Reversal and pinning of Curie point transformations in thin film piezoelectrics

Madhu Bhaskaran,*[a] Sharath Sriram,[a] David Adley,[b] Tatiana S. Perova,[b] and Arnan Mitchell[a]

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Experimental details

PSZT thin film deposition

Silicon (100) samples were dipped in buffered hydrofluoric acid to remove the native oxide. These were subsequently coated with 200 nm of platinum, with a 20 nm titanium dioxide adhesion layer; both layers deposited by electron beam evaporation. The use of the titanium dioxide adhesion layer in place of titanium as in previous work,[S1] was to significantly enhance the rhombohedral *c*-axis texture of the PSZT thin films.[S2]

Table S1 PSZT thin film deposition conditions.

Target	$(Pb_{0.92}Sr_{0.08})(Zr_{0.65}Ti_{0.35})O_3$
Target diameter	100 mm
RF power	100 W
Target to substrate distance	70 mm
Process gas	10 % oxygen in argon
Base pressure	9.0×10^{-6} Torr
Sputtering pressure	1.0×10^{-2} Torr
Substrate temperature	650 ºC
Temperature ramp-up rate	10 ºC/min
Temperature ramp-down rate	5 ºC/min
Sputtering duration	2 h

PSZT thin films were deposited by RF magnetron sputtering under conditions listed in Table S1.[S3] The deposition of PSZT thin films was carried out at 650 ºC and at a process pressure of 10 mTorr which resulted in the optimal thin films composition, without lead/oxygen excess or deficiency.[S3b] Deposition was carried out for 2 hours and the resulting PSZT thin films were 700 nm thick.

In situ micro-Raman spectroscopy

Raman spectra were registered in a backscattering geometry using a Renishaw 1000 micro-Raman system equipped with a CCD camera, a Leica microscope and a long focus 50× objective. A line grating of 1800 lines/mm was used for all measurements, providing a spectral resolution of approximately 1 cm^{-1}. An argon 514 nm laser at 20 mW power was used as an excitation source. An accurate temperature stage (Linkam Scientific Instruments, UK) was used to heat and cool the samples. This enabled controlled heating and cooling of samples (with ±0.5 ºC accuracy) with real-time collection of Raman spectra. An accumulation time of 20 s was used and the data was averaged over 10 accumulations.

Supplementary results

Micro-Raman results for controlled heating and cooling

For the initial experiments to determine Curie point, PSZT thin film samples were heated up to 350 ºC at a controlled rate of 10 ºC/min and cooled at the same rate. Micro-Raman

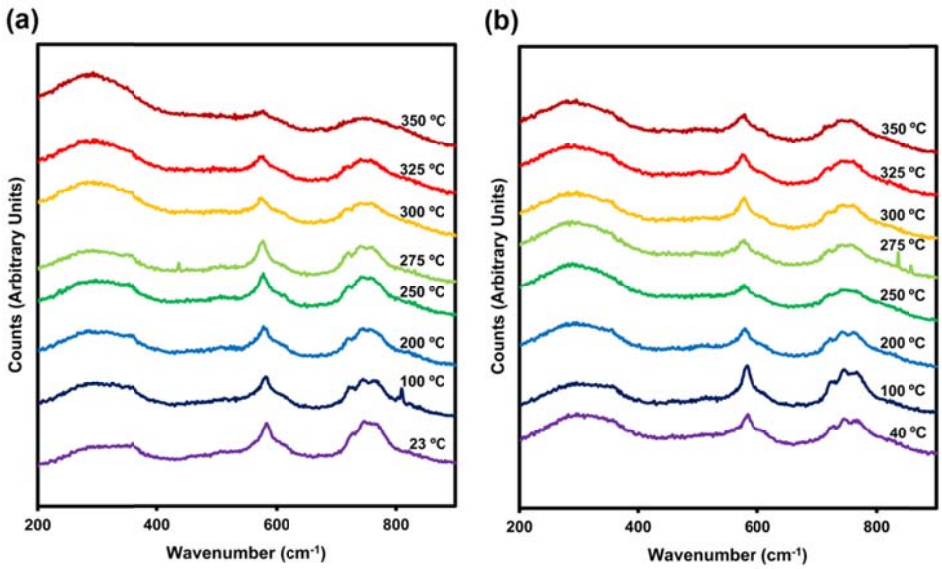

Fig. S1 Raman spectra registered *in situ* on **(a)** heating a PSZT thin film sample to 350 ºC and **(b)** cooling the PSZT thin film sample from 350 ºC. All spectra collected at 514 nm excitation wavelength are presented on the same scale offset with respect to each other to enable comparison.

spectra were collected at regular temperature intervals, under the conditions described above. The complete collection of the spectra recorded during the heating and cooling processes are shown in Fig. S1.

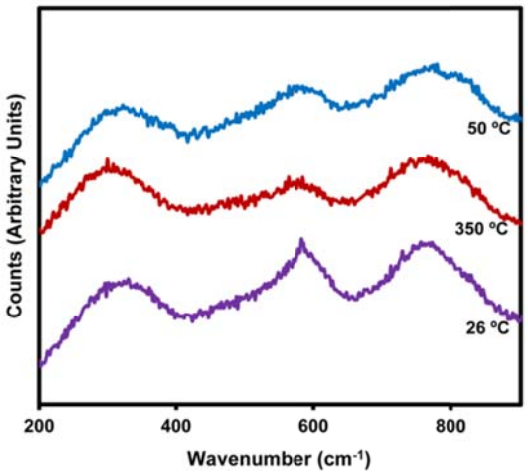

Fig. S2 Raman spectra collected with 514 nm excitation at room temperature, after controlled heating to 350 ºC, and after uncontrolled cooling from 350 ºC to 50 ºC

To study the influence of post-deposition cooling, PSZT thin film samples were heated up to 350 ºC at a controlled rate of 10 ºC/min and cooled without external control. This cooling process took approximately 15 minutes. A comparison of the micro-Raman spectra for the as-deposited thin film, at 350 ºC, and after cooling to 50 ºC are compared in Fig. S2. This clearly shows that pinning to the high temperature phase occurs for uncontrolled cooling.

Notes and references

[a] *Microplatforms Research Group, School of Electrical and Computer Engineering, RMIT University, Melbourne, Victoria 3001, Australia. E-mail: madhu.bhaskaran@gmail.com*

[b] *Microelectronics Technology Group, Department of Electronic and Electrical Engineering, University of Dublin – Trinity College, College Green, Dublin 2, Ireland.*

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