PZT 'composite' ferroelectric thick films

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Abstract

Thick-films of lead zirconate titanate ceramic have been fabricated at low-temperature using a modified sol-gel/ceramic powder technology termed the composite technique. In this process, a ferroelectric powder is suspended in an organometallic solution of the same composition, which is deposited either on metallic or platinised silicon substrates using spin-coating. Dielectric properties have been improved from values around 450–680 by incorporating a novel Cu_2O/PbO liquid-phase sintering aid. Rheology studies were carried out to monitor ageing of both the organometallic solution and composite suspension. Over a trial period of 41 days, the organometallic solution was shown to remain stable. Tests further indicated solution stability down to $-20°C$. Such low temperatures may be experienced during transportation in large-scale manufacturing. By modelling such thick films as 0–3 composites, it is known that electric properties are enhanced with greater powder:solution ratio. This necessary greater loading has been achieved by adjusting the pH of the organometallic solution, allowing the zeta-potential developed on suspended particles to be increased. This considerably lowers the viscosity of the composite suspension and hence allows much greater powder loading. In this way, loadings of up to 2.5 g/ml have been achieved. Optimum permittivities and losses in sintered films of up to 680 and 0.01 have been measured on films 16 μm thick, with associated spontaneous polarisation of 19.8 $\mu C/cm^2$ with 1.6 V/μm applied. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is presently a growing commercial interest for miniaturised 'microsystem' piezoelectric[1] and pyroelectric[2] devices. Size reduction is driven predominantly by the demand for improved device performance, reduced manufacturing cost and better response time. Previously, the fabrication of active piezoelectric and pyroelectric elements for such devices has relied on bulk ceramic technology. This requires high temperatures ($> 1200°C$) for ceramic processing and ultimately the ceramic must be cut, lapped and polished down to the required thickness before hybridisation to a silicon IC.[2] The high processing temperatures needed to sinter the ceramic means that the direct deposition of it onto silicon is impossible. For this reason the active ferroelectric layer must be fully processed and only then attached to the device. This type of hybrid process is time-consuming and costly for large-scale manufacture.

Thin and thick film technologies offer many advantages over the use of bulk ceramics in ferroelectric microsystem devices. If much lower temperatures can be used in the fabrication process, then the ferroelectric layer can be deposited directly onto active semiconductor device components. Such low temperatures ($< 500°C$) have been demonstrated for sol-gel PZT thin films.[3] In respect to thick films, firing temperatures in the range 450–650°C have been reported.[4,5] However, previous reports including phase impurity analysis,[6] indicate possible pyrochlore contamination unless thermal treatments above 700°C are used. It is important that the chosen thick-film deposition method should allow layers of an appropriate thickness (10–100 μm) and with a surface quality such that further processing is minimised. For thick films (> 15 μm), both tape-casting[7] and screen-printing[8] technologies are widely used for manufacturing but pose problems which limit their applications.

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These techniques frequently rely upon inactive glass frits for densification, which act as low dielectric constant phases in the final film, reducing the dielectric constants and other electrical properties.

Thin film techniques, such as plasma sputter deposition[9,10] and sol-gel spin-coating,[11,12] demonstrate the capability of producing films typically at around 1 μm thickness. However, these are too thin for many actuator applications.

A 'composite' ceramic sol-gel processing technique has been investigated to offer a solution to the problems of low temperature thick-film manufacture. This fabrication process has been reported most comprehensively by Barrow et al.[4,5,13] who has published details on many materials including PZT (58/42: Zr/Ti). The 'composite' process entails mixing a ceramic powder with a sol to form a slurry which can be cast onto the substrate of interest. The process has been applied to a variety of ceramic materials (e.g. piezoelectric ceramics and alumina).

In the work reported here, this technique has been investigated in relation to the lead zirconate titanate $(PbZr_{1-x}Ti_xO_3)$, family of ferroelectrics, commonly known as PZT. These materials are already widely used in ceramic form in many electronic applications due to their exceptionally high piezoelectric and pyroelectric responses. The end applications are varied and depend in part on the region of the phase diagram used. However, the most common commercial devices include stress sensors,[14] actuators,[15] 'uncooled' pyroelectric detectors[16] and infra-red thermal imaging[2] equipment.

The basic principle underlying the conventional 'sol-gel' technique is the formation of a solution of the elements making up the ceramic required in an organic solvent. This is partially hydrolysed to form a stable sol. For this stage, the sol can be polymerized to form a gel, which is then dried and fired to displace the organic components and form an oxide powder which is sintered to make a ceramic. Alternatively, to make a thin film, the sol can be spun down onto a flat substrate. After each layer the film generally undergoes an intermediate heat treatment to remove organic material and onto which subsequent layers can be deposited if required. The final film is subjected to a further annealing at higher temperature to form a dense crystalline layer of the desired phase and thickness.

The 'composite' technique is a simple extension whereby a ferroelectric powder is incorporated into the organo-metallic sol, creating a stable 'composite' suspension. This suspension is then deposited on the substrate. Inclusion of the powder:

(1) Increases viscosity and allows relatively thick layers to be made, increasing deposition rates.

(2) In the case of ferroelectric perovskites, the powder particles act as nucleation centres for further perovskite formation during the final heat treatment.

(3) Allows film density to be increased at low temperatures as the organometallic solution fills voids between the ceramic particles.

(4) Reduces costs as a significant proportion of the film originates from powder rather than organometallic solution. The initial raw material expense is therefore significantly reduced in comparison to using conventional sol-gel processing for the same film thickness.

In comparison to previously reported 'composite' investigations,[4,5,13] the new process reported here introduces several novel aspects:[17]

(a) The composite technique was applied to PZT (50/50: Zr/Ti) with commercial dopants Nb, Sb, Mn–a 'hard' piezoelectric composition known as Pz26. The composition of the PZT organometallic solution was precisely matched to the PZT powder, including the addition of commercial dopants. This feature was introduced to give chemical homogeneity and hence increase electrical response. Previous work has reported the use of powders containing dopants in an undoped PZT sol.

(b) Sintered density was promoted by further introducing a liquid-phase sintering aid[18] into the suspension.

(c) The suspension was stabilised by using a suitable dispersant and a ball-milling procedure under nitrogen.

(d) Sol pH was controlled to reduce the viscosity of the composite slurry, allowing more powder to be suspended for a given viscosity.

Combined, these modifications have resulted in substantial physical and electrical property improvements.

2. Experimental

2.1. Organometallic sol preparation

In general, commercial PZT powders contain a number of dopants. In this work a PZT sol close to the morphotropic phase boundary (approximate 50:50 Zr/Ti) was formed with 5 mol% Pb excess included in the organo-metallic solution to compensate for lead loss during the sintering procedure plus the required dopants as ethoxides or acetates. As the organometallic solution is water sensitive, it was made under 'dry' conditions as follows: Lead acetate was refluxed in acetic acid for 3 h, allowed to cool, distilled to remove water and then transferred to storage under dry conditions. Separately, zirconium propoxide (70 wt.% solution in 1-propanol, Aldrich), titanium isopropoxide (99.999%, Aldrich, with further inhouse purification), manganese acetate (98% purity, Aldrich), antimony ethoxide (99.99% Inorgtech), niobium acetate (99.99% Inorgtech) were mixed in 2ME (2-methoxyethanol) in the appropriate molar proportions, refluxed and then cooled. Both solutions were mixed under nitrogen and further refluxed for 2 h.

2.2. Organometallic solution modification

In previous reports,[4,13] the viscosity of the 'composite' suspended fluid is controlled by the weight percentage of ceramic powder to solution used, plus the optional use of additives such as ethylene glycol. A novel feature of this report is the control of the 'composite' viscosity through the chemistry of the organo-metallic solution. Whilst maintaining the molar concentration, further distillation and simultaneous addition of 2ME can be used to change both the viscosity of the solution and the final pH. The variation in pH will result in a different zeta-potential being developed on the surfaces of the suspended ceramic particles. This in turn can be used to alter the electrostatic forces between particles and hence control the viscosity, allowing an increased powder loading (i.e. ceramic powder: organo-metallic solution) to be achieved for a given viscosity.

The optimum conditions for slurry formation were investigated by varying the pH whilst monitoring the resultant 'composite' viscosity. The pH was varied between 2 and 9 by the addition of acetic acid. To monitor the relative effect of powder loading on these optimum conditions, this procedure was carried out with first 1.5 and then 2 g of PZT ferroelectric powder for every 1 ml of metal-organic solution.

The pH modification used in this work was carried out by distilling the organometallic solution prepared in Section 2.1. The temperature was increased slowly to around 84°C to remove alcohol and then finally raised to 104°C to remove any traces of water. The combined volume of removed fluid was then replaced by adding 2ME to maintain PZT molar concentration. By varying the length of this distillation process, this 2ME:acetic acid solvent ratio could be altered. The respective pH was changed from around 5 to 7.5. After final cool down the solution was filtered with a 0.2 μm filter and then ethylene glycol ($HOCH_2CH_2OH$) added to increase slurry stability.

2.3. Fabrication of composite/sol mixture

Suspensions created by ultrasonic mixing were found to be unstable. Ball-milling was found to produce a dispersed powder with high powder loading and good stability. In this procedure, the PZT powder known as Pz26, further known as Ex 2694-D1, was supplied by Ferroperm Ltd, Denmark. On arrival, the ceramic powder was first dried in a vacuum oven to remove moisture. The ceramic powder and water-sensitive organo-metallic solution were sealed in a glass bottle under a nitrogen atmosphere and ball-milled with the 'dry' dispersant KR55 (Ken-React Lica 38, isopropanol isooctyl alcohol). Good quality films were achieved consistently for powder loading levels 1.5 g powder: 1 ml sol and 2 g powder : 1 ml sol. However, a stabilised suspension was achieved up to 2.5 g:1 ml. Electrical measurements were conducted on films made from the 1.5 g: 1 ml suspensions.

To aid densification, a liquid-phase sintering aid was also included during the ball milling procedure. Acceleration of densification and decreasing the required sintering temperature of commercial ceramics by the use of liquid-phase sintering aids have been reported on several occasions[19–21] and are sometimes used in large-scale PZT ceramic manufacture. However, the inclusion of liquid-phase sintering aids to 'composite' thick films is novel. For these investigations the sintering aid was a mixture 1 Cu_2O: 4 PbO[18,22] which has low eutectic temperature of 680°C. This was included at 5 wt.% in relation to the weight of PZT powder loaded into the solution.

2.4. Deposition onto substrate

Numerous substrate materials were investigated including KOVAR (Glass sealing alloy — Fe54/Ni29/Co17 manufactured by Goodfellows), steels (grades 304, 309 & 430 manufactured by Arvesta Precision, Sheffield), platinised alumina (supplied by the University of Oulu, Finland) and platinised silicon [150 nmPt/40 nmTi/500 nmSiO$_3$/Si < 100 > , Radiant Technologies Inc]. The last two substrates exhibited excellent substrate-film adhesion and electrical properties. KOVAR demonstrated the best substrate properties of all the alloys investigated. Thermal mismatch between the substrate and films is minimised and as the alloy is oxidation resistant, it could be fired without significant deterioration of electrical properties due to the formation of interfacial oxide layers.

The substrate cleaning procedure used prior to film deposition was found to greatly affect the adhesion of the PZT films. Substrates used in this report were therefore methodically cleaned using the following steps. After initial spraying with degreaser Volasil440, the substrates were completely immersed in this degreaser and ultrasonicated for 15 min. Followed by a further 15 min ultra-sonication in isopropanol (IPA), any visible residue was removed by washing in high purity IPA (Analar grade). The substrates were then column cleaned in which they were held in refluxing IPA for around 30 min. Cleaned substrates were kept in clean room conditions prior to film deposition.

Spin-coating was used to deposit the composite slurry onto both KOVAR and platinised silicon substrates. The slurry was dripped onto the substrates using a plastic pipette such that a large proportion of the substrate surface was covered. The substrate was then spun at 2000 rpm for 25 s. Intermediate firing was conducted by placing the substrate on a hot-plate at 450°C for 15 s. Sufficient organic material was removed for a stable solid layer to be formed. This allowed further layers to

be deposited. After each successive layer, the films were fired for 15 seconds until a desired thickness was achieved. The thickness of each layer is dependent on powder loading and substrate, although typically each layer increases the film thickness by 2/3 μm. Films in the range 8–40 μm were produced with electrical properties investigated for films of 16 μm.

After deposition, the films were fired to increase density and to form the crystalline perovskite PZT phase. Typically, sol gel ferroelectric thin films are fired for times of the order of 1 min. However, densification through the use of sintering aids relies on a slower sintering process, i.e. by capillary forces and grain re-orientation, and hence requires prolonged firing periods. In these investigations, it was found that optimised film properties were achieved with sintering times of 30–45 min, which is comparable to those of bulk ceramics. Sintering was carried out using an AG210 rapid-thermal annealer (RTA). A sintering temperature of 710 °C was used under an atmosphere of argon. This atmosphere was found beneficial specifically for those films deposited on KOVAR.

2.5. Characterisation

2.5.1. Organometallic solution and composite ageing

It is important that any fabrication process optimised may be easily adapted for large-scale manufacture. For this consideration the ageing and stability characteristics of both the sol and composite suspension were considered. The organometallic solution was characterised by viscosity and particle size measurements. As the ageing process begins, usually through contamination by water, the solution can become viscous via the formation of large molecular clusters or chains. The relative sensitivity of a newly formed solution was therefore monitored over a 41-day period using a Gilmont Instruments falling ball viscometer. Simultaneously the formation of large molecular clusters were monitored using a Malvern 3000 Zetasizer with external 0.5W Ar-ion laser and a minimum particle size resolution of approximately 3nm.

Once the composite is opened to the air, not only will polymerisation take place, but also evaporation of the solvents. This second factor again can cause problems as even within a short period the viscosity may increase from vapour loss resulting in inconsistency in film reproduction. To characterise this effect, viscosity measurements were carried once more but this time with a Bohlin Instruments parallel-plate viscometer in an air atmosphere. The suspensions were tested upon opening the composite suspension to the atmosphere and then periodically over one hour.

2.6. Ceramic film characterisation

To observe the film microstructure, several samples were cross-sectioned and mounted in resin for analysis using a Cambridge 250 SEM. Surface roughness measurements were made using an Digital Instruments 3000 (AFM) atomic force microscope. X-ray diffraction (XRD) was used to determine the phase-purity and crystallinity of the lead zirconate titanate phase. This was carried out on a Siemens D5005 X-ray diffractometer using CuK_α radiation with a step size of 0.01° and a time/step of 5 s.

Circular gold-chrome electrodes (2 mm diameter) were deposited by vacuum evaporation on each film surface for electrical assessment. Dielectric constant and loss values were measured using a GenRad 1689M RLC Digibridge while P-E hysteresis loop measurements were carried out using a Radiant Technology RT66A hysteresis test unit. Piezoelectric measurements of d_{33} were taken from poled films using a Take Control Piezometer System. Poling was carried out in air at 4V μm^{-1} for 2 min at 90 °C. Prior to measurements, all films were electrically discharged in a drying oven at 65 °C for 30 min.

3. Results

3.1. Optimum pH modification

Fig. 1 depicts the change in viscosity of two composite suspensions with pH variation. It can be seen from these results that the maximum viscosity occurs at a pH of around 5 and that this appears to be independent of the powder loading used. The maximum is the isoelectric point at which the zeta potential on the suspended particles is at a minimum. Away from this point, a surface potential develops on the particle surface that results in repulsive electrostatic forces, reducing flocculation and hence reducing viscosity. This in turn allows more powder to be suspended in the solution whilst still maintaining a relatively low viscosity resulting in good spinning quality and increased electrical response as required for these studies.
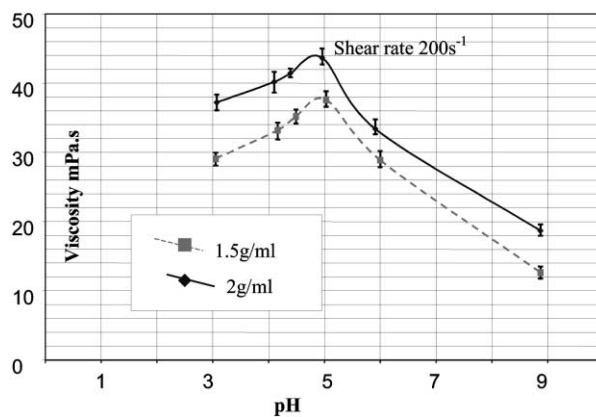

Fig. 1. Depicting the influence of pH on the viscosity of 'composite' powder suspensions.

3.2. Organometallic and composite stability

Table 1 gives the organometallic solution viscosity and particle size of developing molecular clusters, taken over a 41-day period whilst stored under nitrogen. The consistency in values indicates that over the time monitored and within the accuracy of the equipment, the organometallic solution is stable. It is worth noting that viscosity measurements were repeated for an identical organometallic solution that had undergone prolonged low-temperature storage at −20°C. Even when held for up to two weeks, no precipitation or crystallisation could be observed. From an industrial point of view, this temperature stability is important for both storage and transportation.

Viscosity measurements taken on the 'composite' suspension, rather than the pure metal organic solution, indicated that over the time period investigated, the viscosity remained almost constant showing an increase of only 5% after being opened to the atmosphere for over an hour with an average value of around 5×10^{-2} Pa.s (shear rate 20 s^{-1}).

3.3. Film structural analysis

Fig. 2 depicts a SEM cross-section of a typical film with approximate thickness of 18–20 μm. The platinum substrate appears on the left side of the figure. Both

Table 1
Ageing: viscosity of organometalic Pz26 solution and molecular cluster size over time

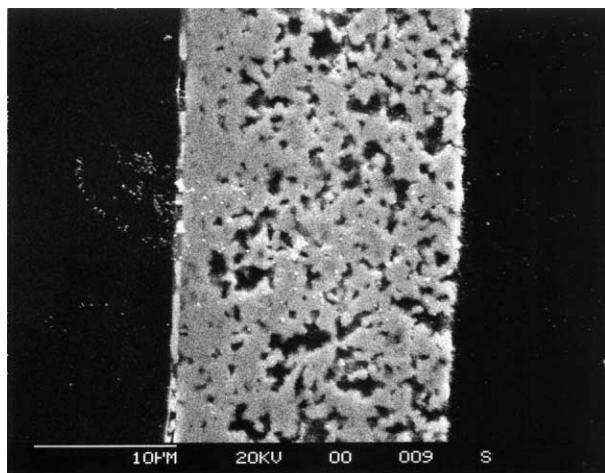| Age of solution	2 Days	5 Days	9 Days	32 Days	41 Days
Viscosity (cP)	4.198	4.197	4.196	4.191	4.181
Particle size (nm)	< 3	< 3	< 3	< 3	< 3

Fig. 2. SEM cross-section of Pz26 'composite' film with 5 wt.% sintering aid fired on platinised silicon.

microstructure and film surface quality (Ra < 200 nm confirmed by atomic force microscopy) can be observed.

It is interesting to note that all films exhibited a greater density near to the substrate in comparison to the surface. This feature is emphasised in Fig. 3(a) and (b) in which greater magnification has been used. A further magnification is shown in Fig. 4, where individual PZT grains can be observed ranging from 40 nm. As the particle analysis of the original suspended ferroelectric powder has a typical grain size of 1.6 μm, it is
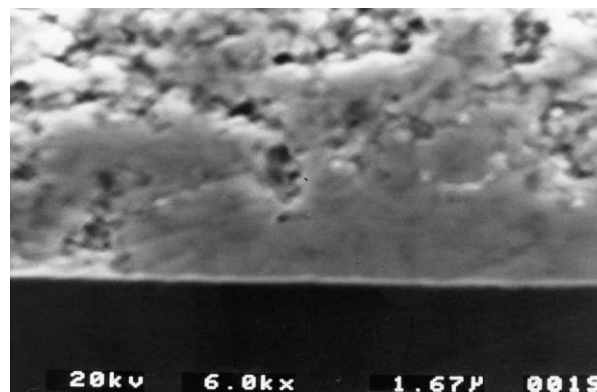
(a)
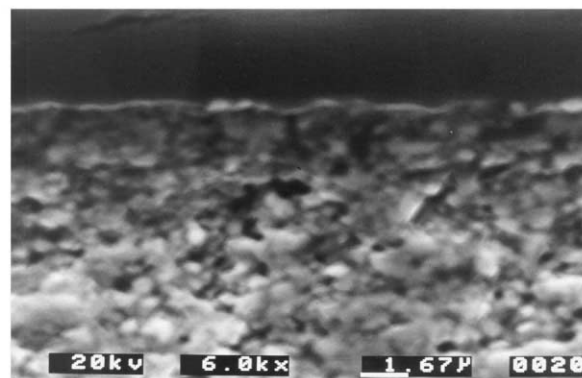
(b)

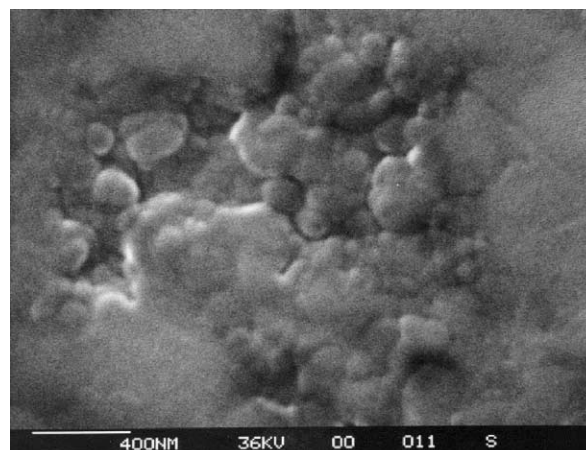Fig. 3. (a) High film density found close to the substrate surface. (b) Porous microstructure close to film surface.

Fig. 4. High magnification of 'composite' film cross-section.

expected that these very small grains originate from the metal-organic solution.

Fig. 5 shows the X-ray diffraction profiles of a PZT thick film fired at 710°C with platinised silicon substrate. All peaks can be indexed for the expected tetragonal perovskite structure. Peak width is broad due to poor crystallinity achieved when firing at such low temperatures but peak splitting of the (2,0,0) is clearly visible. Impurity phases, such as pyrochlore, were not indicated by any additional reflections in the diffraction profile.

3.3.1. Film electrical analysis

Dielectric constants of up to 500 and dielectric losses of around 2% were measured on films incorporating 5 wt.% sintering aid, deposited on KOVAR. Dielectric constants for similar films deposited on Pt/Ti coated silicon were larger. On the best samples, dielectric constants of up to 700 were measured with a decreased dielectric loss of around 1%, although dielectric constant values of 680 were more usual. For films without sintering aid, optimum dielectric constants of around 450 were observed.

Pt/Ti coated silicon would be expected to give a higher dielectric constant as this choice of substrate eliminates the lossy interfacial oxide layers that form on the KOVAR during sintering. However, the flexibility of using a metallic substrate such as KOVAR may have mechanical advantages for certain applications.

P–E hysteresis loops were detected on PZT films prior to final sintering. This indicates that intermediate firing at temperatures as low as 450°C are sufficient for crystallisation of the correct ferroelectric tetragonal PZT perovskite structure. A typical hysteresis loop for a composite film with 5 wt.% sintering aid, fired at 710°C, 16 μm thick film deposited on platinised silicon is shown in Fig. 6. A typical spontaneous polarisation of 19.76 μC/cm^2 was observed at a field of 1.6 V/μm. Measurements over the area of a 6.3 cm^2 film show a dielectric constant variation of ±5%. It should be noted that films of this limited size were prepared due to convenience only and that larger films were successfully produced
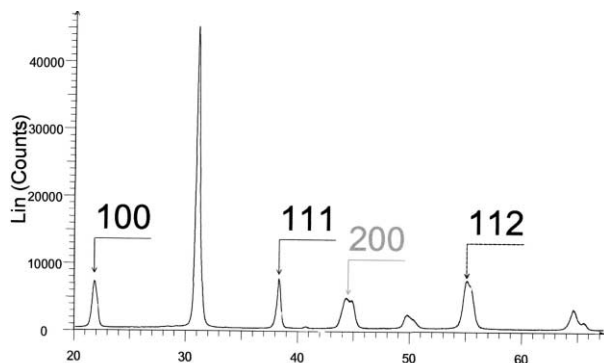

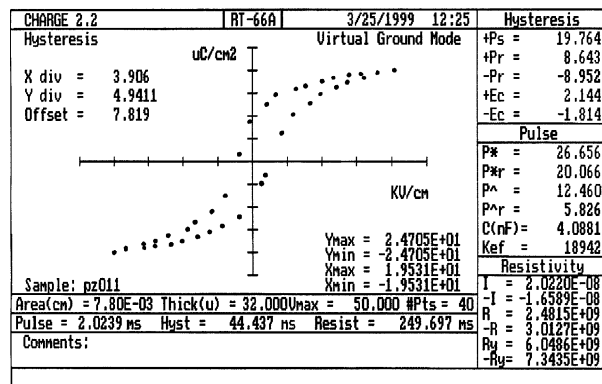Fig. 5. XRD of composite film fired at 710°C on platinised silicon.

Fig. 6. Hysteresis loop using 1.6 V/μm on a 16 μm composite film with 5 wt.% sintering aid, deposited on platinised silicon substrate.

on 4 inch wafers without difficulty. The piezoelectric response was measured on a number of 20 μm films and gave a reproducible d_{33} coefficient of −50 pCN^{-1}.

4. Discussion

A number of novel thick film fabrication modifications have been presented. Thick films have been successfully realised between 10 and 45 μm and covering substrates up to 4 in diameter. Of all novel features, the improvement seen when a liquid-phase sintering aid is introduced is by far the most important. Electrical response increases substantially on its addition due to the increased densification obtained. The extent of porosity that is still present is seen most clearly in the dielectric response rather than piezoelectric response. The electrical 'response' deterioration in comparison to bulk ceramics is therefore application specific.

Electrical response of these films is still substantial lower than in bulk ceramic. Nevertheless exhibited properties are still considered of industrial use and are encouraging considering the lower density of 'composite' films in comparison to bulk ceramic, and also the presence of a second-phase in the form of the sintering aid.

The addition of this sintering aid requires careful consideration. Although the increase in density is hard to quantify accurately, the observed density increase from its incorporation leads to a respective increase in dielectric constant from 450 to almost 700. The main problem seen in trials was over processing. If ball-milled too aggressively, the sintering aid constituent PbO can transform from the orthorhombic to tetragonal phase. Although this second phase is known to be highly reactive, this sintering aid composition relies on a eutectic observed in the phase diagram of orthorhombic PbO–Cu$_2$O, not tetragonal PbO–Cu$_2$O. Furthermore, for an optimised effect the sintering aid should remain in localised regions throughout the sintered film. Prolonged mixing can result in forming a continuous conducting

network through the microstructure that can again reduce film properties.

The variation in density between the film near the substrate and surface needs to be addressed. If a greater consistency is achieved, the film properties will be improved. Investigations which may increase the density and which are related to the sintering aid are:

1. The prevention of sintering aid sinking during the final firing procedure.
2. Modification of PZT particle size distribution suspended in solution.
3. Optimisation of the mixing procedure of the sintering aid throughout the composite to achieve maximum sintering aid properties with minimum wt.% additive.

Many other fabrication details may also prove beneficial with little increase in related production time. For instance, film encapsulation during the sintering procedure may prevent lead loss, particularly near the film surface. A further stage of the process that may have a large impact on the final porosity is the intermediate firing stage. In the hope of minimising processing time, this drying/firing stage was limited to 15 s. Although within this time period a stable solid layer is formed, substantial organic material remains. If not released at this drying stage, this organic material will be released later as vapour in the sintering stage. While the sintering aid is attempting to 'pull' the microstructure into a denser configuration, it is possible that the simultaneous release of vapour is 'pushing' the microstructure apart and hence is responsible for the continued porosity. This would also support the observation that high density is seen nearer the film substrate as lower layers would go through many cycles of intermediate firing. However, other factors such as Pb loss would also result in the same density variations.

An interesting aspect of this investigation is the use of pH modification to control viscosity. Alteration of the zeta potential has long been known to affect suspension stability and is used commercially, for instance in the coatings industry to optimise tape casting slurries.[23] However, the magnitude of its affect in relation to producing composite suspensions is completely novel for techniques such as spin-coating. However, the specific results reported in this study are highly process dependant. The maximum viscosity that is observed at a pH of 5 (the isoelectric point) is not representative of typical PZT. When dispersants are used, it is the interaction of these surface coatings that are being so dramatically altered by the pH modifications, not the PZT–PZT particle interaction directly. Optimised processing conditions must therefore be re-examined if either the solvents or dispersants are changed.

Acknowledgements

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