Preprint of paper: R.A. Dorey, R.W. Whatmore, “Apparent reduction in the value of the d33 piezoelectric coefficient in PZT thick films”, Integrated Ferroelectrics, 50, pp111-119, 2002.

Apparent reduction in the value of the d_{33} piezoelectric coefficient in PZT thick films

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Thick PZT films (1 – 20 µm) have been prepared using a composite sol gel technique whereby PZT powder and a PZT producing sol are formed into a slurry and spin coated onto silicon wafers. The maximum relative permittivity obtained was approximately 80% of that exhibited by bulk PZT of comparable composition. However, the $d_{33,\,f}$ and $e_{31,\,f}$ [1] piezoelectric coefficients were shown to be significantly lower than that of bulk PZT.
It has been proposed that the measured value of $d_{33,\,f}$ is affected appreciably by particle-particle rotation and substrate clamping leading to reduced poling efficiency which may also greatly reduce the value of $e_{31,\,f}$ observed.
Samples with high levels of porosity have been shown to exhibit a reduced value of d_{33}. This was attributed to ‘31’ and ‘51’ mode piezoelectrically generated charges caused by the bending and shearing of particle-particle bridges.
The effect of substrate clamping, on $d_{33,\,f}$ and poling, has been studied by monitoring the changes in position and intensity of the (200)/(002) X-ray diffraction (XRD) peaks of composite films. The presence of the substrate was found to introduce tensile stresses parallel to the film plane which distorted the unit cell. Subsequent permanent polarisation following poling was found to be reduced due to the presence of these stresses.
The discrepancies between the values of d_{33} measured on thick films and bulk ceramics were highlighted as being of particular importance if thick film materials are to be modelled for device applications. Thick film piezoelectric coefficients (i.e. those of the combined film-substrate structure) should not be used in place of material piezoelectric coefficients when attempting to model the behaviour of devices. Such actions would inevitably lead to erroneous results.

Keywords: Lead Zirconate Titanate, PZT, piezoelectric, d33, e31, poling, films

INTRODUCTION

The drive for smaller functional devices has lead to the rapid development of microelectromechanical systems (MEMS) in recent years [2, 3]. Two key requirements for the active materials within these systems are the ability provide sufficiently high/large activation forces/displacements and the ability to integrate the material with the underlying support structure[4,5].
Lead zirconate titanate (PZT) is a favoured active material due to its high piezoelectric coefficients[6]. However, it is typically processed at temperatures above 1200ºC making it unsuitable for direct integration with silicon based MEMS devices[2]. Separate processing of PZT and subsequent grinding, polishing and bonding can be used to achieve an integrated system but the large wastage, long processing times, and non-integrated processing may make this approach unattractive. Alternative approaches used to integrate the production of the PZT thick film with the silicon processing include screen printing[7], electrophoresis[8] and sol gel techniques[9]. Screen printing and electrophoresis require relatively high temperatures for processing (>850ºC) while sol gel techniques are often limited to thicknesses below 10 µm due to the increased risk of cracking[10] and the excessive time required to achieve thicker films[2].
Barrow[11] adapted the sol gel method by mixing the sol with a PZT powder which allowed much thicker PZT films to be deposited at low temperatures. This process was later modified by others who incorporated a low temperature sintering aid[12] and intermediate sol infiltration/pyrolysis steps[13] to produce high density PZT thick films.
The resultant films exhibit relative permittivities comparable to those of bulk ceramics. However the piezoelectric coefficients recorded are typically much lower than those observed for bulk ceramic. This work aims to examine the dielectric, piezoelectric and polarisation behaviour of a series of these thick films to determine how the microstructure and the presence of the rigid substrate may affect the properties of the films. To this end, a series of samples with varying levels of porosity have been made and their microstructure and dielectric/piezoelectric properties assessed.

EXPERIMENTAL PROCEDURE

Film preparation

A sol, designed to yield a hard doped PZT when pyrolysed, was produced using lead acetate, zirconium isopropoxide and titanium isopropoxide as precursors. 2-methoxyethanol was selected as the solvent due to its low viscosity and high surface tension. A full description of the sol synthesis process is given in a previous article[12]. The PZT producing sol was then mixed with PZT powder of comparable composition (PZ26 Ferroperm), a liquid phase sintering aid (0.8PbO-0.2Cu_2O), and a dispersant (KR55, Kenrich Petrochemicals). The final compositional ratio of the composite slurry was 1.5 g PZT powder : 1 ml sol : 4.7 wt% (relative to PZT powder) sintering aid : 2 wt% (relative to PZT powder) dispersant. Before use, the composite slurry was ball milled for 24 hours to ensure thorough dispersion of the constituents.
The composite films were produced by spin coating the composite slurry onto a Ti/Pt coated silicon wafer at 2000 rpm for 30 seconds. Following spinning the films were dried at 200 ºC for 60 seconds and pyrolysed for 15 seconds at 450 ºC. The final film thickness was increased by depositing further layers in an identical manner.

Films of higher density were produced by repeated sol infiltration and pyrolysis of each porous composite layer before the next composite layer was deposited. Each composite/sol infiltration was dried and pyrolysed before the next deposition stage. The resultant films were described using the nomenclature (C+2S)4 which describes a 4 layer film where each layer is composed of a composite layer infiltrated with 2 sol treatments. Once the required film thickness had been obtained the film was subjected to a rapid thermal annealing treatment at 710 ºC for 30 minutes.

Film characterisation

Structural and crystallographic analysis of the films were conducted using X-ray diffraction (XRD) (Siemens D-5005) and scanning electron microscopy (ABT-55) of fracture and polished cross-sections. 1 and 2 mm diameter gold/chrome electrodes were evaporated onto the surfaces of the films to allow their electrical properties to be assessed. Relative permittivity and dielectric loss were assessed at 1 kHz (Wayne Kerr Precision Component Analyser 6425B). Prior to piezoelectric measurements the films were poled at 130 ºC for 5 minutes using a field of 8 V/µm. The piezoelectric coefficients $d_{33,\,f}$ and $e_{31,\,f}$ were measured using flexural method[1] with a modified Berlincourt-type piezometer (Take Control PM25).

RESULTS AND DISCUSSION

Microstructure & Crystallography

Figure 1 shows scanning electron microscope (SEM) photomicrographs of fracture surface cross-section of films with 0, 2 and 4 sol infiltration/pyrolysis steps.

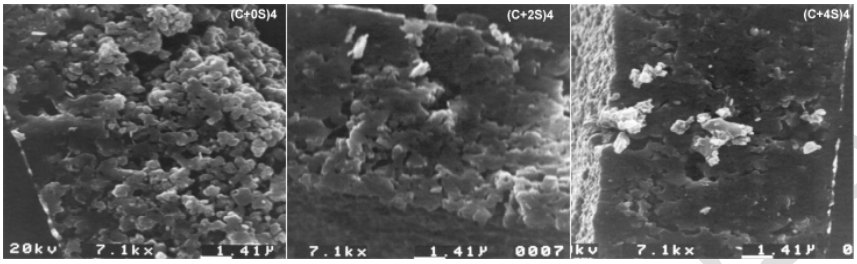

Figure 1 – SEM photomicrographs of fracture surfaces of films with different levels of sol infiltration/pyrolysis

It can be seen that when low levels of intermediate sol infiltration are employed the resultant films exhibit a density gradient with the highest density regions present at the PZT/wafer boundary. This is caused by the infiltration of sol from the composite slurry into underlying porous layers as each new composite layer is deposited. By infiltrating each composite layer before the next is deposited the pores are filled and a homogenous microstructure is obtained. An added advantage of this approach is that the surface quality of the films is greatly improved as each composite layer is deposited onto a smooth surface. When no infiltration is used the surface finish of each successive composite layer is progressively degraded due to the worsening surface finish of the previous layer.
XRD results (figure 2) show the film to be fully perovskite with no evidence of the presence of pyrochlore phases.

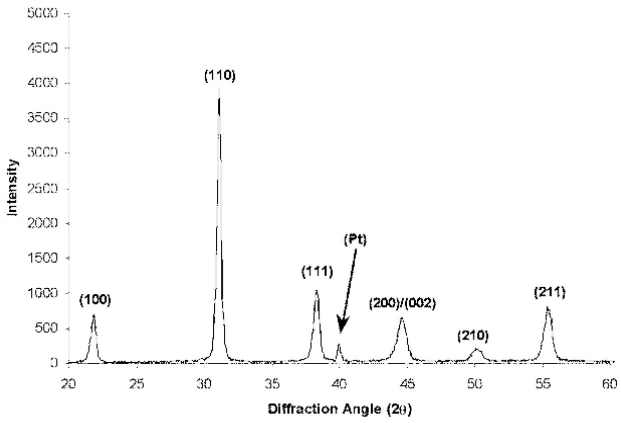

Figure 2 – XRD pattern for a (C+4S)4 film on silicon showing full perovskite phase development

Dielectric properties

Results relating to relative permittivity are presented in figure 3. The relative permittivity can be seen to increase with increasing sol infiltration steps due to the reduction in the level of porosity. The value of relative permittivity obtained for the (C+4S)4 film is close to that measured for unpoled bulk PZ26 (1050). The dielectric loss was found to be independent (~2%) of the number of intermediate sol infiltrations.

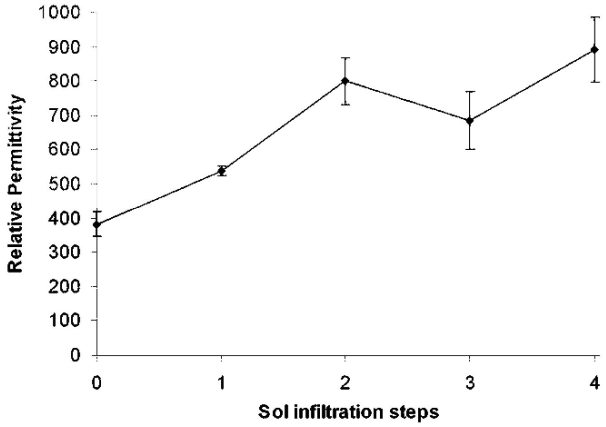

Figure 3 – Relative permittivity of the composite films as a function of intermediate sol infiltration steps

Piezoelectric properties

The variation in $d_{33,\,f}$ and $e_{31,\,f}$ as functions of sol infiltration are presented in figures 4 and 5. It can be seen that $d_{33,\,f}$ is initially lower when no infiltration steps are employed. If sol infiltration is used the $d_{33,\,f}$ piezoelectric coefficient increased to a plateau value of approximately 60 pC/N.

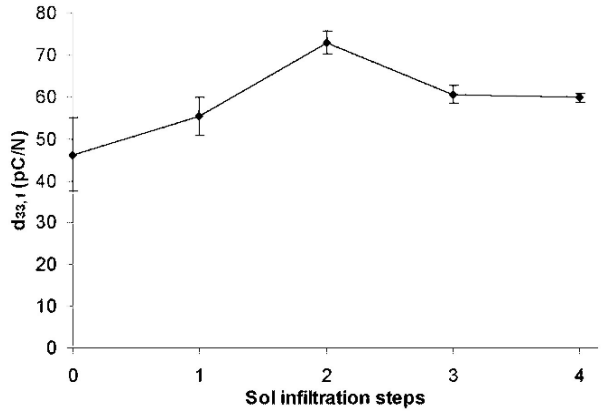

Figure 4 – $d_{33,\,f}$ of the composite films as a function of intermediate sol infiltration steps

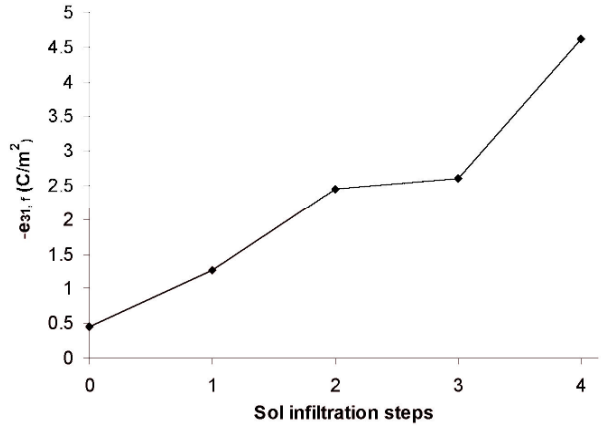

Figure 5 – $e_{31,\,f}$ of the composite films as a function of intermediate sol infiltration steps

The initially low value of $d_{33,\,f}$ is thought to be due to the very high levels of porosity present in the films made with no sol infiltration steps. It is proposed that the structure is such that the application of the measurement stress would cause the PZT film to deform in such a way as to cause bending and shearing of the bridges between particles which may reduce the net charge produced due to the generation of d_{31} and d_{51} charges and/or the reduction in d_{33} generated charges. With the application of sol infiltration steps during processing a more rigid structure is obtained where such deformation does not occur. The $d_{33,\,f}$ plateau value of approximately 60 pC/N is significantly below the value of d_{33} quoted for bulk PZ26 (330 pC/N). However, it should be noted that the d_{33} piezoelectric coefficient is reduced by the presence of a rigid substrate[14, 15] (equation 1). Conversely the e_{31} piezoelectric coefficient is increased in magnitude by clamping[16] (equation 2). This occurs because d_{33}, d_{31} and e_{33} containing terms are positive while the e_{31} term is negative.

$$d_{33,f} = d_{33} - 2\,d_{31}\frac{S_{13}^{E}}{S_{11}^{E} - S_{12}^{E}} \qquad \text{Equation 1}$$

$$e_{31,f} = e_{31} - e_{33}\frac{C_{13}^{E}}{C_{33}^{E}} \qquad \text{Equation 2}$$

If values for the bulk properties of a hard doped PZT comparable to PZ26[17] are substituted into equations 1 and 2 the $d_{33,f}$ and $e_{31,f}$ piezoelectric coefficient would be expected to be approximately 130 pC/N and -16 C/m^2 respectively. Both of these predicted values are greater in magnitude to those observed for the high density thick films.

One of the underlying assumptions that must be considered when using equations 1 and 2 is that the PZT is considered to be fully poled when bonded to the rigid substrate. However, the composite films are initially unpoled and must therefore be poled while bonded to the rigid substrate. Trolier-McKinstry[18] *et al.* and Kholkin[19] showed that domain mobility is reduced in poled piezoelectric materials when they are constrained by a rigid substrate. It is hypothesised here that the presence of the rigid substrate would also reduce domain wall mobility during poling and would therefore have a further deleterious effect on the observed value of $d_{33,f}$ by reducing the degree of poling attainable. To test this hypothesis, an XRD analysis was conducted on bulk PZT and the composite films before and after poling.

Li *et al.*[20] showed that the relative intensities of the (200) and (002) diffraction peaks of the tetragonal phase changed during poling such that the (002) diffraction planes were favoured. Figure 6 shows the XRD diffraction pattern for bulk PZ26, the composite film and a PZT compact containing 4.7 wt% sintering aid, infiltrated with sol and sintered at 710 ºC (nominally identical composition and thermal processing to that of composite films).

The diffraction peaks for the bulk PZT are narrower than those of the compact infiltrated with sol indicating that the grain size of the PZ26 compact is much larger than that of the infiltrated compact. This was confirmed by observations of the microstructures of the two bodies.

The XRD peaks for the composite film are wider, and shifted to higher angles, when compared to the peaks for the infiltrated compact. It is unlikely that this extra broadening is due to the a difference in the grain size between the composite film and the infiltrated compact as the sintering regimes used for the two sample types were nominally identical. The shift in position of the peaks is due to a change in the lattice spacing of the diffraction planes while the extra broadening is caused because this change in spacing is not uniform throughout the sample indicative of non-uniform stress. Due to the high X-ray attenuation within lead based materials the XRD analysis only obtains information about the near surface material. A non-uniform stress within this region could arise due to local stress release in the vicinity of cracks.

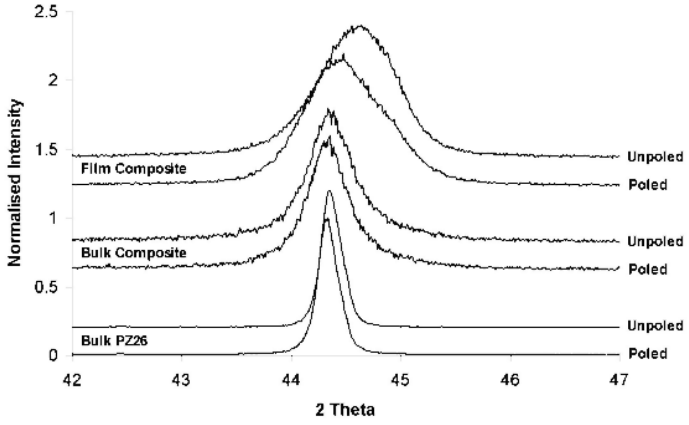

Figure 6 – XRD pattern of the (200)/(002) region for poled and unpoled bulk PZ26, compact infiltrated with sol and sintered at 710ºC and composite film.

The shift of the mean peak position to higher diffraction angles (θ) is indicative of a reduction in the spacing of the diffraction planes. This change could be caused by an increase in the spacing of the atomic planes perpendicular to the diffraction plane. The action of tensile stresses within the plane of the film (perpendicular to the diffraction plane) would be expected to cause such changes. These tensile stresses would be generated by sintering shrinkage and thermal expansion mismatch between the PZT and the silicon substrate. Analysis of the curvature of the silicon wafer with a 10 µm PZT film showed the wafers to be bowed with the PZT film on the inside radius of curvature. This is concurrent with the PZT film being subjected to a tensile stress of approximately 120 MPa.

The deformation of the unit cells (and subsequently the domains) is unlikely to result in a net polarisation as stress is assumed to act uniformly within the plane of the film and hence any local domain polarisation should be cancelled by the random orientations of the domains within the plane of the film.

Following poling, the XRD patterns of both the bulk PZ26 sample and the infiltrated compact show the (200)/(002) peak to be shifted to lower diffraction angles indicating an increase in the spacing of the diffraction planes as would be expected from the orientation of the domains. A similar, but much larger magnitude, change in diffraction angle (and hence d spacing) was observed for the composite thick film. However, there is still a significant diffraction signal present

at high diffraction angles indicating that the composite film has not been completely poled. Hysteresis loops obtained from the composite films show that polarisation similar to bulk PZ26 can be achieved but much higher (~ x 10) fields are required (figure 7).

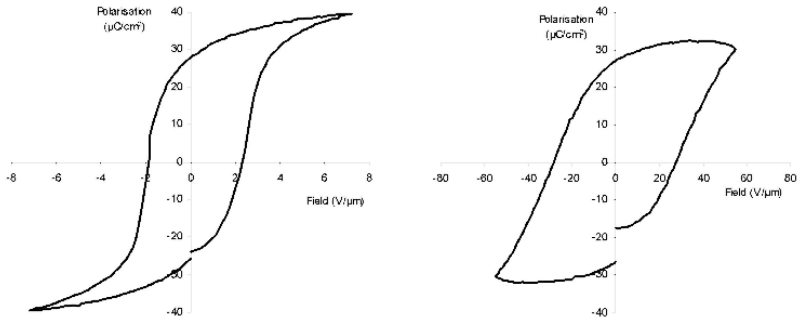

Figure 7 – Comparison of degree of polarisation bulk PZ26 and composite films

The results of the XRD analysis suggest that despite high levels of polarisation during poling, the presence of the tensile stress causes a significant proportion of the domains to reorientate once the poling voltage is removed. Similar depoling behaviour has been observed in PZT[21] and $BaTiO_3$[22] subjected to compressive stresses parallel to the poling direction. The action of a compressive stress parallel to the poling direction would be expected to have a similar effect to that of a tensile stress perpendicular to the poling direction as the same type of crystallographic deformation would be expected to occur.
The in-plane tensile stresses will be further increased by domain/grain shape changes during the poling process.

CONCLUSIONS

PZT composite films with a range of densities have been deposited onto silicon wafers at 710 ºC. The resulting films exhibit values of relative permittivity approximately 80% of those of bulk PZT of comparable composition.
The piezoelectric coefficients $d_{33,\,f}$ and $e_{31,\,f}$ were found to be approximatly 60 pC/N and -4.5 C/m^2 respectively. These values are below those predicted for bulk ceramics bonded to rigid substrates (130 pC/N and -16 C/m^2). This discrepancy was attributed to the need to pole the thick films while bonded to the rigid substrate.
The change in position and width of the (200)/(002) diffraction peak for bulk PZT indicated that poling increased the spacing of the diffraction planes perpendicular to the poling direction.
Analysis of the (200)/(002) diffraction peaks for the composite film PZT and wafer bowing studies showed the film to be subject to tensile stresses. These tensile stresses oppose the poling induced orientation of domains. The accompanying shape change during poling will result in further increases in the magnitude of the tensile stress.
The presence of the rigid substrate, and the subsequent tensile stresses generated by sintering, thermal expansion mismatch and poling, limits the maximum level of retained polarisation. Alternative processing conditions may reduce the stresses generated by sintering. The stresses generated by thermal expansion mismatch and poling can not be altered and will affect all silicon-PZT thick film based technologies including those based on bonding bulk unpoled PZT to silicon substrates.
Finally, it should be noted that the d_{33} piezoelectric coefficients measured on thick films will always be lower that those quoted for bulk materials due to the clamping constraints. Hence, care should be taken when applying these values to figure-of-merit calculations and modelling.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the European Commission and the Engineering and Physical Sciences Research Council under grant GR/N05970 for their financial support during this project.

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