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Pyroelectric energy harvesting with Black-Al/Pt/Pb($Zr_{0.2}Ti_{0.8}$)O_3/Pt thin films.

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Abstract

Energy harvesting from heat is an important option for powering autonomous devices. Pyroelectric converters use temperature time variations to transform thermal energy into electricity. Black-Al/Pt/PZT/Pt and Pt/PZT/Pt were grown on SiO2/Si to enable pyroelectric conversion from a pulsed light source. Black-Al electrodes serve to effectively absorb radiation, and the superior pyroelectric $PbZr_xTi_{1-x}O_3$ (PZT) serve as the working body for the conversion. Our modeling results indicate that the device operates efficiently in the temperature range from 25 to 465 °C. Monopolar and asymmetric bipolar cycles, where the voltage is synchronized with the thermal oscillations are used for harvesting. The output power density may reach 2 kW/kg for a device operating at 200 Hz.

1. Introduction

Conversion of heat into thermoelectricity may be directly done using Seebeck principle, or alternatively using the pyroelectric effect. Conventional thermoelectric energy harvesters work on the Seebeck effect [1]. Nowadays, their efficiency is usually in the range from 5% to 10%, furthermore, it is expected that the efficiency will increase up to 15% in the foreseeable future [2]. Unlike the thermoelectric converters, the pyroelectric ones utilize temperature time variations. The effect is comparable to piezoelectric effect for energy harvesting from vibrations [3]. Sebald et al defined the fundamental principles of energy harvesting using the pyroelectric effect [4]. Achievement of efficiency up to 50% of the Carnot efficiency is considered to be realistic [5].

the working element of converter is formed of a ferroelectric plate between electrodes. The plate is subject to thermodynamic cycles, where its temperature varies simultaneously with voltage on the sample. The cycles may optimize to provide maximum output power with account for technical limitations (breakdown threshold, etc.). A cycle with two isotherms and two parts with constant electric field is named Olsen cycle. The Olsen cycle has been shown to be optimal in terms of specific power under constraints on the voltage and temperature ranges for low-frequency (usually under 1 Hz) generators. During the past decade pyroelectric harvesting moved towards the use of thin films, where a giant electrocaloric effect was discovered, in particular in Pb(Zr,Ti)O_3 (PZT) [6]. The other advantage of the thin film converters, is that they may operate at higher frequencies, and render higher specific powers, in proportion to the frequency of operation. For high-frequency cycles, in the range of 10^2-10^3 Hz, sinusoidal change of parameters is natural [7], as controlled by faster decay of high-order harmonic oscillations. Also, the problem of the transfer of the high-frequency thermal oscillations into the working material is is crucial.

In this work, we study pyroelectric energy harvesting from a source of radiation (incident light) using highly absorptive Black-Al (BAl) electrodes, allowing effective conversion of illumination to heat. Only few hundred nanometers thick, the electrode allows rapid delivery of the heat into the working material and allows operation in the frequency range of up to kHz. Black-Al/Pt/PZT/Pt structures were deposited on SiO2/Si substrates. The experiments are accompanied with phase field modeling of the pyroelectric material using "Comsol Multiphysics" software. A representative harvesting cycle for 200 nm thick Pb($Zr_{0.2}Ti_{0.8}$)O_3 films operating at 200Hz renders specific electric power of 2kW/kg.

2. Deposition and modeling of Pt/PZT/Pt samples.

The Pt/PZT/Pt stacking structures were prepared on Pt/TiO2/SiO2/Si substrates. First, Pb($Zr_{0.2}Ti_{0.8}$)O_3 layer (200 nm in thickness) was deposited at 150°C on Pt(120nm)/TiO_2(5nm)/SiO_2(100nm)/Si(400 lm) substrate by multitarget sputtering in mixed argon (95%)–oxygen (5%) gas. The PZT layer was then annealed in a conventional furnace at 650°C during 30min in air for crystallization. Heating and cooling ramps were 2°C/min for all annealing treatment employed in this study. After annealing, X-Ray Diffraction was performed in order to check the crystallization of the PZT film. An argon ion milling, with an acceleration voltage of 700V, was used for to etch the sample on which 500 × 800 μm^2 pads were protected by a photoresist (1.5 μm in thickness). Finally, BAl layers of 500 nm with dimensions of 250 × 400 μm^2 were deposited by DC spu-

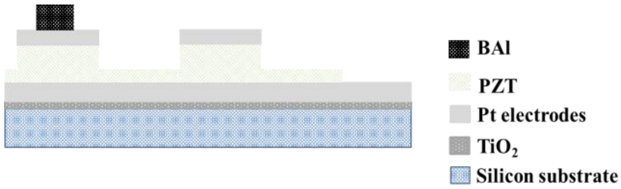

Fig 1: Cross section of BAl/Pt/PZT/Pt stack and Pt/PZT/Pt stack deposited onto SiO2/Si substrate.

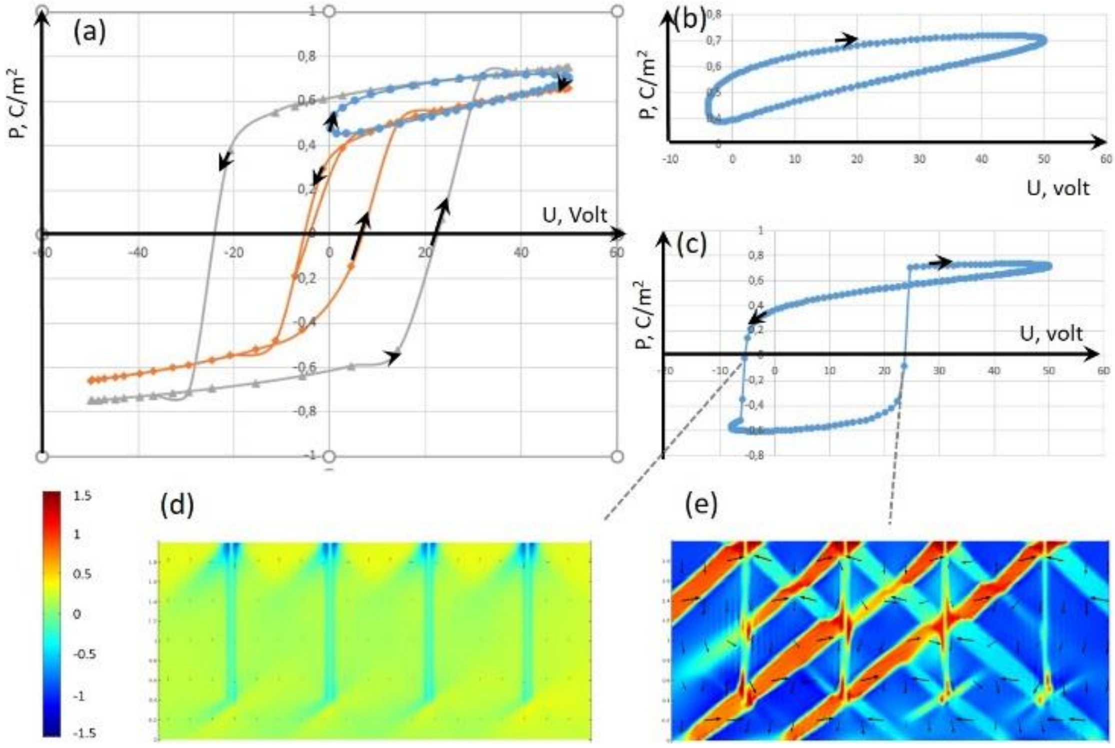

Fig 2: Thermodynamic cycles for a thin film of a ferroelectric PZT with a thickness of 200 nm, obtained by numerical simulations involving domain nano-structure (shown in color in (d), (e).) and the columnar boundaries (vertical lines). (a) - dependence of the mean vertical polarization component on the applied voltage (sinusoidal) for bipolar cycles at a constant room temperature and 465 ° C (hysteresis loops) and a unipolar cycle with a variable temperature from 25 to 465 °C, varying sinusoidally with a phase shift of quarter period relative to the voltage. (b) -Asymmetric thermodynamic cycle corresponding to the maximum output power with a sinusoidal temperature change. (c) - Asymmetric thermodynamic cycle, with ferroelectric switching, and negative energy accumulated per cycle. (d, e) illustrate the process of switching in the ferroelectric up and down, respectively.

ttering at a pressure of 0.5 Pa, in a mixture of Ar and N_2. The Nitrogen gas promotes the growing of nanostructural BAl onto the surface of half Pt pads using a lift-off technic. Figure 1 presents a cross-section of the device after processing. Comparisons between both stacks have been performed for all electric and pyroelectric measurements.

Modeling results demonstrating the thermodynamic cycles of pyroelectric energy harvesting in the structure are shown in Figure 2. The figure illustrates the results of simulation for a fragment of a 200 nm thick PZT film containing four columnar boundaries. Fig. 2 (a) presents hysteresis loops, obtained with an alternative applied voltage of 50 V at 200 Hz, for temperatures of 25 and 465 °C and the harvesting cycle traveled in the clockwise direction. The harvesting cycle is a unipolar cycle with sinusoidally varying temperature (in the range from 25 to 465 °C) and voltage, with a phase shift of a quarter of the period between them. Figure 2 (b) shows an asymmetric cycle corresponding to the largest accumulated power (with a sinusoidal change in the parameters). Figure 2 (c) shows an asymmetric cycle, with an electric field exceeding the critical value for repolarization of the sample. The process of repolarization is started with the nucleation of domains at grain boundaries (d, e). In this case, when the polarization reverses downward, which occurs at a temperature of about 250 °C, the ferroelectric passes through a state close to the paraelectric phase (d). In contrast, when repolarized upwards, which occurs at a temperature close to room temperature, the sample switches via the formation of ferroelastic domains (e). A power density of 2kW/kg is calculated for the system operating at 200 Hz.

3. Conclusion

BAl/Pt/PZT/Pt thin films were grown using rf sputtering technique on SiO_2/Si substrate. The experiments are accompanied with phase field modeling of the thermal processes and electrodynamics in the pyroelectric material. A representative harvesting cycle for $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films of 200 nm thickness operating at 200Hz renders specific electric power of 2kW/kg.

Acknowledgments

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