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Micromoulding of lead zirconate titanate (PZT) structures for MEMS

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Abstract Thick (>10 μm) ceramic structures for applications in micro-electromechanically systems are typically fabricated using screen printing techniques or by printing a continuous film and subsequently etching the structure. This work presents a thick film lift off technique to create high aspect ratio thick Lead Zirconate Titanate (PZT) features on silicon substrates. In this technique, a photoresist material is used to produce a mould, on a silicon substrate, and so define the shape of structures to be created. A composite sol gel ink (mixture of ceramic powder and sol) is then cast into the polymeric moulds and heat treated at low temperature (<250°C) to dry the ink. The use of these low temperatures means that the polymeric mould maintains its shape whilst still allowing the sol to be converted to an amorphous ceramic precursor. Subsequent deposition of further composite sol gel ink can then be used to increase the thickness of the features. The density of the structures can also be increased through the use of repeated sol infiltrations once the structure has been created. A final heat treatment is used to remove the polymeric moulds and crystallise the ceramic material.

Keywords Ceramics · PZT · MEMS · Micromoulding

1 Introduction

Dense, crack-free piezoelectric thick films can be integrated with silicon substrates and used for many MEMS applications [1, 2]. One such application of micro-machined silicon wafers with integrated piezoelectric thick films is in the field of ultrasonic transducers for medical imaging and non destructive testing [3]. Films, 30–50 μm thick, have potential application as high frequency (>20 MHz) ultrasonic transducers if they can be structured to produce high aspect ratio features capable of resonating in the thickness direction [4].

Thick ceramic structures, for MEMS applications, are typically fabricated using screen printing techniques or by depositing a continuous film and subsequently etching the structure. However, isotropic etching of ceramic films can lead to sloping side walls and limited resolution. Conversely, the resolution of screen printing is limited to between 25 and 100 μm due to the construction of the mesh and ability to accurately deposit multiple layers on top of each other. In addition to these issues, thick film technologies tend to produce films with low density and so require temperatures higher than 850°C for adequate densification of the particles to occur. During such high temperature processing the multi-material MEMS structures can be damaged. A lower temperature sintering route (<720°C) can be achieved while maintaining the film thickness by using a composite sol–gel method in conjunction with spin coating to build up the layer thicknesses [5–7]. This composite sol–gel method is preferred due to the reduced temperature of processing and the compositional control that it offers. As with conventional thick film processing, the composite sol gel route can be used to produce structured thick features by etching or screen printing [3]. However, similar limitations in resolution and feature shape are still observed. One potential route to overcome this limitation is to use a moulding process where the size and shape of the features is dictated by the photolithographic process used to create the polymer photoresist moulds.

This paper highlights the work used to produce PZT features using micromoulding where lead zirconate titanate

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(PZT) free standing ceramic structures have been produced by casting a composite sol gel slurry into polymeric micromoulds created using UV photolithography.

2 Experimental procedure

The PZT sol was synthesized from lead acetate trihydrate (Fisher), zirconium isopropoxide (Sigma Aldridge), titanium propoxide (Sigma Aldridge), using a sol–gel method, as described in Fig. 1. The final concentration of the sol solution was 0.4 M on addition of acetic acid and 1-propanol. A composite sol gel slurry was then made by mixing commercial PZT powders (Ferroperm PZ26, mean diameter 0.5 μm) with the PZT sol to form a slurry with a power loading of 1.5 g of powder per ml of sol with 1wt% (relative to PZT powder) of KR55 (Kenrich Petrochemicals) dispersant added to stabilise the slurry. The composite slurry was then ball milled for 24 h to ensure thorough mixing of the individual components in the slurry.

The polymeric micromoulds were produced by spinning a 12 μm thick layer of photoresist (AZ4562-Clariant) onto a silicon wafer at 1,000 rpm for 60 s. The photoresist material was then dried at 90°C for 3 min prior to UV exposure for 45 s. After UV exposure the photoresist material was developed using AZ351B developer (Clariant) in a 1 to 4 ratio in deionised water. After development the micromoulds were baked at 90°C for 1 min to ensure thorough drying.

There exist two conflicting requirements for the production of PZT features using the micromoulding process. On the one hand the polymeric micromoulds have a limited temperature capability above which the photoresist material will begin to degrade and disrupt the shape of the micromoulds. Conversely, it is desirable to process the ceramic material at a high temperature in order to maximise

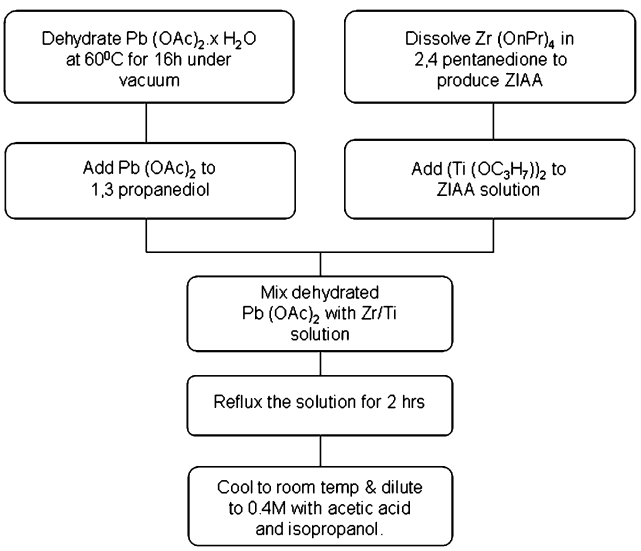

Fig. 1 Flow chart showing the sol preparation route

Table 1 Summary of processing conditions used to produce PZT microfeatures.

	Photoresist pre-treatment (°C)	Drying (°C)	Sintering configuration
1	90	Room temperature	Face down
2	90	250	Face down
3	250	Room temperature	Face down
4	250	250	Face down
5	90	250	Face up
6	250	250	Face up

the decomposition of the sol gel material during intermediate drying stages so that the green density of the features can be maximised prior to the final high temperature densification stage. To determine the maximum stability of the photoresist material samples of exposed and developed photoresist were heated to the following temperatures: 100, 150, 200, 250, 300, 350, 400°C.

Once a suitable processing window had been determined photoresist micromoulds were produced on a silicon substrate using UV photolithography. The substrate/micromoulds were coated with the composite slurry and the excess removed by spinning the substrate/micromoulds at 2,000 rpm for 60 s. The slurry was then dried prior to the repeating the process to build up the layer thickness. The dried slurry film was approximately 2.5 μm thick per layer. Two sol infiltrations, with intermediate drying, were conducted in order to increase the final density of the PZT structures prior to sintering. PZT films were sintered at 650°C for 30 min in a box furnace using a ramp rate of 3°C/min and furnace cooling.

Different photoresist pretreatments, drying and sintering configurations were examined to determine the optimum processing conditions to achieve highly defined samples. Two hundred fifty degree Celsius was determined to be the maximum temperature that the photoresist could withstand without the mould shape degrading. Face down sintering (features in underside of suspended wafer) was selected as a sintering configuration to ensure that unwanted PZT material would drop away from the substrate. Table 1 summarises the processing conditions used.

3 Results and discussions

3.1 Thermal stability of photoresist material, AZ4562

From the study it was found that the photoresist material survived heat treatment up to 250°C, with significant cracking of the photoresist micromoulds occurring at temperatures greater than 400°C (Fig. 2). It is evident that shape of the

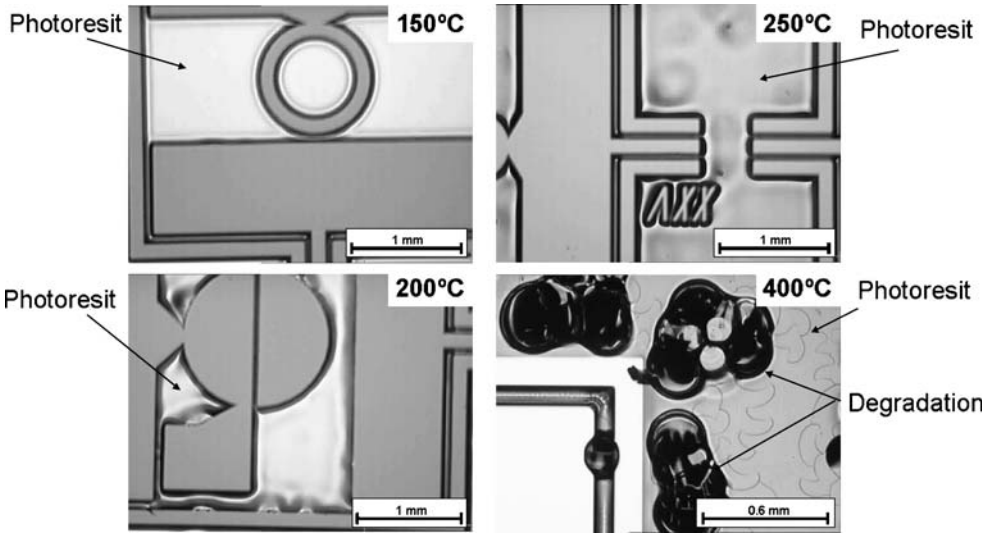

Fig. 2 Light micrographs of photoresist micromoulds after heat treatments at 150, 200, 250 and 400°C

micromoulds has been retained after heat treatment at 150°C. Heat treatments at 200 and 250°C appear to show some degree of deformation as evidences by the appearance of dark fringes on the light micrographs. However, examination of a SEM micrograph (Fig. 3) and measurement of the height of micromoulds after heat treatment at 250°C indicate that there is only a minimal shape change (<5% shrinkage). Comparison of the samples treated at 200 and 250°C shows there to be change in the colour of the photoresist material with a darker colour evident after heat treatment at 250°C. Such a change in colour indicates that the photoresist has undergone a chemical change which is confirmed by a reduced solubility (in acetone and propanol) of the 250°C treated photoresist. Heat treating at 250, 300, or 350°C produced no appreciable change in the appearance of the photoresist. Heat treatment above 400°C results in large scale decomposition of the micromould shape as can be seen by the bubbling of the micromoulds.

From the characterisation study of the photoresist material it was found the micromoulds treated at 200°C and below exhibited a degree of solubility in the sol used to create the composite slurry. For this reason it was decided to examine the effect of pre-treatment at 250°C as a method of preserving mould shape during casting.

3.2 Characterisation of the PZT deposited film

Figure 4 shows an SEM micrograph of micromoulds coated with PZT and dried at 250°C but prior to the pyrolysis and crystallisation steps. At this stage the whole wafer is coated with PZT but it can be observed that the filled shapes of the micromoulds are visible as flat uncracked regions which show good adhesion to the substrate. The PZT is shown to be partially released around the micromould shape due to poor adhesion of the PZT material to the photoresist.

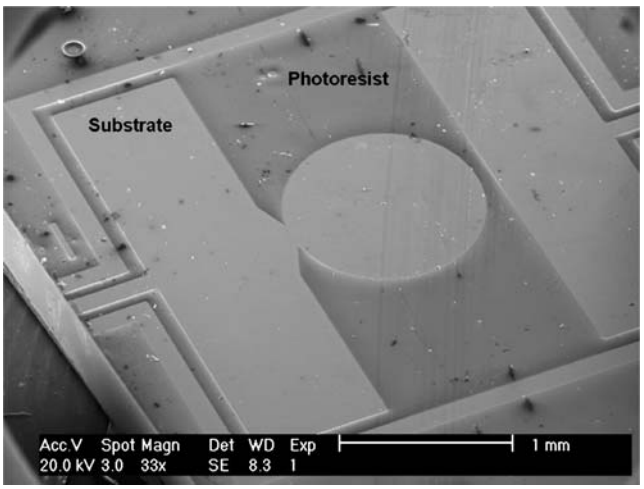

Fig. 3 SEM micrograph of photoresist micromould after heat treatment at 250°C showing clear retention of mould shape

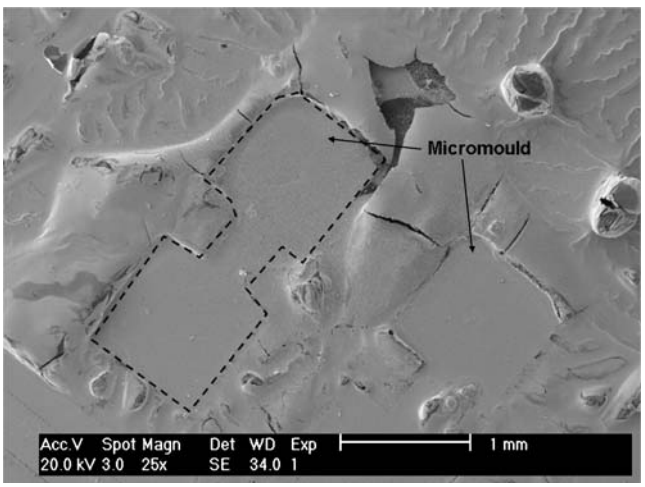

Fig. 4 SEM micrograph of micromoulds filled wit PZT dried at 250°C before pyrolysis and crystallisation

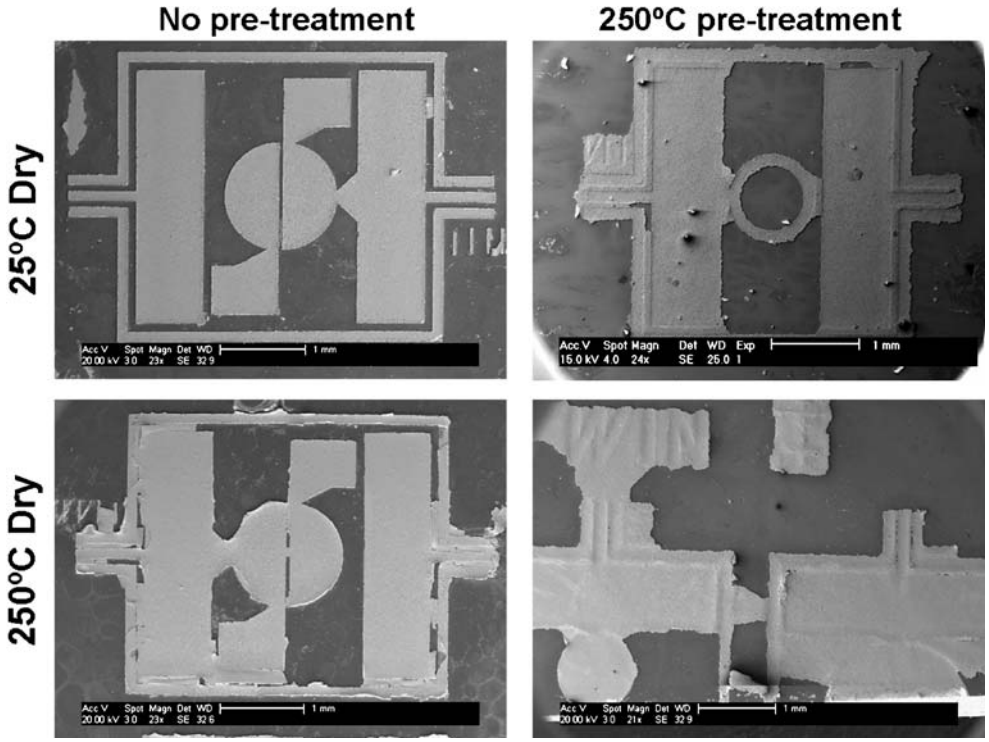

Fig. 5 SEM micrographs showing a comparison of the effect of 250°C pre-treatments and drying on the final features

Figure 5 shows a comparison between the final shapes achieved with the different photoresist pre-treatments and drying treatments. It can be seen that the best features are achieved when neither a pre-treatment nor high temperature drying are used during the processing of the PZT features. The edge definition and resolution decrease when 250°C drying is employed which can be seen in Fig. 5 by the residue material between the moulds positioned close to each other. Further degradation in edge definition and resolution are observed when a 250°C pre-treatment is employed with the worst performance being observed for samples employing both a pre-treatment and a drying stage at 250°C.

The effect of sample orientation during mould burnout/sintering can be seen in Fig. 6. When the structures are sintered face down excess material is able to fall away from the wafer thus ensuring a relatively clean substrate where no PZT is required. When the sample is sintered face up a greater amount of residual PZT is observed on the substrate away from the features. This clearly shows the importance of processing the wafer in such a way so as to ensure unwanted material is able to fall away from the substrate. The quality of resultant features was uniform across the wafer so allowing a near 100% yield for optimally processed wafers.

The surface profile of a PZT feature is shown in Fig. 7. The scan was conducted across the three lines at the edge of the features. The three main lines (150 μm wide) are evident and highlighted in the figure. Additional features are also present due to residue remaining on the surface of the wafer as the sample measured was one dried at 250°C. The characteristic 'U' shape profile of the features is an

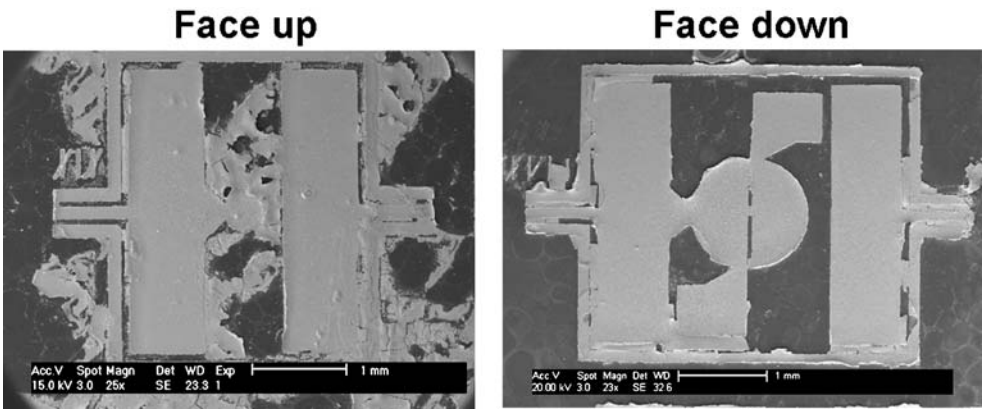

Fig. 6 Comparison of face up and face down processing for features dried at 250°C with no photoresist pre-treatment

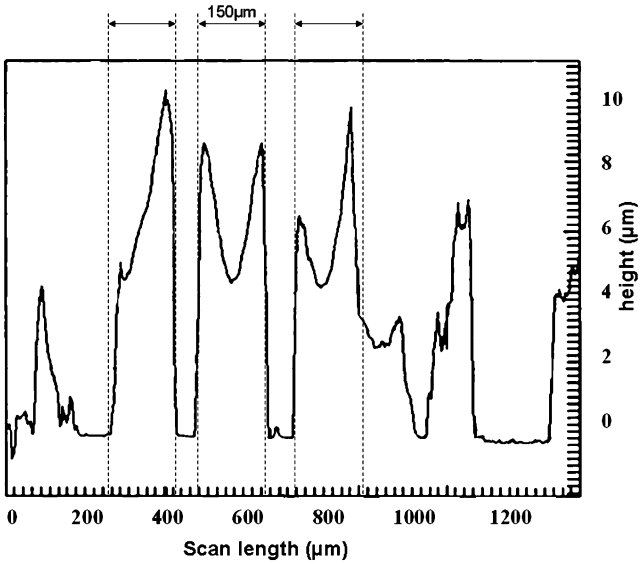

Fig. 7 Surface profile of three micromoulded PZT features after sintering at 650°C for 30 min

artefact of drying and is caused by the shrinkage of the slurry as carrier fluid and fugitive phases are removed. The mould cavity is initially filled completely. As drying proceeds the slurry shrinks but is constrained by the side walls of the mould such that the centre of the feature shrinks to a greater extent than the edges resulting in the characteristic 'U' shape profile. Further layers of slurry would be expected to reduce the severity of this U shape by filling in the trough preferentially.

Figure 7 shows the maximum height of the features to be between 8 and 10 µm which compares with a 12 µm mould depth. There was no PZT edge delamination evident from SEM analysis (Fig. 6) indicating that the curved nature of the features arises purely during drying/pyrolysis. The features produced in this work had a resolution of 50 µm and it is expected that still finer resolution could be obtained with appropriate photomasks for patterning the photoresist.

The X-ray diffraction pattern of the deposited PZT features crystallised at 650°C for 30 min is shown in Fig. 8. At this stage the photoresist material has been burned off leaving only PZT features on the substrate. The XRD plot shows there to be single phase PZT with no evidence of a second phase due to pyrochlore or the sol gel material. An examination of the microstructure of a PZT feature (Fig. 9) shows the PZT structures to have a reasonable relative density with a narrow distribution of particle sizes and uniform packing of particles. The mean relative permittivity of the material was determined to be 178 with a mean loss of 0.03. These values compare well with results obtained in previous work [6] for continuous films with comparable microstructure where the mean relative permittivity and loss were 220 and 0.025 respectively. The previous work has shown that through the use of infiltration stages and a low melting point sintering aid the density can be increased with associated increases in relative permittivity (to ca 900) and decreases in loss (to ca 0.017). This indicates that a similar approach could be used to increase the properties of these micromoulded features. Work is currently underway to examine this.

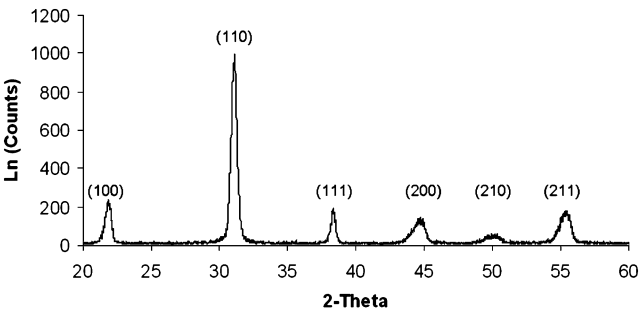

Fig. 8 XRD pattern of a crystallised PZT composite film (650°C)

4 Conclusions

Micromoulds were created successfully using AZ4562 photoresist and UV photolithography. The photoresist was found to be compatible with the PZT composite sol gel processing stages allowing shaped PZT structures to be obtained. The thermal treatment used for drying and pre-treating the polymeric material was shown to be critical in determining the quality of the achievable features. The best features were obtained when low temperature drying and pre-treatment was used as this did not appear to cause a change in the structure of the photoresist.

After crystallisation it was found that the PZT structures were self supporting and showed good adhesion to the substrate. SEM micrographs of the microstructure of the PZT structures after crystallisation showed that the features have a reasonable relative density with a narrow distribution of par-

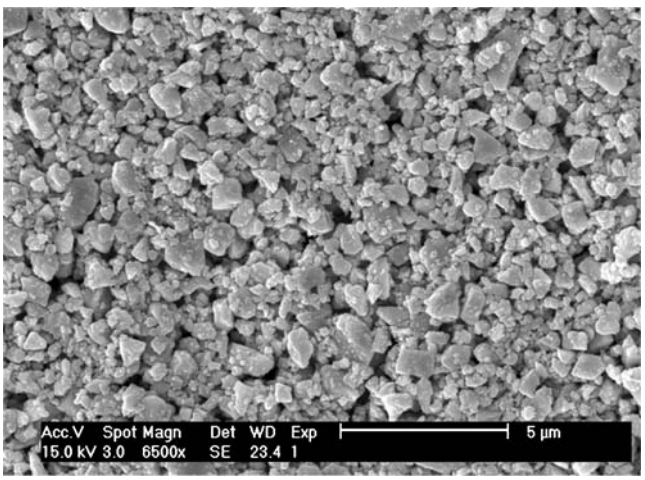

Fig. 9 SEM micrograph showing the microstructure of a micromould PZT feature

ticle sizes. The features tended to exhibit a 'U' shaped profile caused by the shrinkage of the PZT slurry during drying.

Preliminary electrical measurements show the features to have comparable properties to that of continuous films with comparable microstructures. The micromoulding process shows potential as a viable process for producing micro-features for MEMS applications such as ultrasonic transducers.

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