Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 30 (2010) 365–368
www.elsevier.com/locate/jeurceramsoc

Development of PLZT dielectrics on base metal foils for embedded capacitors☆

U. Balachandran*, D.K. Kwon[1], M. Narayanan, B. Ma

Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, United States

Available online 2 June 2009

Abstract

We have deposited $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ (PLZT) films on nickel and copper substrates to create film-on-foil capacitors that exhibit excellent dielectric properties and superior breakdown strength. Measurements with PLZT films on $LaNiO_3$-buffered Ni foils yielded the following: relative permittivity of 1300 (at 25 °C) and 1800 (at 150 °C), leakage current density of 6.6×10^{-9} A/cm^2 (at 25 °C) and 1.4×10^{-8} A/cm^2 (at 150 °C), and mean breakdown field strength ≈2.5 MV/cm. With PLZT deposited directly on Cu foils, we observed dielectric constant ≈1100, dielectric loss (tan δ) ≈0.06, and leakage current density of 7.3×10^{-9} A/cm^2 when measured at room temperature.

Keywords: Ferroelectric film; PLZT; Dielectric property; Chemical solution deposition

1. Introduction

The development of power electronic devices with improved performance, increased reliability, small size, and reduced weight requires the passive components to be embedded within a printed wire board (PWB). This technology could free up surface space, increase device reliability, and minimize electromagnetic interference and inductance loss. Although the technology has primarily received attention for decoupling capacitors in microelectronic applications,[1–3] it can also be extended to high-power applications at higher voltages, such as plug-in hybrid electric vehicles. However, the integration of high-permittivity films into PWBs is a difficult task because of the incompatibility in the processing conditions for the different materials involved. Polymer layers in a PWB cannot withstand the high temperatures (600–800 °C) required for processing the ceramic film dielectrics to obtain the desired crystalline structures. Development of these crystalline structures becomes extremely challenging at reduced processing temperatures.[4] However, success has been demonstrated through a film-on-foil approach where the ceramic dielectrics are first coated on a thin base metal foil by chemical solution deposition and then crystallized at high temperature.[5–10] These coated foils can subsequently be embedded into a PWB. Kingon and Srinivasan[5] reported the deposition of PZT (52/48) films directly on copper foils using a complex heat-treatment process and obtained dielectric constant of ≈1100 and loss <5%. Maria et al.[7] reported fabrication of PLZT (15/52/48) on nickel plated copper foils that achieved capacitance density of 350 nF/cm^2 and loss of 2%. Zou et al.[8] reported growth of PZT on various metal substrates and observed dielectric constant up to ≈450. In this paper, we report our recent results on the dielectric properties of PLZT film capacitors deposited on nickel and copper foils.

2. Experiment

Prior to being coated, the base metal (Ni or Cu) substrates were polished with diamond paste to 1-μm finish, ultrasonically cleaned in distilled water, and then wipe-cleaned with acetone and methanol using Texwipe Alpha swabs. $LaNiO_3$ (LNO) and $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ (PLZT 8/52/48) precursor solutions were prepared by a modified 2-methoxyethanol synthesis route.[8] Detailed experimental conditions were reported earlier.[9] For

☆ The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the government.

* Corresponding author. Tel.: +1 630 252 4250; fax: +1 630 252 3604.
E-mail address: balu@anl.gov (U. Balachandran).
[1] Current address: Materials Engineering Department, Korea Aerospace University, Gyeonggi-do, Korea.

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.05.006

the deposition of PLZT on Ni substrates, LNO precursor solution (0.2 M) was first spin coated on Ni substrates, pyrolyzed at 450 °C for 5 min, and annealed at 650 °C for 2–5 min. This process was repeated three to five times to build a buffer film with desired thickness. Subsequently, PLZT precursor solution (0.5 M) was spin coated on LNO-buffered nickel substrates at 3000 rpm for 30 s. Pyrolysis was at 450 °C for 10 min and subsequent annealing at 650 °C for 2–5 min, with a final annealing at 650 °C for 20 min. All pyrolysis and annealing were performed in air. Solution coating and firing were repeated to produce films of a desired thickness. For the deposition of PLZT on Cu substrates, the 0.5 M PLZT precursor solution was spin coated onto the substrate at 3000 rpm for 30 s and dried in a furnace at 250 °C for 10 min. The film was then pyrolyzed at 450 °C for 18 min under flowing N_2 (99.999%, 500 sccm) at a heating and cooling rate of 4 °C/min. The spin, dry, and pyrolysis steps were repeated up to three times, and then the sample was crystallized at 650–700 °C for 18 min (2 °C/min ramp rate) in 500 sccm of flowing ultrahigh purity N_2 ($pO_2 \approx 10^{-7}$–10^{-8} atm). The entire process up to and including crystallization was repeated two or three times to yield the desired thickness of PLZT films. Platinum (Pt) electrodes of ≈250-μm diameter and ≈100-nm thickness were deposited on PLZT films by electron-beam evaporation.

The film-on-foil capacitor samples were analyzed by several methods. A Bruker AXS diffractometer with General Area Detector Diffraction System was used for X-ray diffraction (XRD) analysis. An HP 4192A impedance analyzer was employed for measuring the capacitance and dissipation factor with a 0.1-V oscillating signal at 10 kHz; a Keithley 237 high-voltage source meter for leakage current and breakdown field strength; and a Radiant Technologies' Premier II dielectric testing system for hysteresis loops. The samples were immersed in silicon oil during the dielectric breakdown measurements.

3. Results and discussion

The PLZT films grown on LNO-buffered Ni foils were phase pure with no preferred crystallographic orientation and no crack or delamination. Fig. 1 shows the relative permittivity and dielectric loss of a 2.5-cm × 2.5-cm PLZT/LNO/Ni sample measured at room temperature as a function of applied bias field. The thickness of the PLZT was ≈1.15 μm, deposited on top of a ≈0.4-μm-thick LNO buffer. A relative permittivity of 1300 and dielectric loss (tan δ) ≈0.05 were measured at room temperature.

Fig. 2 shows the temperature-dependent relative permittivity of a 2.5-cm × 2.5-cm PLZT/LNO/Ni sample along with that of PLZT on platinized silicon substrate. As evident in the figure, the Curie temperature for the PLZT/Pt/Si sample (≈150 °C) is higher than that for the PLZT/LNO/Ni sample (≈200 °C). The Curie temperature of the PLZT/Pt/Si sample agrees well with that reported earlier.[11] In addition, for this sample, the capacitance varies by about 20% in the temperature range between 25 and 275 °C. The capacitance of the PLZT/LNO/Ni sample increases more rapidly with increasing temperature from 25 to 200 °C. Its relative permittivity was 1300 at 25 °C and reached 1800 at 150 °C. A possible reason for the higher Curie temperature and strong temperature dependence in the PLZT/LNO/Ni sample is a lower concentration of lanthanum[12] in the PLZT grown on LNO-buffered Ni foil when compared with that grown on platinized silicon substrate. Further investigation is underway.

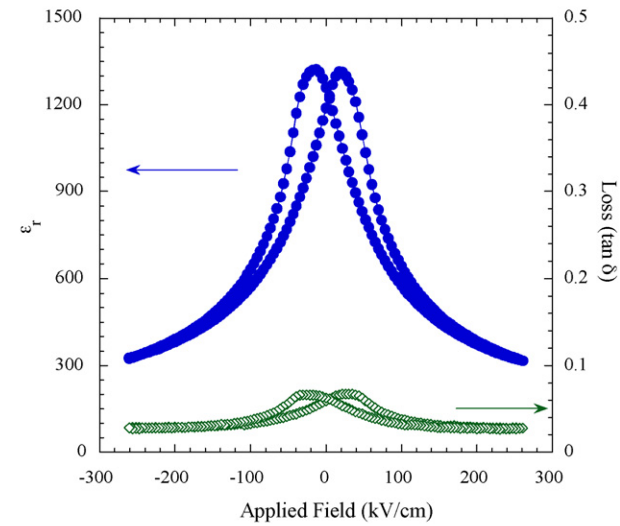

Fig. 1. Relative permittivity and dielectric loss measured as a function of applied field on a Pt/PLZT/LNO/Ni capacitor.

Fig. 3 shows the time relaxation for the current density measured on the 2.5-cm × 2.5-cm PLZT/LNO/Ni sample (1.15-μm-thick PLZT) at 25 and 150 °C with a constant bias potential of 10 V (corresponding to an applied electrical field ≈90 kV/cm) across the top and bottom electrodes. The measurements were conducted by keeping the top Pt electrode positive and the bottom Ni electrode grounded. Both curves show strong initial time dependence, indicating depolarization. The current density measured at 150 °C is roughly a factor of two higher than that measured at 25 °C. The decay in dielectric relaxation current

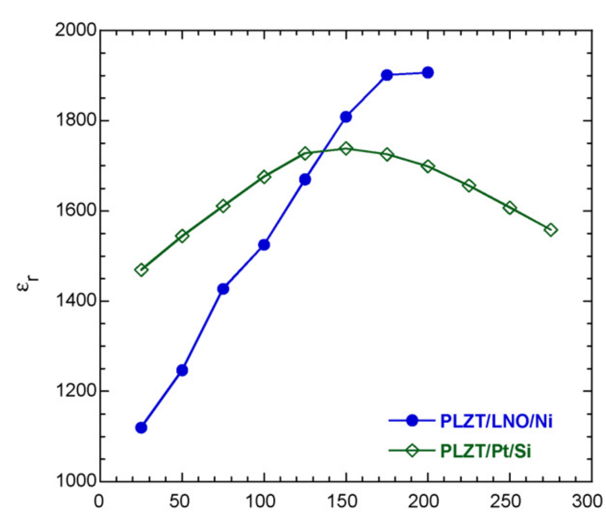

Fig. 2. Relative permittivity as a function of temperature for a Pt/PLZT/LNO/Ni capacitor, in comparison with PLZT grown on a platinized silicon substrate.

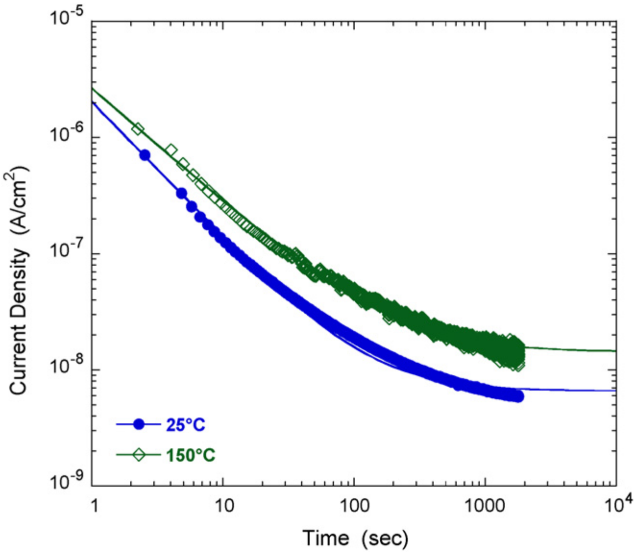

Fig. 3. Current density measured as a function of time on a PLZT/LNO/Ni sample at room temperature and 150 °C.

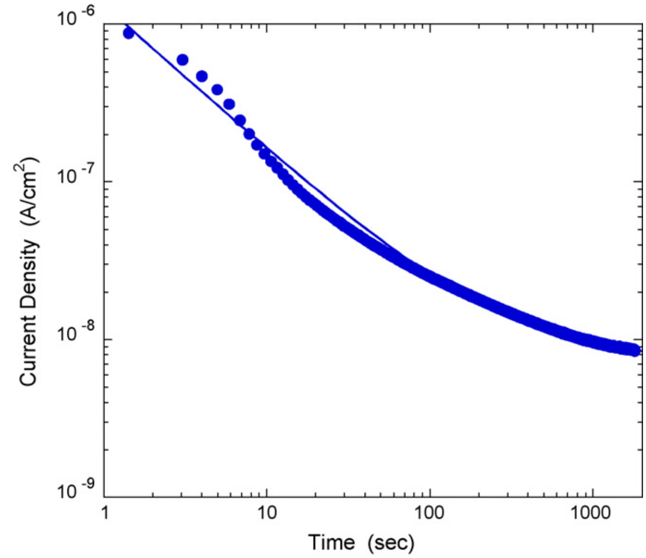

Fig. 5. Relaxation current density measured as a function of time on PLZT/Cu at room temperature.

obeys the Curie-von Schweidler law[13]:

$$J = J_s + J_0 t^{-n} \quad (1)$$

where J_s is the steady-state current density, J_0 is a fitting constant, t is relaxation time in seconds, and n is the slope of the log–log plot. Fitting the data to Eq. (1), we found n values of 0.99 and 0.97 and leakage current densities of 6.6×10^{-9} A/cm^2 and 1.4×10^{-8} A/cm^2 for the measurements at room temperature and 150 °C, respectively. The leakage current densities measured on our samples is approximately three orders of magnitude smaller than that reported by Zou et al.[8]

Fig. 4 shows the relative permittivity and dielectric loss of a 1.2-cm × 1.2-cm PLZT/Cu sample measured at room temperature as a function of applied bias field. The thickness of the PLZT was ≈1.04 μm, deposited on polished copper substrate. A relative permittivity of 1100 and dielectric loss (tan δ) ≈0.06 were measured at room temperature. With a simple heat-treatment procedure,[10] the dielectric constant and loss we measured are comparable to that reported by Kingon et al.[5] Fig. 5 shows the relaxation current density measured as a function of time at room temperature on Pt/PLZT/Cu capacitor, along with the fitting of the data to Eq. (1). From the curve, we obtained $n = 0.99$ and leakage current densities $J_s = 7.3 \times 10^{-9}$ A/cm^2. This value is comparable to that we obtained on Pt/PLZT/LNO/Ni capacitors.[9] Fig. 6 shows the relative permittivity and dielectric loss as a function of temperature measured on a 1.2-cm × 1.2-cm Pt/PLZT/Cu film-on-foil sample. Relative permittivity increases while dielectric loss decreases with increasing temperature between room temperature and 175 °C. A relative permittivity of ≈1400 and dielectric loss of ≈5.5% were determined at 150 °C. These results mea-

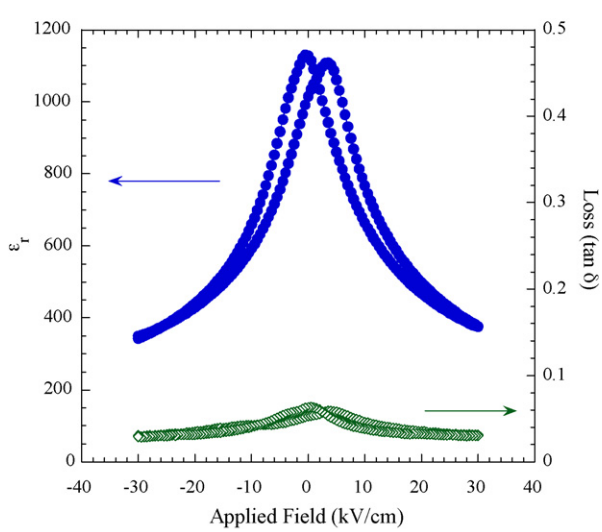

Fig. 4. Relative permittivity and dielectric loss measured as a function of applied field on a Pt/PLZT/Cu capacitor.

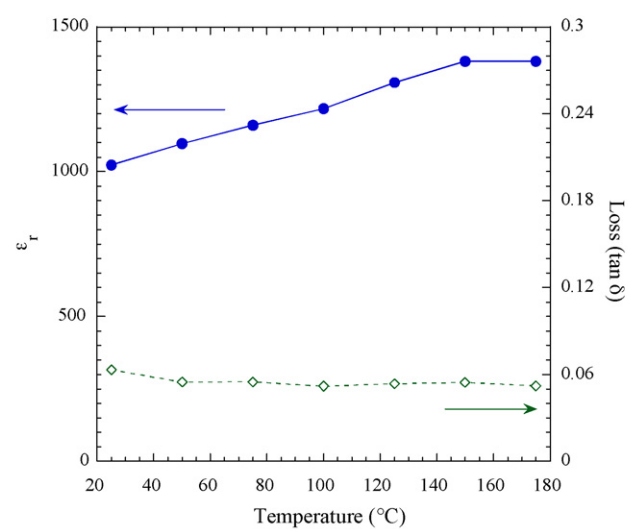

Fig. 6. Relative permittivity and dielectric loss measured as a function of temperature of Pt/PLZT/Cu capacitor.

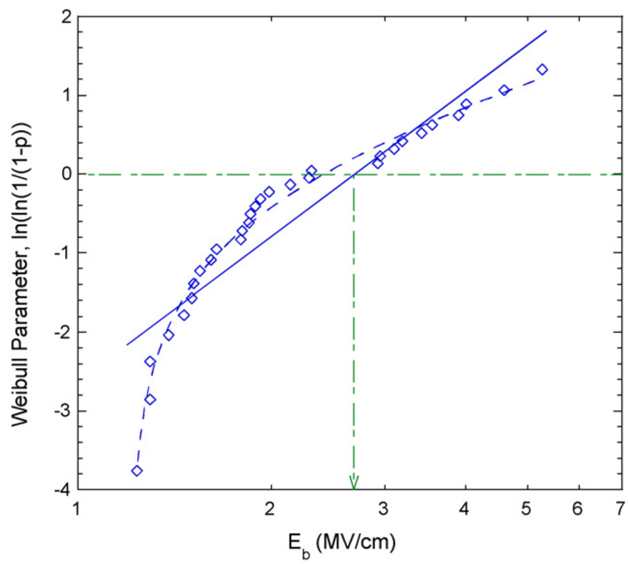

Fig. 7. Weibull plot for breakdown field strength of PLZT/LNO/Ni capacitors with 1.15-μm PLZT layer. The straight solid line and curved dotted line are fittings to two- and three-parameter functions for failure probability.

sured on Pt/PLZT/Cu are comparable to these obtained on Pt/PLZT/LNO/Ni samples.

The breakdown field strength was measured with a "top-to-bottom" electrode configuration. The applied voltage was increased by 1 V/s, soaking time was 1 s, and the breakdown voltage was determined by using a 1-μA criterion. Weibull statistics[14–16] were employed for failure behavior analysis. Fig. 7 shows a Weibull plot of breakdown field strength obtained from 30 measurements with Pt/PLZT/LNO/Ni capacitors (with 1.15-μm-thick PLZT). The solid straight line is a fitting to the two-parameter distribution function and led to the mean breakdown field strength of 2.7 MV/cm. The dashed curve is a fitting to the three-parameter distribution and resulted in smaller mean breakdown field strength of 2.4 MV/cm. When an electric field of 1.2 MV/cm (≈50% of mean breakdown strength) is applied on the film-on-foil capacitor, the probability of failure is <1% based on the three-parameter Weibull analysis. The breakdown strength measured on our samples is roughly three times higher than that reported by Zou et al.[8] on PZT deposited on LNO-buffered nickel substrates, and ≈2.5 times better than that on PZT directly on titanium metal substrates.

4. Conclusions

The PLZT film-on-foil capacitors deposited on base metal substrates by chemical solution deposition exhibited excellent dielectric properties. For PLZT grown on LNO-buffered nickel substrates, we measured a dielectric constant of 1300 (at 25 °C) and 1800 (at 150 °C), leakage current density of 6.6×10^{-9} A/cm^2 (at 25 °C) and 1.4×10^{-8} A/cm^2 (at 150 °C), and mean breakdown field strength ≈2.5 MV/cm. With PLZT films deposited directly on Cu foils, we observed dielectric constant ≈1100, dielectric loss (tan δ) ≈0.06, and leakage current density of 7.3×10^{-9} A/cm^2 at room temperature. These film-on-foil capacitors are promising for high-power electronic applications.

Acknowledgment

Work funded by the U.S. Department of Energy, Office of Vehicle Technologies Program, under Contract DE-AC02-06CH11357.

References

1. Borland, W., Doyle, M., Dellis, L., Renovales, O. and Majumdar, D., Embedding ceramic thick-film capacitors into printed wiring boards. *Mater. Res. Soc. Symp. Proc.*, 2005, **833**, 143–151.
2. Nelms, D., Ulrich, R., Schaper, L. and Reeder, S., In *Proceedings of the 48th IEEE Electronic Components and Technology Conference, "Anodization for Forming Thin Film Embedded Capacitors in MCM-D and MCM-L Substrates,"*. Institute of Electrical and Electronic Engineers, Piscataway, NJ, 1998, pp. 247–251.
3. Chiang, C. and Fraser, D. B., In-plane on-chip decoupling capacitors and method for making same, US Patent # 6949831B2, 2005.
4. Zhu, Y., Zhu, J., Song, Y. J. and Desu, S. B., Laser-assisted low temperature processing of Pb(Zr,Ti)O thin film. *Appl. Phys. Lett.*, 1998, **73**, 1958–1960.
5. Kingon, A. I. and Srinivasan, S., Lead zirconate titanate thin film on copper electrodes for ferroelectric, dielectric and piezoelectric applications. *Nat. Mater.*, 2005, **4**, 233–237.
6. Ma, B., Narayanan, M. and Balachandran, U., Dielectric strength and reliability of ferroelectric PLZT films deposited on nickel substrates. *Mater. Lett.*, 2009, **63**, 1353–1356.
7. Maria, J.-P., Cheek, K., Streiffer, S. K., Kim, S.-H., Dunn, G. and Kingon, A. I., Lead zirconate titanate thin film base-metal foils: an approach for embedded high-permittivity passive components. *J. Am. Ceram. Soc.*, 2001, **84**, 2436–2438.
8. Zou, Q., Ruda, H. E. and Yacobi, B. G., Improved dielectric properties of lead zirconate titanate thin films deposited on metal foils with $LaNiO_3$ buffer layers. *Appl. Phys. Lett.*, 2001, **78**, 1282–1284.
9. Ma, B., Kwon, D. K., Narayanan, M. and Balachandran, U., Dielectric properties of film-on-foil capacitors. *Mater. Lett.*, 2008, **62**, 3573–3575.
10. Narayanan, M., Kwon, D. K., Ma, B. and Balachandran, U., Deposition of sol–gel derived lead lanthanum zirconate titanate thin film on copper substrates. *Appl. Phys. Lett.*, 2008, **92**, 252905.
11. Haertling, G. H. and Land, C. E., Hot-pressed (Pb,La)(Zr,Ti)O_3 ferroelectric ceramics for electrooptic applications. *J. Am. Ceram. Soc.*, 1971, **54**, 1–11.
12. Dai, X., DiGiovanni, A. and Viehland, D., Dielectric properties of tetragonal lanthanum modified lead zirconate titanate ceramics. *J. Appl. Phys.*, 1993, **74**, 3399–3405.
13. Jonscher, K., *Dielectric Relaxation in Solids*. Chelsea Dielectrics Press, London, 1983.
14. Weibull, W., A statistical distribution functions of wide applicability. *J. Appl. Mech.*, 1951, **18**, 293–297.
15. Dissado, L. A., Theoretical basis for the statistics of dielectric breakdown. *J. Phys. D: Appl. Phys.*, 1990, **23**, 1582–1591.
16. Tuncer, E., James, D. R., Sauers, I., Ellis, A. R. and Pace, M. O., On dielectric breakdown statistics. *J. Phys. D: Appl. Phys.*, 2006, **39**, 4257–4268.