHz.

The difference of frequencies of the measured and simulated data is due to clamping or structure imperfections.

In the electrical characterization, the cantilever was excited with a voltage amplitude of 2 V, and the voltage response was measured at several loads (figure 3a). The voltage amplitude measured at resonance with different loads ranged roughly from 1 V to 3 V for PiEH-1. The power collected at the maximum was found when internal impedance and external load were matching, this represents the
maximum power point of the curve. From this data, information were collected on instant power that our harvester can produce, a maximum of 14 μW was attained at 275 kΩ. The electrical characterization carried out on PiEH-2 by using input amplitude of 1 V showed the generated voltage comparable with the former sample. The voltage amplitude at different loads was in the range of 0.4-1.5 V (figure 3b). The measured power had a maximum at 300 kΩ, and the dissipated power was 4 μW. On both cantilevers, we measured the frequency shift (Δν) due to the electrical damping of the structures derived from the load. The higher the value of the resistor, the higher was the damping on the structure. This shift was 3 Hz in the first case and 1.5 Hz for the second structure. A comparison of power generated by the two PiEls is given in figure 4. The power for PiEH-1 is higher due to the higher excitation voltage (Vin=2 V), but the advantage of PiEH-2 is the lower bending frequency, giving wider span for applications.

Two geometries of pyroelectric chips were characterized, measuring voltage response for different threshold temperatures. The electrodes had circular (ThEH-1) or square (ThEH-2) shape, but the same conductive surface. The typical pyroelectric voltage behavior during one cycle is shown in figure 5.
After increasing the temperature of the furnace to 100 °C, it was possible to observe that the voltage was slowly ascending, reaching 1 mV when at the maximum cycle temperature. While the temperature was steady, the voltage was quickly reaching zero, mainly because there was no change in polarization of LiNbO3. This proved a fast response of the device to external heating sources. Finally was possible to make a comparison between the two geometries (figure 6). The collected voltages using different geometries of electrodes were identical taking into account the error ranges. Both of them increased with the temperature reaching the maximum value $V_{\text{max}}=2.6$ mV at 200 °C. The pyroelectric voltage increased nonlinearly with the increase average cycling temperature and this relationship can be described by the second order polynomial function. The slope of the curve is related to $P_V$, the pyroelectric voltage coefficient. $P_V$ is found in the equation: $\Delta V = P_V h \Delta T$ [8] where $h$ is the thickness of the crystal, $\Delta T$ and $\Delta V$ are the gradient of temperature and voltage respectively. With further measurements we will be able to obtain an estimate of this parameter.

4. Conclusion
In our paper we presented a fabrication route for a piezoelectric cantilever and pyroelectric chip using LiNbO3 Y-36° wafer cut. The vibrometer characterization of PiEHs showed a good agreement with eigenfrequency simulations, while from dynamic characterization, we demonstrated that the cantilevers with substrate thicknesses of 500 µm and 250 µm were able to generate spontaneous power of 4 µW at 485 Hz and 14 µW at 1.26 kHz, respectively. With ThEHs we found out that we can collect pyroelectric voltage reaching 2.6 mV with 5 °C ramp at 200 °C. More measurements are underway to have an estimate of the pyroelectric voltage coefficient.

In the future we will optimize the design of the PiEHs and ThEHs, using LiNbO3 wafer cuts or thin films with different orientations. The aim is develop a hybrid system with dedicated electronics able to harvest energy from both thermal and vibrational sources.

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