Enhanced Ferroelectric Properties in Highly Epitaxial and Fatigue-Resistant PZT Thin Films Deposited Using Dual-laser Ablation

UNIVERSITY OF SOUTH FLORIDA
DEPARTMENT OF PHYSICS

Devajyoti Mukherjee, Robert Hyde, Tara Dhakal, Hariharan Srikanth, Pritish Mukherjee, and Sarath Witanachchi

Abstract

Epitaxial $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) films were deposited on single crystal MgO (100) and $SrTiO_3$ (STO) (100) substrates using a dual-laser deposition (DLD) process. This technique combines a pulsed KrF excimer and CO_2 laser outputs by overlapping them spatially and synchronizing them temporally. The PZT films made using DLD process exhibited ferroelectric properties much superior to those of the single-KrF laser ablated films. Hysteresis loops with higher values of remnant polarizations and coercive fields were observed. Optimum coupling of the combined laser energies produced enhanced plume excitation and higher ionization of the background ambient O_2 which eventually reduced the defects related to O_2 vacancies within the films. This not only reduced the leakage through the PZT capacitors but also improved their fatigue response. AFM surface analysis of the PZT films grown using DLD revealed a smoother surface with root mean square roughness (Rrms) value of 1.6 nm compared to 11.5 nm for single-KrF laser ablated films. Further the broader transverse expansion of plume in DLD allowed for the deposition of particulate free films that were uniformly thick over a larger area making them ideal for incorporation in multilayered multiferroic structures. The PZT capacitors made using $La_{0.7}Sr_{0.3}MnO_3$ top and bottom electrodes were highly resistant to fatigue even after 10^9 cycles of polarization switching.

Introduction

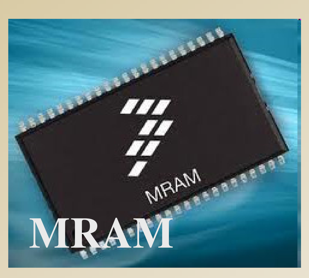
Applications of PZT films:
- non-volatile Random Access Memory devices (FeRAMs)
- micro actuators and ultrasonic sensors (MEMs)

Ferroelectric Random Access Memory (FeRAM)

Motivation: Future memory devices

Magneto-Electric Random Access Memory (MERAM)

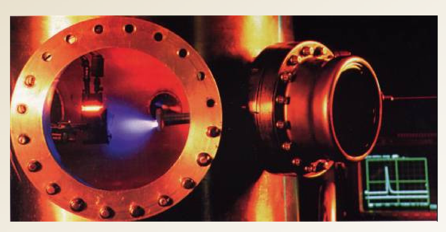
- Fast access speed
- Low-power electrical write operation
- Non-destructive magnetic read operation
- Four state memory
- High density storage

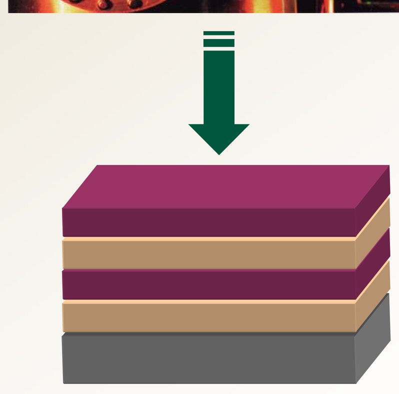


Magnetoresistive Random Access Memory (MRAM)

Demand for high quality epitaxial heterostructures for multiferroic applications

Laser ablation for film growth

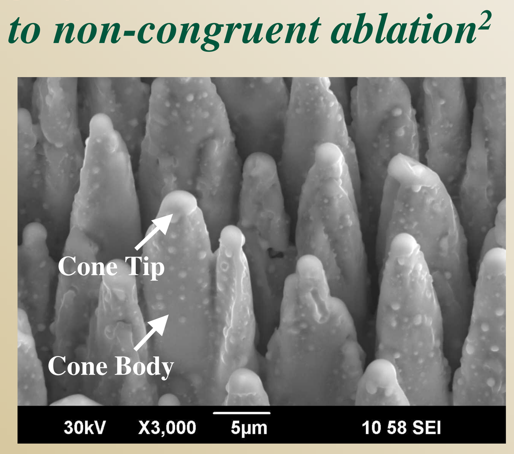




Horizontal / Ferroelectric / ferromagnetic hetero-structures[1,3]

Experiment

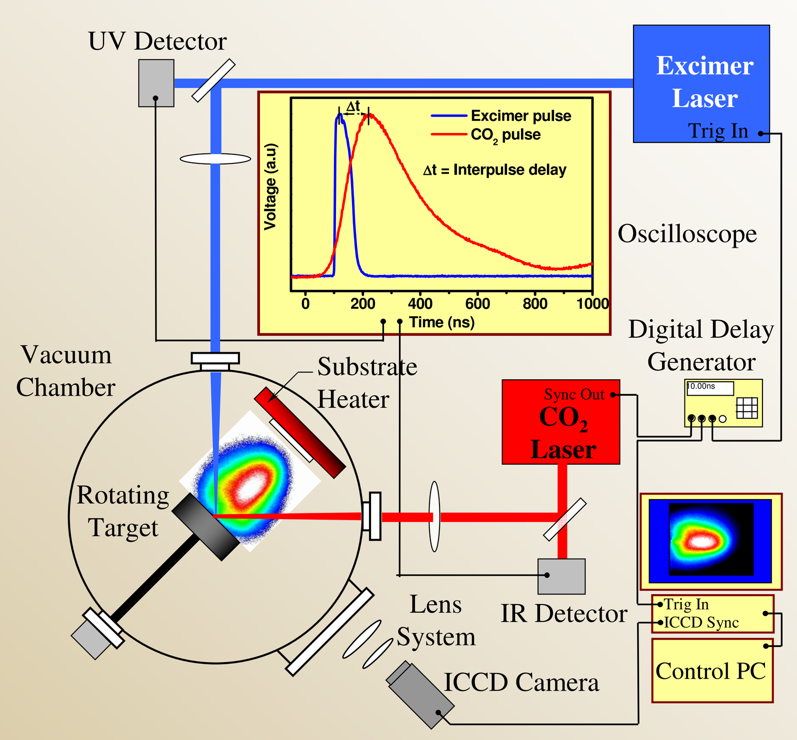
Preferential evaporation of highly volatile Pb in PZT leads to non-congruent ablation[2]



SEM image of conical structures formed on a PZT target surface after repeated ablation by KrF excimer laser.

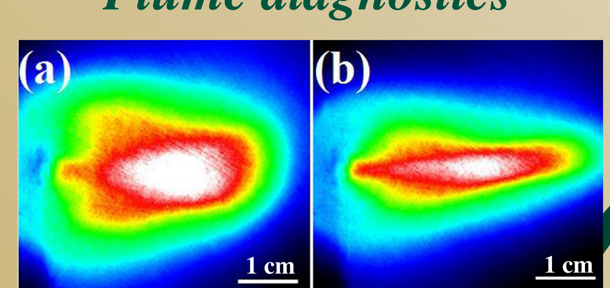
Complications in laser ablation of PZT:[2]

- At low laser energy Pb deficiency in PZT films degrade the ferroelectric properties
- At high laser energy undesirable particulates on films



Dual Laser Deposition (DLD) System[4]

Plume diagnostics



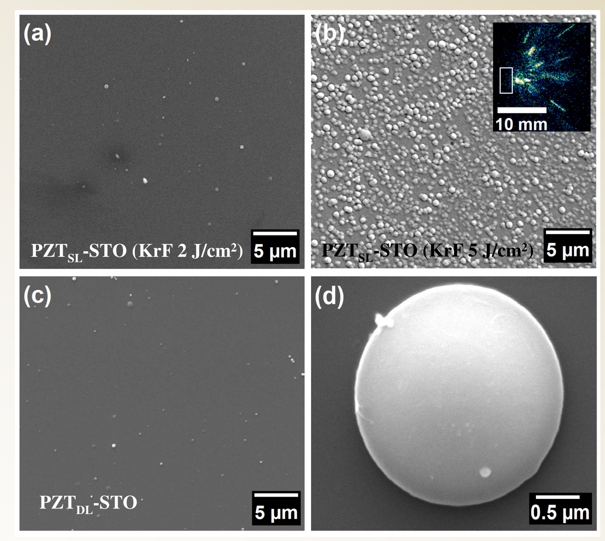
Time integrated ICCD images of the visible emission spectra of laser-induced plumes in 500 mT ambient O_2 for (a) dual-laser ablation, and (b) the KrF single-laser ablation.

The broader transverse expansion of the plume in DLD (28.0 mm FWHM) compared to single–laser (18.7 mm FWHM) allowed for the growth of more uniform film over a larger area.

Results

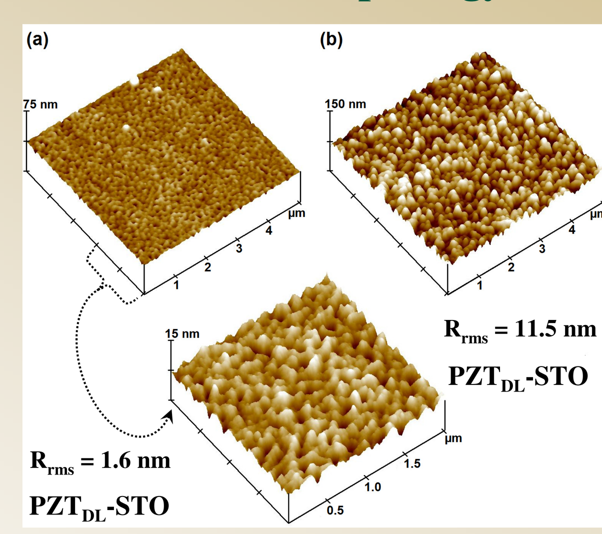
Structural properties

Particulates on films



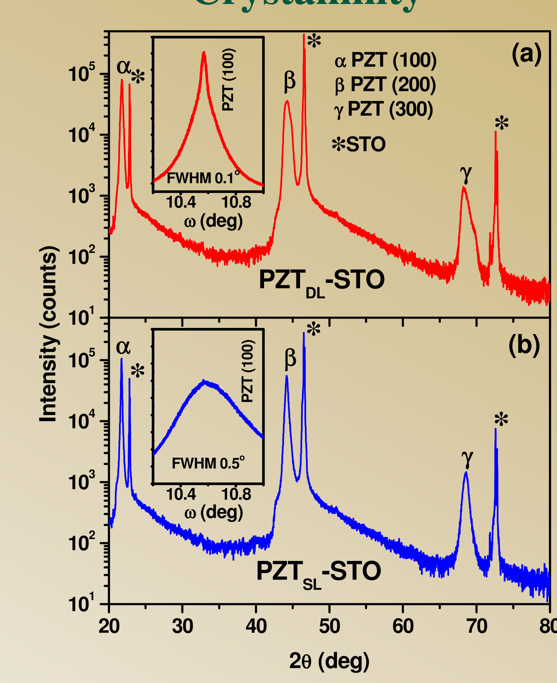
SEM images of single laser PZT films on STO substrates (PZT_{SL}) at (a) low fluence of 2 J/cm² and (b) high fluence of 5 J/cm², and (c) dual laser film (PZT_{DL}), (d) one of the "splashed" particulates on PZT_{SL} film ejected from target.

Surface morphology



AFM images of PZT films on STO substrates deposited using (a) dual-laser (PZT_{DL}-STO), and (b) single-laser (PZT_{SL}-STO) ablation, respectively.

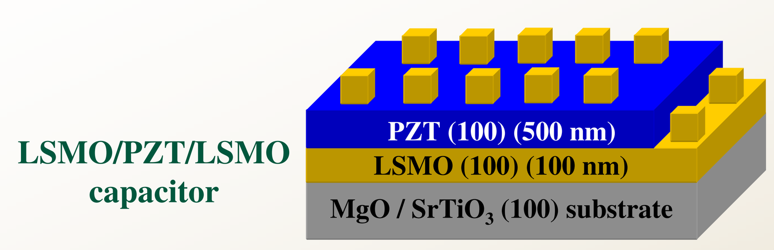
Crystallinity

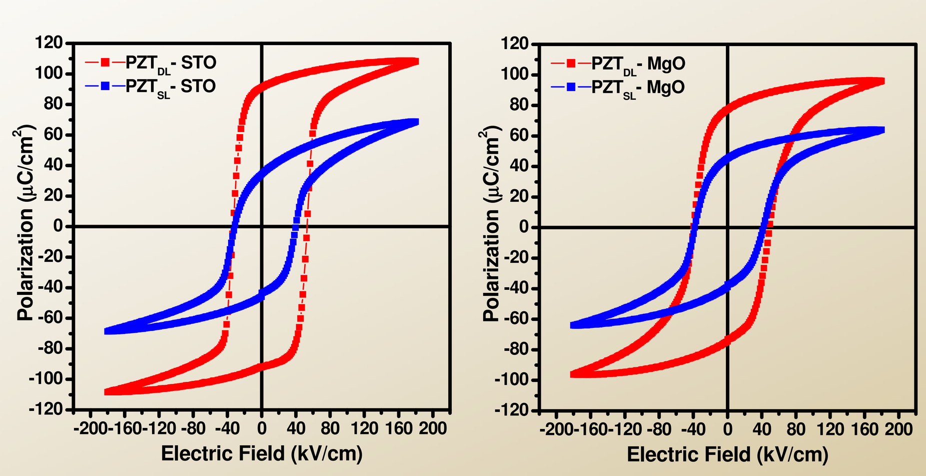


XRD patterns of PZT films on STO substrates grown by (a) dual and (b) single-laser ablation, respectively. Insets show the rocking curves about the PZT (100) peak.

Ferroelectric properties

Polarization





P-E hysteresis loops for PZT films deposited using DLD (PZT_{DL}) and single laser ablation (PZT_{SL}) on STO and MgO substrates.

Leakage

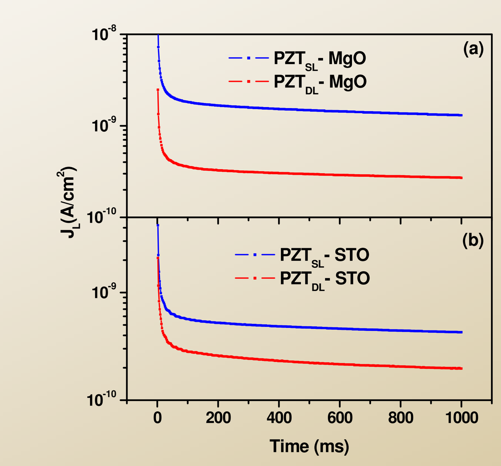
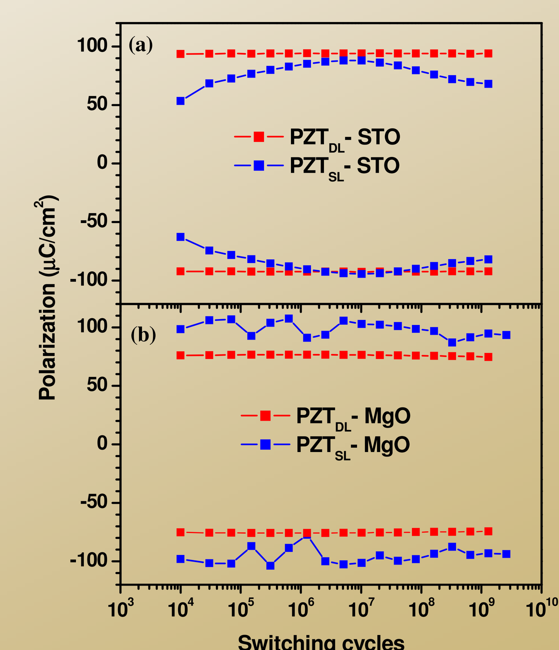


Table of values

Sample	P_{max} (μC/cm²)	P_r (μC/cm²)	V_c (V)	E_c (kV/cm)	J_L x 10^{-9}(A/cm²)
PZT_{SL}-STO	68	34	1.99	35.7	0.43
PZT_{DL}-STO	108	91	2.65	43.2	0.20
PZT_{SL}-MgO	64	45	2.09	40.0	0.43
PZT_{DL}-MgO	96	77	2.45	44.4	0.27

Fatigue



Fatigue tests at 10 kHz using +/- 9 V read/write voltages for LSMO/PZT/LSMO capacitors.

Summary

- **Successful growth of stoichiometric, particulate-free, and smooth PZT films with the desired perovskite structure and no impurity phases using dual laser deposition technique.**
- **Enhanced ferroelectric properties with higher remnant polarization and better fatigue response desired for device application.**
- **DLD as a generalized technique for all multi-component thin film growth where a highly volatile element leads to non-stoichiometric transfer of materials.**

References

1. D. Mukherjee, T. Dhakal, R. Hyde, P. Mukherjee, H. Srikanth, and S. Witanachchi, J. Phys. D: Appl. Phys. **43**, 485001 (2010).
2. D. Mukherjee, R. Hyde, T. Dhakal, H. Srikanth, P. Mukherjee and S. Witanachchi, Mater. Res. Soc. Symp. Proc. 1199, 37 (2010).
3. T. Dhakal, D. Mukherjee, P. Mukherjee, R. Hyde, M. H. Phan, H. Srikanth, and S. Witanachchi, J. Appl. Phys. 107, 053914 (2010).
4. S. Witanachchi et al., Appl. Phys. Lett. **66**, 1469 (1995).

This work was supported in part by:
National Science Foundation (Grant Nos. DMI-0217939 and DMI-0078917)
Department of Defense (Grant No. W81XWH-07-1-0708).