Dielectric and Piezoelectric Properties of $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ Thin Films

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Tunable ferroelectric capacitors, which exhibit a decrease of the dielectric permittivity (ε) under electric field, are widely used in electronics for RF tunable applications (e.g. antenna impedance matching). Current tunable devices use barium strontium titanate (BST) dielectric. Improving on BST performances is one key for a tighter energy management. Finding alternative lead-free piezoelectric materials to the most performing solutions like (1-x)$PbZrO_3$-x$PbTiO_3$ and (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ is also highly desirable. For this dual purposes, we chose to investigate the $BaTiO_3$-$CaTiO_3$-$BaZrO_3$ ternary phase diagram (BCTZ) where morphotropic phase boundaries (MPB) are expected. Indeed, increased dielectric, piezoelectric and ferroelectric properties have been reported in (1-x)$BaTi_{0.8}Zr_{0.2}O_3$–x$Ba_{0.7}Ca_{0.3}TiO_3$ ceramics in the vicinity of a MPB for x=0.5 [1]. More recently, thin films of BCTZ with composition at the MPB have shown interesting tuning ratios of 5/1 under a field of 300kV/cm [2].

We report here on libraries of BCTZ thin films deposited on $IrO_2/SiO_2/Si$ substrates using combinatorial pulsed laser deposition (CPLD) allowing for gradients of composition on one sample [3]. The dielectric properties of 8 samples, each one containing 480 capacitors (40 different compositions with 12 capacitors per composition), were statistically investigated. Effective piezoelectric coefficient d_{33} were also measured across the ternary phase diagram by dual beam laser interferometer.

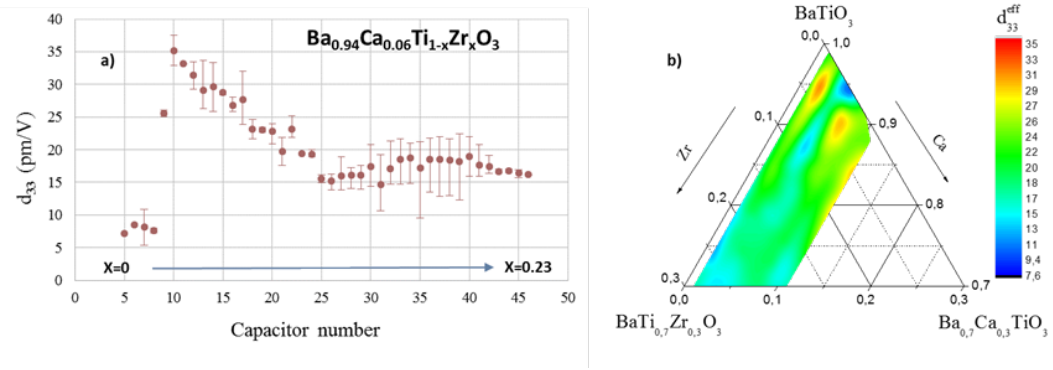

Figure 1. Effective d_{33} versus composition for one BCTZ library (a). Contour map of the effective d_{33} versus compositions in the ternary phase diagram (b).

We show that tunability >70% can be obtained under an electric field of 250kV/cm. Calcium and zirconium contents influence the breakdown voltage in the same way, while Ca is beneficial to tunability and Zr to low losses. Thus lowest dielectric losses and maximum tunabilities are not obtained for a single composition and call for compromise. Rapid variation of the d_{33} versus composition were observed, reminiscent of d_{33} behavior across MPBs. Composition with effective d_{33} of 35 pm/V, about 2/3 of effective d_{33} for PZT thin films of the same thickness (48 pm/V @ 130 nm) [4], were identified. Piezoelectric and dielectric properties versus temperature are being investigated and will be reported. Finally we show that CPLD is a powerful screening tool to identify the best compromise depending on the needs (high tunability at low voltage, low dielectric losses, high d_{33}...).

References

[1] W. Liu et X. and Ren, Phys. Rev. Let. 103, 257602 (2009).
[2] A. Piorra, P. A., H. Kohlstedt, M. Wuttig and E. Quandt, J. Appl. Phys. 109, 104101 (2011).
[3] G. Liu et al., J. Appl. Phys. 108, 114108 (2010).
[4] Y. Bastani et al., J. Appl. Phys. 109, 014115 (2011).