Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1091–1094

www.elsevier.com/locate/jeurceramsoc

Electrical properties of high density PZT and PMN–PT/PZT thick films produced using ComFi technology

R.A. Dorey*, R.W. Whatmore

School of Industrial and Manufacturing Science, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

Abstract

To achieve high actuation forces in piezoelectric film actuators and transducers it is desirable to have relatively thick films. Sol-gel derived films are often limited in the maximum thickness that is obtainable due to the increased probability of cracking and delamination during processing. Composite film (ComFi) technology combines conventional sol-gel processing with ceramic powder processing to enable thick (>2 μm) ferroelectric films to be deposited onto silicon substrates at temperatures as low as 710 °C. Ten micrometre thick films have been fabricated using three different piezoelectric powders [hard doped PZT, soft doped PZT and PMN–PT(85–15)]. The resultant films have high densities with relative permittivities of 800, 900 and 1800, respectively. The d_{33} piezoelectric coefficients were found to be lower than corresponding values for the bulk material. This has been attributed to a combination of small grain size and the clamping effects of the rigid substrate. Hysteresis loop measurements show that greater fields are required to achieve a similar degree of polarisation to that of the bulk material. This indicates that the presence of the substrate also affects the ability to pole the material so further reducing the observed piezoelectric coefficient.

Keywords: Composites; Dielectric properties; Functional applications; Piezoelectric properties; PZT

1. Introduction

Piezoelectric ceramics in the doped lead zirconate titanate (PZT) system are well known for their excellent piezoelectric properties. When deposited in the form of thick films (1–100 μm) onto silicon they offer the possibility of producing micro-electro-mechanical system (MEMS) type devices with high actuation forces and sensitivities due to their high piezoelectric coefficients.[1,2] One of the main obstacles to overcome for their successful applications is the issue of integration with low thermal stability materials (i.e. silicon) which are widely used as substrates in MEMS devices. Conventional solid oxide ceramic powder processing requires high processing temperatures (ca. 1200 °C) and hence necessitates the use of separate forming, machining and bonding stages to be completed to produce a MEMS device. Low temperature processes such as sol gel, sputtering and evaporation, are slow and often limited by the maximum thickness that can be attained due to stress induced cracking.[3] An alternative approach[4] is to combine the processing of a PZT powder with that of a PZT producing sol. A slurry, consisting of mixed PZT powder and sol, is used to rapidly deposit thick films which can be fired at temperatures as low as 600 °C. This process can result in a relatively porous film, but the addition of a sintering aid[5] and the use of repeated sol infiltration and pyrolysis has been shown to yield high density films.[6] This composite sol-gel route has now been applied to the production of hard and soft doped PZT composite films (ComFi) and to a composite lead magnesium niobate–lead titanate (PMN–PT)/PZT composite film. The resultant dielectric and piezoelectric properties of these films ($d_{33,\ f}$ & $e_{31,f}$) are reported as a function of film density in this paper.

2. Experimental

The hard and soft PZT producing sols ($Pb_{1.05}(Zr_{0.46}Ti_{0.48}Sb_{0.02}Nb_{0.02}Mn_{0.02})O_3$ and ($Pb_{1.05}(Zr_{0.51}Ti_{0.47}Nb_{0.02})O_3$) were prepared from metal-organic precursors with 2-Methoxyethanol (2ME) as the solvent.

* Corresponding author. Tel.: +44-1234-750111x2505; fax: +44-1234-751346.
E-mail address: r.a.dorey@cranfield.ac.uk (R.A. Dorey).

0955-2219/$ - see front matter
doi:10.1016/S0955-2219(03)00542-9

4.7 wt.% $0.2Cu_2O–0.8PbO$[5] sintering aid and 2 wt.% dispersant were added to the PZT powder to aid densification of the film and stability of the slurry. The composite slurry was prepared using a sol:PZT powder ratio of 2:3. A single composite layer was deposited onto a Ti/Pt coated silicon wafer and fired at 450 °C to yield a porous layer. This layer was then repeatedly infiltrated with sol and fired to increase the film density. The desired film thickness was obtained by depositing further composite layers as described above. Once the required film thickness was obtained the film was sintered at 710 °C for 30 min in a rapid thermal annealer (AG associates Heatpulse 210). 710 °C was selected as this is approximately 30 °C above the eutectic melting point of the sintering aid. Full details of the production of the sol, composite slurry and film deposition have been presented elsewhere.[6] The composition of the sol was matched to that of the PZT powder (Ferroperm PZ26 and PZ27) for the hard and soft doped PZT composite films. The PMN–PT/PZT composite film was produced using PMN-PT powder (TRS Ceramics PMN-15) and the soft PZT producing sol. It was hoped that this approach would yield a film with higher piezoelectric coefficients than pure PZT.

To perform the electrical measurements 2 mm diameter gold electrodes were deposited by evaporation (Edwards E480). The capacitances of the electroded areas were measured using a Wayne Kerr Component analyser (6425B). The relative permittivity was then calculated from the capacitance and a knowledge of the system geometry. The films were poled at 130 °C for 5 min using a field of 8 V/μm. The field was maintained during cooling to room temperature. $d_{33,\ f}$ and $e_{31,\ f}$ were measured using a modified Berlincourt piezometer[7] (TakeControl PM25). Hysteresis loops were acquired using a Radiant Technologies RT66A looptracer.

3. Results and discussion

3.1. Relative permittivity

The relative permittivities for the films are shown in Fig. 1. The values quoted by the manufacturer for the PZ26 and PZ27 are 1300 and 1800 respectively. These are greater than those obtained for the high density ComFi thick films. The values obtained experimentally are also very similar in value to each other. Some of the reduction in the relative permittivity in the films relative to the bulk can be attributed to the presence of residual porosity.[8] However, as the level of residual porosity is approximately the same in the hard and soft PZT films it is unlikely to account for the much larger decrease in the relative permittivity of the soft PZT relative to the hard PZT. Such behaviour is a result of the action of the rigid substrate which reduces the degree of domain wall motion within the ferroelectric material[9] and also reduces the piezoelectric contribution to relative permittivity due to clamping.[10] The domain walls in hard PZT are already 'pinned' by the dopants[11] hence the clamping effect of the substrate is unlikely to have a significant effect on the value of relative permittivity obtained. However the domain walls are not 'pinned' in soft PZT, hence the rigid substrate can have a much greater effect on the relative permittivity of the soft PZT. Similar values of relative permittivity are attained for the hard and soft PZT films as the ferroelectric deformations (i.e. atomic and domain wall movement) within the clamped films are comparable.

The PMN–PT/PZT composite film exhibits a marked increase in the value of relative permittivity due to the presence of the high permittivity PMN–PT phase. The manufacture's quoted relative permittivity for the PMN–PT ceramic is 20,000. The combination of the presence of the PZT material and the effect of the rigid substrate will lead to the reduction in this value of relative permittivity. PMN–PT exhibits a larger intrinsic contribution to permittivity[12] which will also help maintain high permittivity values.

3.2. Piezoelectric coefficients

The hard and soft PZT materials exhibit very similar values of $d_{33,\ f}$ and $e_{31,\ f}$ (stress and strain piezoelectric coefficients for clamped films) as shown in Figs. 2 and 3. This can again be attributed to the clamping of domain walls through the action of the rigid substrate, indicating that this process is active in reducing the relative permittivity. It is not a trivial matter to compare the piezoelectric coefficients of films with those of bulk materials. By only considering the stress states it is possible to obtain equations[13,14] for predicting the piezoelectric properties of a poled bulk material constrained by a rigid substrate. However, to successfully apply

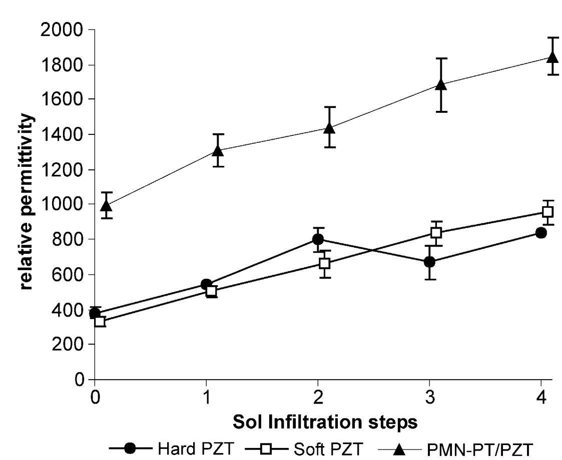

Fig. 1. Relative permittivity of hard PZT, soft PZT and PMN–PT/PZT composite.

these equations in reverse it would be necessary to have detailed knowledge of the elastic properties of the thick films. Simply using those of the bulk material is unlikely to result in accurate predictions of 'free' piezoelectric properties due to the different processing conditions used and the resultant microstructures obtained, which will result in different mechanical properties. Furthermore, this approach would neglect any effect that the substrate has on the ability to pole the material fully.[15]

The piezoelectric properties of the dense PMN–PT/PZT composite are comparable with those of the PZT thick films. The PMN–PT powder selected for this study has a composition such that the highest piezoelectric coefficients are only achievable at room temperature through the application of a DC bias field. The observed gradual increase in value of $d_{33,f}$ is primarily a result of the increased levels of piezoactive PZT with increased infiltration. Application of a DC bias during $d_{33,\,f}$ measurements was not conducted in this study.

All of the PZT thick films exhibit a value of $d_{33,\,f}$ that is approximately constant irrespective of the level of infiltration. The value of $e_{31,\,f}$ is shown to increase with

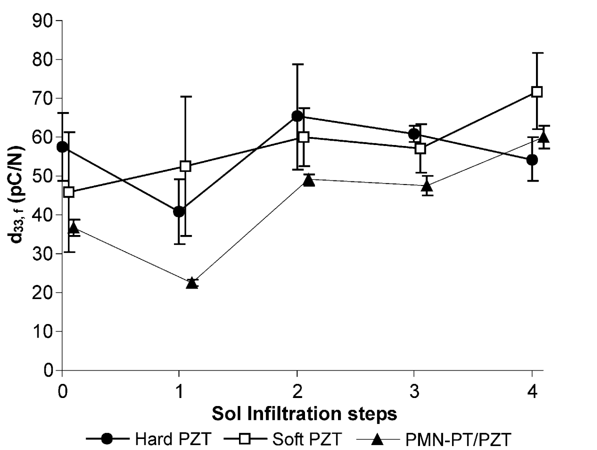

Fig. 2. Piezoelectric coefficient $d_{33,\,f}$ of hard PZT, soft PZT and PMN–PT/PZT composite.

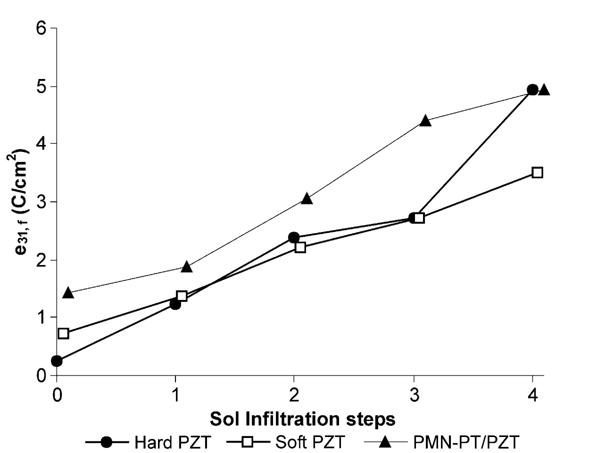

Fig. 3. Piezoelectric coefficient $e_{31,\,f}$ of hard PZT, soft PZT and PMN–PT/PZT composite.

increasing levels of sol infiltration. This is due to the increased proportion of active material that is stressed during use due to increased stress transfer within the higher density films.[8]

3.3. Hysteresis loops

Hysteresis loops for the hard and soft doped PZT are shown in Fig. 4a and 4b. Both films exhibit weaker remnant polarisations than the corresponding bulk materials at comparable fields. However, the films are not fully saturated at these levels and the remnant polarisation can be increased to levels similar to those of the bulk by utilising higher field strengths (Fig. 4d). A consequence of this behaviour is an increase in the area of the hysteresis loop indicating an increase in loss.[11] This increased loss is due to the greater resistance to 90° domain wall motion. Domain wall motion would lead to a crystallographically induced strain which in turn would be opposed by the rigid substrate. The resultant stresses can be overcome, and bulk level polarisation obtained, through the application of higher fields. Due to the small defect size the films are capable of supporting fields in excess of 60 V/μm.

Fig. 4c shows the hysteresis loop for the PMN–PT/PZT composite material. Here it can be seen that the loop is more closed than those of the PZT films. This is due to the contribution of the PMN–PT which exhibits narrow loops and weak remnant polarisation close to

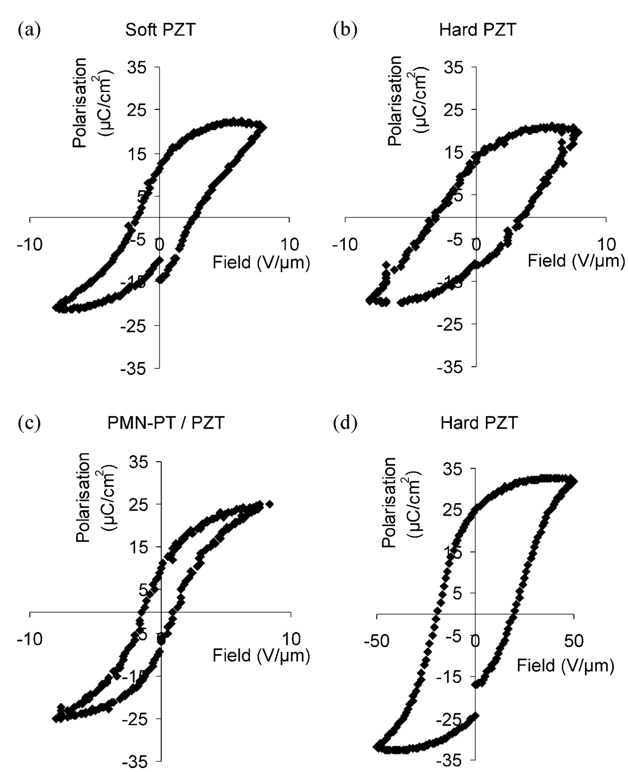

Fig. 4. Thick film hysteresis loops.

the transition temperature.[16] The PMN–PT material selected for this study has a transition temperature close to room temperature.

4. Conclusion

Hard and soft doped PZT and PMN–PT/PZT thick films have been produced using a composite slurry consisting of an oxide route derived powder and a PZT producing sol. The dielectric and piezoelectric properties of the resultant films were assessed. It was found that the hard and soft doped PZT films exhibited similar properties indicating that the domain wall motion, which accounts for the higher properties of the soft doped PZT, was suppressed when the material was constrained by a rigid substrate.

The high density PMN–PT/PZT composite film exhibited comparable piezoelectric properties to the PZT films. The relative permittivity of the films was enhanced greatly through the incorporation of the high permittivity PMN–PT powder.

References

1. Damjanovic, D., Demartin, M., Shulman, H. S., Testorf, M. and Setter, N., Instabilities in the piezoelectric properties of ferroelectric ceramics. *Sensors and Actuators*, 1996, **A53**, 353–360.
2. Prudenziati, M., ed., *Thick Film Sensors, Volume 1 of the Handbook of Sensors and Actuators*. Elsevier, Amsterdam, 1999 ISBN 0444897232.
3. Zhou, Q. F., Chan, H. L. W. and Choy, C. L., PZT ceramic/ceramic 0–3 nanocomposite films for ultrasonic transducer applications. *Thin Solid Films*, 2000, **375**, 95–99.
4. Barrow, D. A., Petroff, T. E. and Sayer, M., Thick ceramic coatings using a sol-gel based ceramic–ceramic 0–3 composite. *Surface and Coatings Technology*, 1995, **76-77**, 113–118.
5. Corker, D. L., Zhang, Q., Whatmore, R. W. and Perrin, C., PZT 'composite' ferroelectric thick films. *J. Eur. Ceram. Soc.*, 2002, **22**, 383–390.
6. Dorey, R. A., Stringfellow, S. B. and Whatmore, R. W., Effect of sintering aid and repeated sol infiltrations on the dielectric and piezoelectric properties of a PZT composite thick film. *J. Eur. Ceram. Soc.*, 2002, **22**, 2921–2926.
7. Southin, J. E. A., Wilson, S. A., Schmitt, D. and Whatmore, R. W., $e_{31,\ f}$ determination for PZT films using a conventional 'd_{33}' meter. *J. Phys. D: Appl. Phys.*, 2001, **34**, 1456–1460.
8. Bowen, C. R. and Kara, H., Pore anisotropy in 3–3 piezoelectric composites. *Materials Chemistry and Physics*, 2002, **75**, 45–49.
9. Damjanovic, D., Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. *Rep. Prog. Pys.*, 1998, **61**, 1267–1324.
10. Nye, J. F., *Physical Properties of Crystals*. Oxford University Press, Oxford, 1957.
11. Moulson, A. J. and Herbert, J. M., *Electroceramics*. Chapman & Hall, London, 1990 ISBN 0412473607..
12. Bellaiche, L. and Vanderbilt, D., Intrinsic piezoelectric response in perovskite alloys: PMN-PT versus PZT. *Physical Review Letters*, 1999, **83**(7), 1347–1350.
13. Steinhausen, R., Hauke, T., Seifert, W., Mueller, V., Beige, H., Seifert, S. and Lobermann, P., Clamping of piezoelectric thin films on metallic substrates: influence on the effective piezoelectric modulus d_{33}. In *Applications of Ferroelectrics 1998, Proceedings of the 11th IEEE International Symposium*, 1998, pp. 93–96.
14. Cattan, E., Haccart, T., Velu, G., Remiens, D., Bergaud, C. and Nicu, L., Piezoelectric properties of PZT films for micro-cantilevers. *Sensors and Actuators*, 1999, **74**, 60–64.
15. Dorey, R. A. and Whatmore, R. W., Apparent reduction in the value of the d_{33} piezoelectric coefficient in PZT thick films. *Ferroelectrics*, 2002, **50**, 111–119.
16. Shrout, R. R. and Fielding, J., Relaxor ferroelectric materials. In *Proceedings of the Ultrasonics Symposium*, 1990, pp. 711–720.