Effect of sintering aid and repeated sol infiltrations on the dielectric and piezoelectric properties of a PZT composite thick film

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Abstract

Thick PZT films have been produced using a combination of spin coating of a composite slurry and subsequent infiltration of PZT producing sol. The effect of adding a Cu_2O–PbO sintering aid and repeated sol infiltrations have been studied with the aim of producing dense PZT films. Relative permittivity has been shown to increase with the addition of sintering aid and increased levels of sol infiltration. Measurements of piezoelectric properties indicate that sol infiltrations have no effect on d_{33} once a critical density has been exceeded. A sample with approximately 10% closed porosity was obtained following the incorporation of sintering aid and four infiltration steps per layer. This resulted in a mean relative permittivity of approximately 700 and a d_{33} of 62 pC/N (poling conditions: 8 V/μm for 5 min at 200 °C). © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Sol-gel technology allows thin oxide films (< 1 μm) to be deposited onto a variety of substrates at temperatures well below those conventionally used for bulk ceramic processing. Typically temperatures as low as 600–700 °C are used, so allowing the ceramic deposition to be incorporated into the silicon processing stages.[1,2] In addition, the lowering of the processing temperature reduces the interdiffusion of atomic species between the different layers and the vaporisation of PbO.[2,3] Thin PZT films have been deposited to produce devices such as membrane sensors, accelerometers and micromotors.[4] However, devices requiring larger actuation forces (i.e. high frequency transducers, vibration control devices) require thicker (> 10 μm) piezoelectric films.[5] It is not practical to produce thick PZT coatings using the standard sol-gel technique because of the increased risk of cracking due to shrinkage and the time required to produce very thick layers by repeated layering.[6,7]

In a study of bulk sintering of PZT ceramics Villegas et al.[8] found that the addition of 1–2 wt.% colloidal sol derived PZT powder resulted in a lowering of the sintering temperature which in turn lead to an increase the piezoelectric properties due to lower lead volatilisation. An alternative approach used by Barrow et al.[6] was to mix the PZT powder with the PZT sol and form the colloidal PZT powder in situ. Higher levels of sol were utilised in the in situ technique resulting in the formation of a composite structure where the sol derived PZT formed an interconnecting network. The thick film was built up by depositing a series of composite layers. Each layer was spin coated and fired at an intermediate temperature designed to pyrolise the sol. Once the required number of coatings had been applied the whole film was subjected to a crystallisation stage where the sample was sintered at higher temperatures designed to develop the perosvkite phase. Using this technique, thick, crack free PZT films have been deposited. Barrow et al.[6] attributed the crack free nature of the films to a) the presence of large amounts of powder which resulted in a decrease in the level of sol present and hence lower shrinkage; (b) strong bonding between the sol-gel and the PZT particles making cracking less likely.

The incorporation of PZT powder into the sol may also have an additional benefit. Wu et al.[2] showed that the addition of 1 wt.% PZT powder lowered the perovskite formation temperature by 50 °C and increased

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the dielectric and ferroelectric properties of the film. The incorporation of the PZT micro-powder should promote heterogeneous nucleation of the perovskite phase from the sol and may, therefore, result in randomly orientated nano PZT.

Using the composite layering technique Barrow et al.[6] obtained thick films and quoted properties comparable to those of bulk ceramics. However, in a later paper[4] lower values of relative permittivity were reported. This was attributed to the presence of the sol derived PZT with a low relative permittivity of approximately 400 compared to 1300 for the bulk PZT. The different value of relative permittivity obtained for the sol derived PZT and bulk PZT is probably due to the small size of the sol derived PZT grains.[7] Similar low values of relative permittivity have also been reported by other investigators working on thick films.[5,9] In these cases the decrease was attributed to the presence of significant levels of porosity. In reality thick films are likely to be affected by both of these factors indicating that relative permittivity of the thick films will always be lower that that expected for bulk ceramics.

The effect of various processing parameters on the relative permittivity of composite films between 0.1 and 1.5 μm thick was studied by Ohno et al.[1] It was found that the major factors affecting the film performance were powder loading and sol concentration. High powder loadings (maximum of 70 wt.%) and high sol concentrations (maximum of 0.6 M) were shown to result in thicker films with high polarisation and coercive fields. However, high powder loading and sol concentrations were also found to result in lower values of dielectric constant due to the formation of pores. A subsequent sol infiltration and annealing stage resulted in an increase in the relative permittivity of the material through a reduction in the level of porosity. Improvements in relative permittivity of PZT composite films (from 200 to 1350) were also observed by Kholkin et al.[10] following repeated sol infiltration.

It is also possible to reduce the level of porosity through increased sintering. Corker et al.[11] showed that the addition 5 wt.% Cu_2O–PbO sintering aid improved the density of PZT compacts sintered at 710 °C. The same level of the Cu_2O–PbO sintering aid was later incorporated into a composite slurry to produce thick films (> 15 μm).[12] The resultant films exhibited a density gradient (higher density closer to substrate) with a relative permittivity and d_{33} of approximately 680 and 52 pC/N respectively.

The aim of this work was to combine these two approaches to improved sintering and so produce thick composite films with improved structural homogeneity and electrical properties. It is envisaged that this combined approach will also significantly reduce the shrinkage on sintering and hence the stresses generated within the constrained film.

The work examined the variation in relative permittivity and piezoelectric properties of 10 μm thick hard doped PZT composite films with increasing levels of sol infiltration and the addition of 4.7 wt.% (the actual amount added by Corker et al.[12]) Cu_2O–PbO sintering aid. A high powder loading (1.5 g PZT/ml of sol) was selected to maximise the ferroelectric properties of the thick film and the thickness of the deposited layers. Repeated sol infiltration and pyrolysis of the individual composite layers was then conducted in an attempt to maximise the dielectric properties of the film. The variation in the film properties was recorded as a function of sol infiltration.

2. Experimental procedure

2.1. Composite slurry production

A hard doped PZT [$Pb_{1.05}(Zr_{0.46}Ti_{0.48}Nb_{0.02}Sb_{0.02}Mn_{0.02})O_3$] sol was produced using the route described in Fig. 1.[12] A composite slurry was then made by mixing the PZT producing sol with a hard doped PZT powder (mean diameter 0.5 μm, Ferroperm PZ26) to produce a powder loading of 1.5 g/ml. 2 wt.% (relative to the PZT powder mass) of a dispersant (Kenrich Petrochemicals, KR55) was also added to ensure thorough dispersion of the PZT powder. To examine the effect of sintering aid addition 4.7 wt.% (relative to the PZT powder mass) of sintering aid (0.2 CuO_2–0.8 PbO)[11,12] was added to the slurry. Prior to use, the slurry was ball milled for 24 h to ensure thorough mixing of all of the constituent parts.

2.2. Spin coating and infiltration

The PZT thick films were deposited onto platinised silicon wafers (Pt/Ti/SiO₂/Si). Prior to coating the wafers were cleaned in acetone, followed by isopropanol and finally any residual organics were removed using a plasma etching process in a 20% oxygen–80% argon atmosphere (Polaron PT7160 RF plasma barrel etcher, 13.56 MHz, 3 min @ 12 W power). The PZT thick films were built up by depositing a series of layers. Each layer consisted of an initial composite layer which was deposited by covering the entire wafer surface with the composite slurry and then spinning at 2000 rpm for 30 s. The layer was then subjected to a heat treatment (200 °C/60 s and 450 °C/15 s) designed to remove the organic component and crystallise the sol. Various numbers of sol infiltrations were then conducted ensuring that each sol treatment was subjected to an identical spinning and firing regime before the next sol treatment was applied. Once the required number of layers had been deposited the wafer was subjected to a rapid thermal annealing process (710 °C/30 min) designed to

develop the perovskite structure. The nomenclature adopted during this study describes the deposition treatments such that (C+2S)4 relates to a sample made up of four layers where each layer was composed of one composite layer with two sol infiltration steps.

2.3. Electrical measurements

Prior to the deposition of electrodes the crystalline state of the samples was assessed using X-ray diffraction (Siemens D-5005). Circular Cr–Au electrodes were evaporated onto the surface of the PZT films for electrical measurements. Contact was made with the back electrode by removing a small section of PZT by mechanical abrasion. Capacitance measurements between the back electrode and Cr–Au top electrodes were made using a Wayne Kerr precision component analyser 6425 at 1 kHz. The thickness of the films was determined from optical microscopy and SEM observations of cross-sectional fracture surfaces. Values of thickness and capacitance were then used to calculate the relative permittivity.

The thick films were poled at 200 °C for 5 min using a field of 8 V/μm. The piezoelectric coefficient d_{33} was measured using a piezometer (TakeControl PM25).

3. Results and discussion

3.1. Dielectric constant

XRD analysis of the films following the 710 °C treatment showed the films to be composed only of perovskite phase PZT. Figs. 2 and 3 show the variation in relative permittivity and dielectric loss for films produced using the (C+XS)4 procedure where X was varied between 0 and 4. It can be seen that the relative permittivity is increased by both sol infiltration and the addition of sintering aid. Dielectric loss decreases slightly with increased sol infiltration but is largely independent of the presence of sintering aid.

Samples containing the sintering aid exhibit a consistently higher relative permittivity for a given level of sol infiltration. Both sets of results show the same trend with an initially rapid increase in relative permittivity followed by a region of less rapid increase. This difference in the rate of change of relative permittivity is due to the reduced efficiency of the later infiltration stages. Initially the structure is open and the sol is able to infiltrate fully and result in large reductions in pore volume. As the pore size is reduced infiltration becomes more difficult and the degree of pore size reduction becomes smaller. However, the continued increase in relative permittivity indicates that infiltration and pore size reduction is still occurring for all samples. Examination of the fracture surfaces of the two sets of samples (Fig. 4) confirms that the level of porosity is reduced for each

infiltration step. Examination of Fig. 4 also highlights the effect of adding the sintering aid to the composite slurry. It can be seen that the presence of the sintering aid significantly alters the fracture mode. When no sintering aid is present the fracture mode appears to be intergranular as individual grains are clearly visible on the fracture surface (Fig. 4). This indicates that the sol derived PZT phase is relatively weak. However, when sintering aid is added to the composite slurry the fracture mode changes to one that is primarily intragranular where individual grains are no longer discernible. This change in fracture mode is significant when the material strength and mechanical fatigue resistance are to be maximised.

The sol infiltration technique employed in this study leads to a homogenisation of the film structure. Examination of Fig. 5 shows that a graded structure is obtained when no sol infiltration occurs (i.e. density greater closer to the substrate). Corker et al. assumed the graded structure resulted from 'sinking' of the sintering aid. However, inverted sintering experiments produced the same results and it is believed that the graded structure results because sol is drawn from the slurry into the underlying porous composite layer. As the number of layers increases the lower composite layers become further enriched with sol. The bottom composite layer of a four layer structure will effectively be infiltrated three times. The formation of the graded structure is detrimental from a processing point of view because as each new composite layer is deposited the amount of sol drawn from the slurry will increase (due to the increased thickness of porous film). Hence as each successive layer is deposited the composite slurry will become more viscous resulting in thicker layers, poorer surface finish and an increased risk of cracking. By repeatedly infiltrating the structure with sol, prior to the deposition of the next composite layer (to produce a dense layer), it is possible to produce composite films with uniform densities (Fig. 4) and a good surface finish.

3.2. Piezoelectric properties

Fig. 6 shows the variation in piezoelectric strain coefficient d_{33} with different levels of sol infiltration for samples with and without sintering aid. There is a large degree of scatter associated with the results which is primarily due to the sensitivity of the measurement technique to the placement of the probes relative the electrodes. This sensitivity arises because the stress state within the poled part of the film changes if the probes are not located centrally on the electrode. To overcome this problem five electrodes were analysed per sample with each electrode being measured three times. The results shown in Fig. 6 represent the mean value of d_{33} with error bars of 1 standard deviation from the mean.
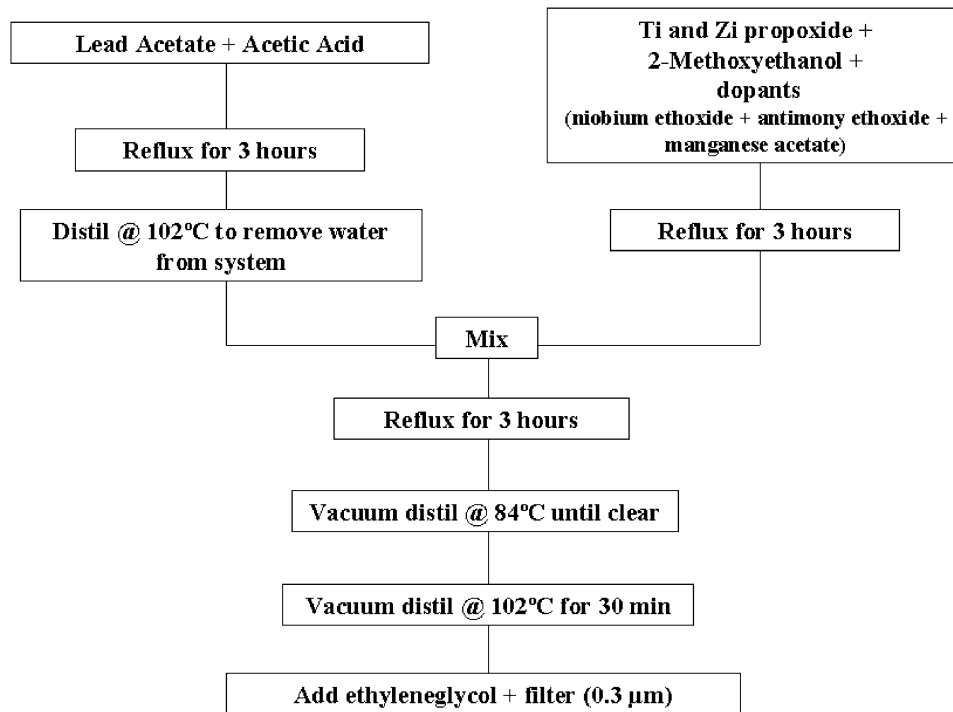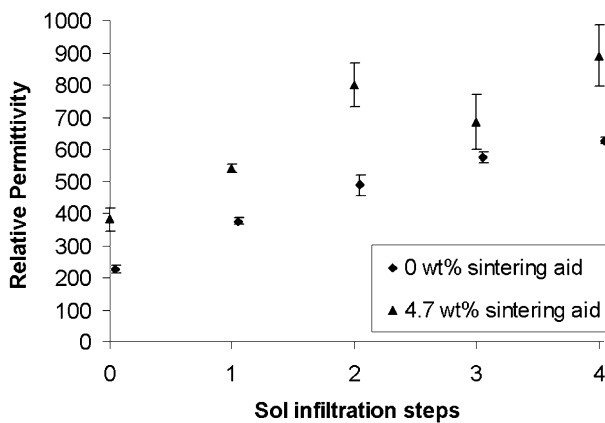
Fig. 1. PZT processing route.

Fig. 2. Variation in mean relative permittivity with increased levels of sol infiltration (C + XS)4 710C30M (error bars represent 1 standard deviation).

Fig. 3. Variation in mean dielectric loss with increased levels of sol infiltration (C+XS)4 710C30M (error bars represent 1 standard deviation).

It can be seen, for the case of films containing sintering aid, that the infiltration of sol does not appear to have a significant effect of the value of d_{33} obtained. The mean value of d_{33} observed is approximately 62 pC/N. However, when no sintering aid is present the value of d_{33} obtained initially is lower ($\sim$35 pC/N) but increases to a plateau value approximately equal to that exhibited by the films containing sintering aid.

Due to the dependence of the piezoelectric properties on the chemistry of the material—in particular the nature and level of dopants—it is not possible to offer a comparison of the results obtained with those found in literature. PZT thin films made using the sol used in this study typically exhibit a d_{33} of approximately 40 pC/N.
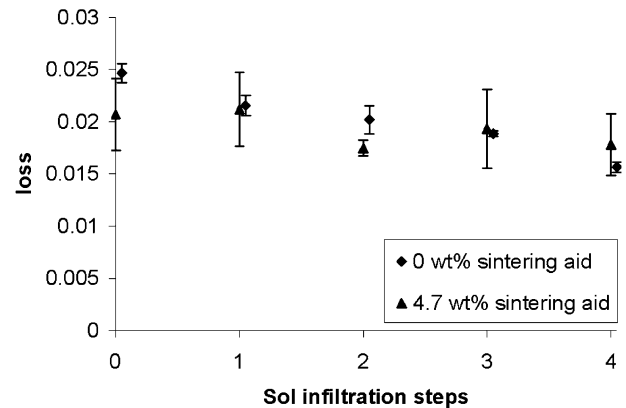
It is also not possible to directly compare values of d_{33} for bulk PZT and thick films due to the substrate clamping stresses which significantly reduce the observed the value of d_{33}.[13,14] However, it is reasonable to assume that the addition of the sol-gel derived PZT will either have no effect ($d_{33\text{sol-gel}} = d_{33\text{ powder}}$) or reduce the value of d_{33} ($d_{33\text{ sol-gel}} < d_{33\text{ powder}}$).[15] This is not observed in practice. Instead the addition of sol-gel derived PZT leads to an increase in the value of d_{33}.

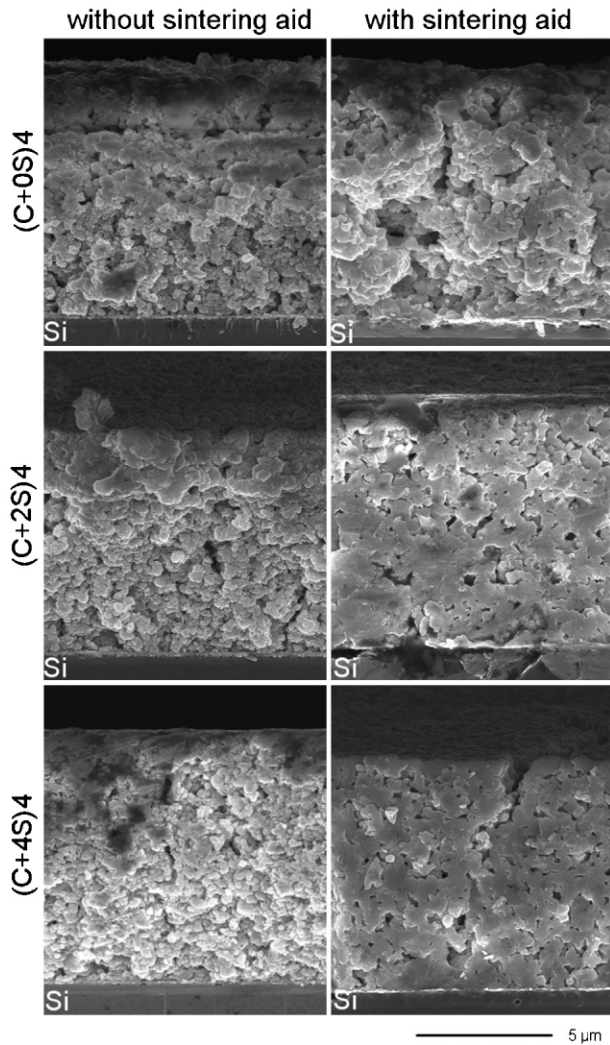An explanation for the observed results could be attributed to the deformation nature of the highly porous

Fig. 4. Fracture surfaces of (C + XS)4 710C30M films produced with and without sintering aid.

material. For films produced with no sol infiltration the structure is very porous and weakly bonded (Figs. 4 and 5). The application of a load could cause the structure to deform such that the resultant crystallographic deformation would not yield a maximum piezoelectric response. Increased levels of sol infiltration would result in a more rigid structure where the applied load would be more likely to result in crystallographic deformation. This change in the deformation mode of the structure could explain the initial low value of d_{33} and the subsequent increase with increasing sol infiltration steps. Samples prepared with 4.7 wt.% sintering aid exhibit a plateau value of d_{33} after fewer infiltration steps because the sintering aid promotes densification.

3.3. Influence of copper

Samples containing the Cu_2O/PbO sintering aid generally exhibit superior properties to the samples without the sintering aid. This is thought to be solely due to the
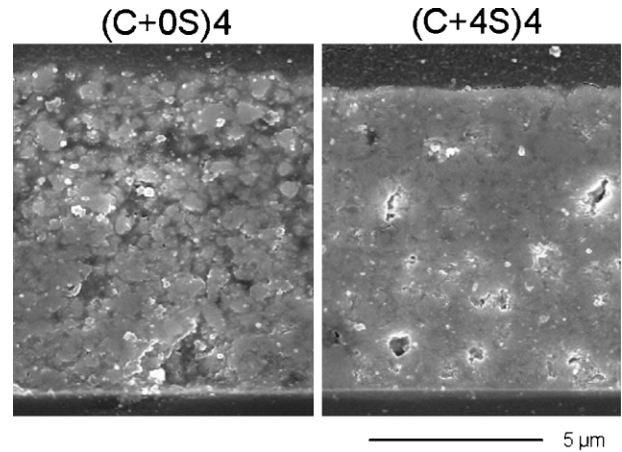

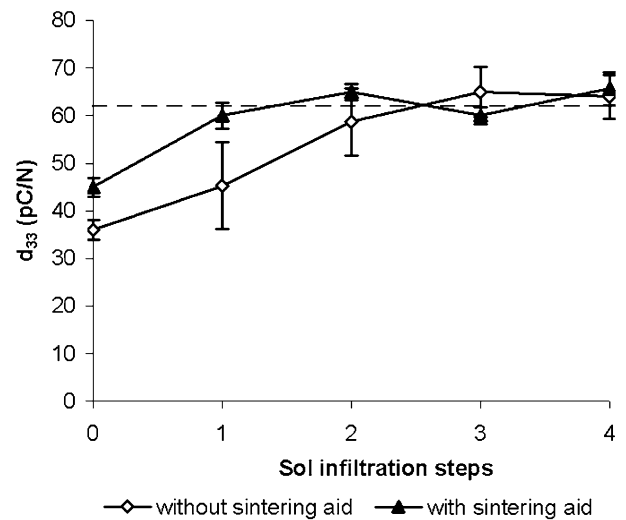Fig. 5. Polished cross sections of (C + 0S)4 and (C + 4S)4 films without sintering aid.

Fig. 6. Effect of sol infiltrations on the piezoelectric strain coefficient (d_{33}).

increased sintering kinetics. The processing temperatures are very low, and are unlikely to result in large scale atomic redistribution/mixing. Hence it is unlikely that the copper would be incorporated into the PZT crystal structure. Due to the extremely low concentration of copper in the system (0.7 at.%) it was not possible to determine its location in the film. Further more, Sugihara and Koyama[16] reported that the doping of PZT with copper lead to a decrease in piezoelectric and dielectric properties which was not observed in this case. Hence is it reasonable to argue that the increased sintering kinetics (and hence final density) are responsible for the improved properties.

4. Conclusion

It has been shown that the incorporation of a series of sol infiltration stages gives rise to an increase in the

relative permittivity. This is primarily due to the reduction in the level of porosity.

Incorporation of 4.7 wt.% $0.2Cu_2O$–$0.8PbO$ sintering aid leads to an additional increase in density and relative permittivity for a given level of sol infiltration.

For thick films produced with 4.7 wt.% sintering aid there was no change in the piezoelectric strain coefficient d_{33} with increased levels of sol infiltration. When no sintering aid was added to the composite slurry the resultant films exhibited an initially low value of d_{33}. This subsequently increased as the structure became more rigid following increasing number of sol infiltrations.

Incorporation of 4.7 wt.% sintering aid into the composite slurry was shown to change the mode of fracture from intergranular to intragranular, indicating a strengthening of the grain boundary phase.

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