Novel patterning of composite thick film PZT

F. Tyholdt · R. A. Dorey · H. Ræder

Abstract There is a clear need for thick PZT films (10–100 μm) in micro-electromechanical systems (MEMS). Some applications, like high frequency transducers operating in the thickness mode, require frequencies in the MHz region and thus thicker films, which in addition will provide more power. Thicker films are also important in actuator systems and sensors as it will generate more force and voltage, respectively. Integration of complex structures of thick films in thick films in MEMS is challenging. The use of normal thin film patterning techniques is difficult for thick films due to the amount of material that has to be removed and the isotropic nature of wet etching. A new patterning technique suitable for composite thick films using an epoxy mould is presented. By filling a micro mould of SU-8 photoresist with PZT paste details down to 20 μm with vertical feature walls could be patterned in a 15 μm thick film.

Keywords PZT · Composite thick film · Pattern · Micro-mould

1 Introduction

A vast amount of research has been carried out on PZT films with thicknesses ranging from 100 nm to 3–4 μm for implementation in microelectronic devices [1–6]. There are several fabrication methods for such films; e.g. sputtering [7], chemical solution deposition (CSD) [8–11], metal-organic chemical vapour deposition (MOCVD) [12–14] and pulsed laser deposition (PLD) [15, 16]. The key points about these films are that they are generally textured or even epitaxially oriented to the substrate, they are obtained in crystalline form at low temperature and they are 100 % dense. Some applications, like high frequency transducers and vibration control devices, require higher actuation forces, lower frequencies when operating in thickness mode and thus thicker films (>10 μm) [17, 18]. It is, however, difficult to fabricate films with such thicknesses with the methods mentioned. In practice a barrier can be drawn at ~5 μm, even if there are examples of thicker films that have been made [19]. The main problem in this respect is that it is very time consuming to make thick films by these techniques to avoid cracking and thus securing the film quality.

The main industrial method for making thick films of a variety of materials is screen printing, where a paint consisting of fine particles suspended in a binder matrix is pressed through a fine mesh. The problem that arises when moving from low temperature processes like sol–gel to a powder process is the high temperature required to obtain a dense object [20]. For integration with other technologies, especially silicon based, this temperature requires the PZT based component to be manufactured separately and post mounted. The high temperature also requires the use of substrate materials other than Si, which has been traditionally used in thin film processes [21, 22].

Some measures to reduce the sintering temperature have been proposed. The use of low melting sintering aids, which are also often used for sintering of bulk ceramics, brings the sintering temperature down to 700 to 800°C [22,

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23]. A way of lowering the porosity, without having to increase the processing temperature, is to use a hybrid technology in which the PZT powder is mixed with a PZT forming solution [24–27]. This solution will add an interconnecting network of the same material between the PZT particles, hence decreasing porosity. As an extra benefit it has been shown that addition of PZT powder to a PZT forming solution lowers the perovskite formation temperature by 50°C [28]. The firing could then be done at as low a temperature as 650°C. This composite method was recently improved by Dorey et al. by making 1 to 4 PZT sol impregnations with intermediate pyrolysis steps before final densification. In addition a Cu_2O–PbO sintering aid was used. After 3 to 4 infiltrations of spin coated composite films the porosity dropped significantly and it is possible to make dense thick films of PZT at as low temperature as 710°C using this method [29–32]. The increased density is indeed important as studies of the piezoelectric properties of thick films show that even if $d_{33,f}$ is not significantly affected by the processing method, ε_r and $e_{31,f}$ are very sensitive towards porosity [32, 33]. During e.g. bending of a cantilever porosity opposes stress transfer in the film and so results in reduced performance, especially in transverse operation mode. The accepted values for $d_{33,f}$ and $e_{31,f}$ for a 2 μm PZT 53/47 film made my CSD is ~85 pm/V and from −12 to −15 C/m^2, respectively [11, 34]. For a composite thick film, however, the effective transversal piezoelectric coefficient, $e_{31,f}$, after 4 infiltrations is −3 to −4 C/m^2, which still is a substantial improvement from non-infiltrated films which have values of ~ −1 C/m^2 [32]. The low processing temperature simplifies integration with microsystems as it is possible to use Si-wafers as substrates.

The use of normal thin film patterning techniques is limited for thick films due to the amount of material that has to be removed. Wet etching by HCl/HF mixes is applicable, even though severe undercutting will take place as a consequence of the isotropic wet etching and the thickness of the film. Etching of 8 μm sol–gel films by a two step HF/HCl process has been demonstrated. In this study a undercut of 2:1 lateral/thickness was observed, which is typical for dense chemical solution deposited PZT films [35, 36]. However, the presence of excess porosity in a thick film increases the undercutting additionally as the etchant penetrates the film. This, in combination with high thicknesses, in turn lowers the resolution that can be obtained substantially. A typical 30 μm thick film will have an underetch of 50–60 μm which indeed puts restrictions on the resolution that can be obtained, and the number of devices that can be fabricated on a single Si-wafer.

A promising technique for fabricating ceramic structures by filling a photoresist mould with a ceramic suspension has been presented by Schönholzer et al. [37]. In this work a mould was made in 3 μm resist (AZ 4562, Clariant,

Germany) and filled with an alumina suspension. After drying the resist was dissolved before sintering and structures with a height of 3 μm and a width down to 7 μm could be made. However, in a typical ultrasonic transducer operating in thickness mode the PZT thick film must have a thickness often higher than 10 μm [38]. There are very few resist types that can be made very thick using only one coating. SU-8 is, however, a high aspect ratio epoxy resist which can provide vertical walls of several hundred microns. Thus, SU-8 moulds can prove very suitable for making high aspect ratio structures of composite thick films. Equally important is the fact that SU-8 is a highly cross linked epoxy that can withstand quite high temperatures [39], as the films made by this method must be impregnated and pyrolyzed at temperatures up to 450°C several times. This work will present a method for successfully patterning composite PZT thick films, which are preferred due the piezoelectric properties and low processing temperatures, by the use of SU-8 moulds.

2 Experimental

A composite slurry was made according to literature using Pz27 powder from Ferroperm Piezoceramics [31]. The PZT powder was milled in ethanol in a zirconia ball mill for 60min together with PbO and Cu_2O that was used as sintering aid. After drying the power mixture a paste was made by mixing the PZT powder with an alkoxide solution that had approximately the same metal stoichiometry as the powder. 2 g of powder was mixed with 0.5 g of solution. A platinized Si substrate was cleaned in a piranha etch (H_2SO_4:H_2O_2 3:1) at 130°C for 10 min and rinsed in DI-water and dehydrated at 350°C for 5 min. Microchem SU-8 5 was spun on the substrate at 1000 rpm, corresponding to a final thickness of 15 μm and soft-baked. The standard processing guidelines from the manufacturer was followed to pattern the resist by lithography. A Karl-Süss MJB56 mask aligner in soft contact mode was used with a test pattern for lithography to investigate the limits of the method. The resist mould was filled by dropping small amount of PZT slurry into the mould and the excess was wiped off using a doctor blade. After drying at 200°C for 60s the film was pyrolyzed using RTP (Jipelec JetFirst 150) at 450°C for 15 s. A temperature of 450°C was required to completely convert the sol–gel material to an amorphous oxide ceramic. At this temperature the SU-8 material retained its structure but a change in colour was observed indicating that the SU-8 had begun to degrade. However, the SU-8 still had the mechanical strength necessary to avoid sol intrusion into unwanted areas. In order to increase the density of the film it was infiltrated using the same alkoxide solution as previously used using spin coating at

2000 rpm for 30 s. This was done 3 times using the same procedure of drying at 200°C and pyrolyzing at 450°C. Final densification was done, above the eutectic temperature of the sintering aid, at 710°C for 30 min. Any PZT covering the now decomposed resist was removed using ultrasonic treatment in ethanol for 60 s. The patterned sample was investigated by SEM (JEOL JSM-5400LV). The processing route is described schematically in Fig. 1.

3 Results and discussion

SEM images of the patterned sample can be seen in Fig. 2. As can be seen in Fig. 2(a) sections of the PZT lines break off from the substrate when the line width drops below 25–30 μm. However, for more supported structures, such as 20 μm diameter holes and 30 μm depressions, with near vertical side walls, such break off is not observed (Fig. 2(c) and (d)). Details, like concentric rings, for which problems with resist flaking due to acid undercutting during wet etching is likely to occur, can also be patterned successfully (Fig. 2(b)). This is a very promising result, especially if even thicker films can be made, as normal underetch when wet etching is often 2:1 lateral/thickness.

Fracturing of the finest sub 20 μm details is observed in Fig. 2(a). The sonication step necessary to remove a thin layer of excess PZT that still covered the resist details after wipe off may have damaged the finest details. In Fig. 2(d) the remains after 3 20 μm wide pillars can be seen in the open area to the right. Structures of this type are very fragile due to high aspect ratio and small area anchored to the substrate. It is clear that to keep such structures intact is very demanding, and they were likely destroyed during sonication. These results indicate that the sonication step should be avoided. In order to be able to do this the thin slurry film left on top of the resist details by the doctor blade must be eliminated. A polymer squeegee might be better for making closer contact to the resist mould during wipe off.

The fracturing of the finest detail can also originate from volume changes in the resist during decomposition as reported by Schönholzer et al. [37]. In this case the problem was avoided by dissolving the resist before crystallization. However, SU-8 is a highly cross linked epoxy that is very hard to remove, which again was the reason why it was chosen in the first place. It is likely that an epoxy stripper like MS-111 (Miller-Stephenson, US) can remove SU-8. However, it is unsure how such a stripper attacks the uncrystallized PZT material. Strippers can also induce

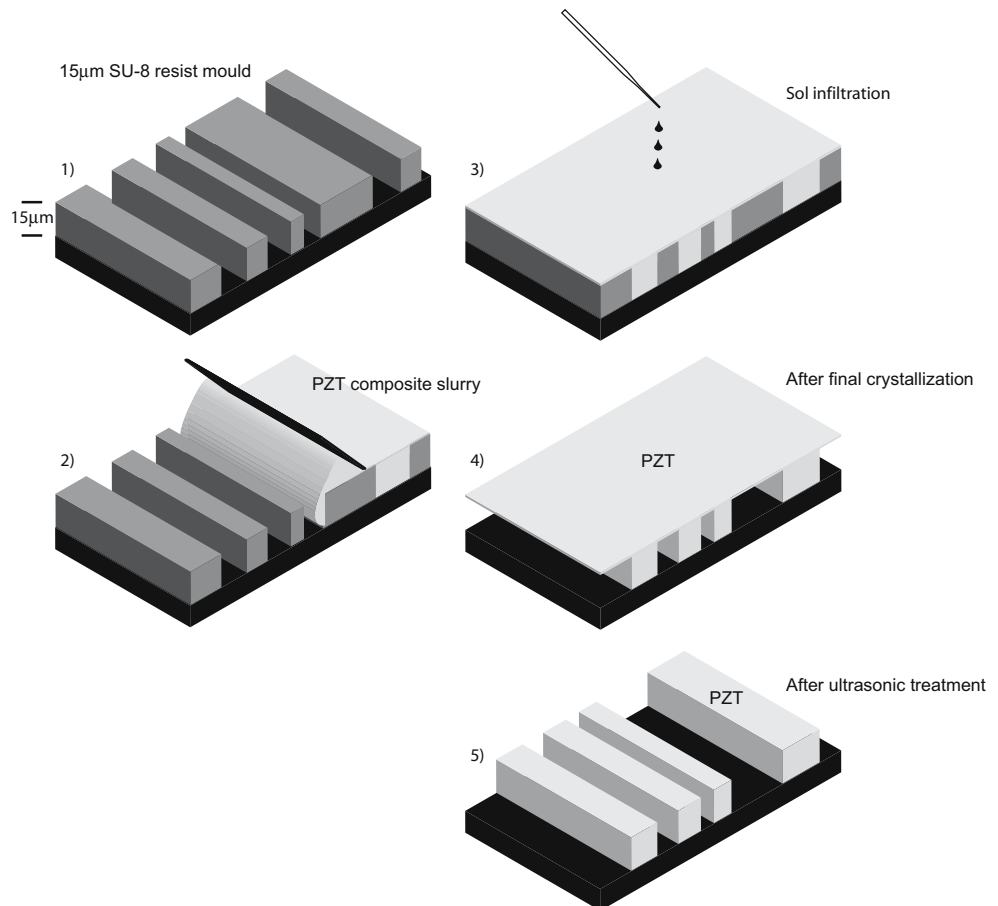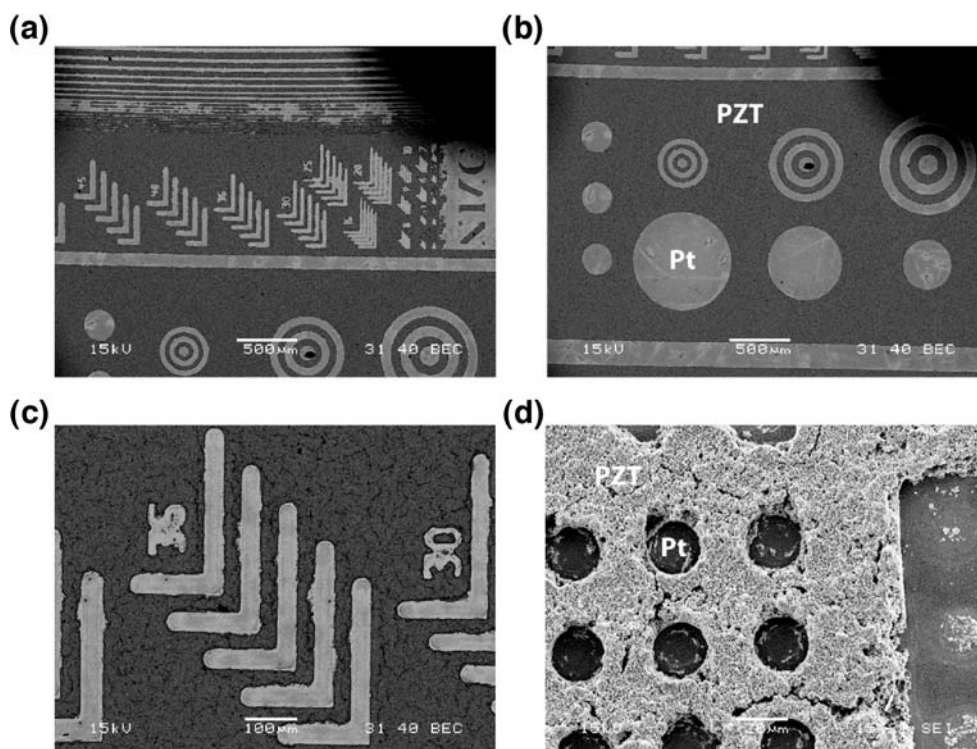**Fig. 1** Composite PZT film formation using a sacrificial mould of SU-8 photoresist

swelling in the SU-8 that undermines the reason for removing it. One should, though, not forget that if the lower practical limit of this method is ~15 μm after optimizations it will still be a significant improvement from wet etching. Particularly if even thicker films of 30–50 μm can be patterned using this method. If very fine details are needed removal of SU-8 with dry etching techniques can be considered before final sintering.

It is unclear what amount of porosity is formed in the SU-8 resist during the partial decomposition after the step at 450°C. Even if some PZT solution comes into contact with the platinum covered by SU-8 during the infiltration steps the formed layer will be very thin and will neither contribute electrically nor acoustically. Remains of the resist edge can be observed in Fig. 2(d) and Fig. 3. Thus, if PZT solution has leaked into resist covered areas the amount was very limited.

There is some residual porosity in the film in Fig. 3. This indicates that even though 3 infiltrations suffice for 2 μm thick films [31], additional infiltration cycles are needed for thicker films. The volume to be infiltrated is much higher in a 15 μm film than in a 2 μm film. To successfully infiltrate such a thick film it is possible that vacuum must be utilized to get the gas in the open pores out. This result also illustrates the importance of using very fine PZT powder in the slurry to minimize the amount of sintering needed. Compared to this work Schönholzer et al. [37] milled the powder for 18 h, which suggest that there is some potential in reducing the particle size further. Even though the

amount of sintering aid can be increased as well to lower the porosity it will lead to degradation of the piezoelectric properties.

Some cracks can also be seen in the film shown in Fig. 2(d) which probably originate from large shear forces arising during the excess slurry wipe-off. The powder:sol ratio is clearly influencing the filling and drying behaviour of the paste and its behaviour during paste wipe-off. Too low powder loading will lead to cracking during drying after wipe off whereas too high powder loading will lead to cracks due to high shear forces during wipe off. The
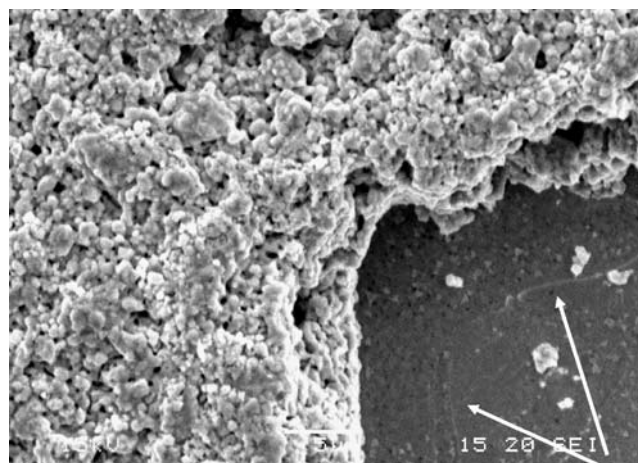

Fig. 3 Detailed SEM picture of a side wall in the patterned thick film. Arrows show remains of resist edge

powder loading is indeed a very important parameter which has to be optimized further.

4 Conclusions

A new patterning method for composite thick films using SU-8 as a micro-mould is proposed. The temperature stability of this epoxy makes it withstand several short pyrolysis steps at 450°C, which from previous experience are necessary for infiltration. By using a mould depth of 15 μm features down to 20 μm could be patterned depending on feature support. Near vertical feature walls were observed. This is a very promising result. Even finer features are expected to be successfully patterned after optimizations. Further work will concentrate on eliminating the sonication step, optimizing the powder loading and decrease the powder particle size. The possibility of patterning of thicker films (~50 μm) using this method is also very interesting. The piezoelectric and dielectric properties of such films will also be investigated.

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