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Formation of PZT micro-scale structures using electrohydrodynamic atomization filling of metallic moulds

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Abstract

In our previous work electrohydrodynamic atomization (EHDA) combined with a photolithography polymeric micromoulding technique was used to form PZT ceramic micro-scale structures. The major drawback of this technique was the deformation of the polymeric mould resulting in irregular PZT structures.

In order to overcome the above drawback, nickel micromoulds were used in this work to form PZT structures. It was observed that the PZT structures presented more regular features compared with those obtained from polymeric micromoulds. The smallest PZT square sizes and separations achieved were 78 μm and 31 μm, which correspond to the minimum nickel micromould cavity obtainable. The side wall angle was increased by using a release agent to prevent excessive build up of PZT at the edges of the mould cavity. The resulting PZT structures exhibited a relative permittivity of 240, $d_{33,f}$ of 70 pCN^{-1} and remnant polarisation of 9.3 $\mu C\,cm^{-2}$ at 35 $V\,\mu m^{-1}$.
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Keywords: PZT; Films; Suspensions; Micromoulding; Ferroelectric properties

1. Introduction

Lead zirconate titanate (PZT) is an important piezoelectric material in microelectromechanical systems (MEMS) because of its high piezoelectric constant, relative permittivity and electromechanical coupling coefficient.[1] It has been used in a large variety of micro-device applications, such as sensors,[2] transformers,[3] transducers[4] and actuators.[5] The commonly used deposition methods of forming PZT films include sol–gel coating[6] and sputtering.[7] These two methods are usually used to produce thin PZT films, typically less than 5 μm.[8] However, some MEMS devices such as micro-power harvester, micro-piezoelectric transformer, and high resolution piezoelectric transducers need thicker piezoelectric films of 10–100 μm.[9,10] Thick film fabrication methods such as screen printing, based on the sintering of oxide ceramic particles, require high temperatures normally above 1200 °C and are likely to result in the damage of substrate and electrode materials.[11] The use of conventional bulk ceramic processing with subsequent machining and bonding is wasteful of material and time consuming.[12] In addition, the level of difficulty increases largely as the size of the devices decrease, especially when the device has constrained and complex structures.[13]

Effective deposition techniques are important to produce high quality PZT thick films and structures. Electrohydrodynamic atomization (EHDA) is a physical process where an electrified liquid/suspension is dispersed to fine droplets due to an electrostatic force working on the charged surface of a liquid, first reported by Zeleny.[14] With the growing usage in bio, functional and composite materials, EHDA has attracted considerable attention and has been used to form microstructures in bioengineering[15] and chemical engineering.[16] EHDA has three distinct advantages when used with suspensions[17–19]: (a) fine and uniform droplet can be obtained, (b) the size of deposition product is independent of nozzle diameter and (c) there is less risk of nozzle blockage.

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With the use of sol–gel combined with PZT powder it is possible to produce PZT thick films greater than 20 μm at low temperatures.[20] In our previous work the EHDA deposition technique, coupled with PZT composite sol–gel slurry, was used to produce crack free 30 μm thick PZT films with the advantages of high deposition speed and low processing temperature.[21] The EHDA technique has also been employed in the micromoulding process to form PZT thick film structures by depositing dense and crack free PZT films from a PZT composite sol–gel slurry into polymeric moulds.[22] This delivers a higher resolution over chemical wet etching and screen printing techniques, avoids the use of hazardous solutions such as hydrofluoric acid used in chemical wet etching, and the high temperature (850–1200 °C) employed in sintering screen printed structures. However, the polymeric micromould material (AZ9260) used in our previous work is intolerant to high temperatures where temperatures higher than 110 °C resulted in its rapid deformation and degradation, leading to irregular PZT features. In this work nickel micromoulds were used to form PZT ceramic structures with greater precision than when using polymeric micromoulds.

2. Experimental details

2.1. Formation of nickel micromoulds

Three types of features were designed on a 4 in. Chromium/glass photomask for forming the nickel micromoulds in order to explore the capabilities of the technique in term of feature size and resolution. Features varied in size between 1 μm and 2000 μm with the separations ranging from 1 μm to 300 μm. The procedure of forming the nickel micromoulds includes Ti/Pt bottom electrode deposition, formation of sacrificial photoresist dry film structures, nickel plating and removal of photoresist dry film structures (Fig. 1). Prior to coating of the photoresist sacrificial film structures, the Si wafer was coated with a blanket layer of Ti/Pt (8/100 nm) using RF magnetron sputtering (Nordiko Ltd., Hampshire, UK), cleaned using acetone/propan-1-ol on a spinner and then dried at 100 °C for 3 min. Two layers of dry film photoresist 350 were formed using a hot-roll laminator (Dynachem 350 HR laminator) at a roller temperature of 68 °C, which gave approximately 58 μm thick films. The pressure between the top and bottom rollers and working speed were set at 300 kPa and 0.5 m/min. The dry film photoresist was then exposed to UV light on a MLB21 mask aligner (SUSS MicroTec. Lithography GmbH, Garching, Germany) at a beam intensity of 12.5 mW cm^{-2} for 18 s. The sacrificial dry film structures were developed in a 1% potassium carbonate solution for 7 min and cleaned with distilled water. Prior to nickel plating any residual organics on the dry film structures was cleaned using a plasma etching process (PT 7160 RF Plasma Barrel Etcher, Polaron PLC, Whatford, Hertz, UK) at the power of 15 W for 5 min. The wafer, with dry film structures, was then immersed in a mixed solution of nickel sulphamate and boric acid (15:1) at the plating condition of 15 mA, 0.32 V and 50 °C for 90 h, which gave a nickel film thickness of 33 μm. Finally the dry film structures were removed by immersing in the 10% MFS 1102 stripper (PMD Ltd., Coventry, UK) for 40 min to obtain the nickel micromoulds for the deposition of PZT film structures.

2.2. EHDA deposition of PZT composite slurry

The PZT composite sol–gel slurry was prepared from PZT sol, PZT powder (PZ 26, Ferroperm, Denmark), dispersant KR 55 (Ken-React Lica 38, KenRich) and Cu_2O/PbO sintering aid. The PZT sol was prepared from the precursors lead (II) acetate trihydrate, titanium (IV) isopropoxide and zirconium (IV) propoxide, which has the final chemical stoichiometric ratio of metal ions of Pb 1.10: Zr 0.48: Ti 0.52. The details of the components and preparation routes of the PZT sol and PZT composite sol–gel slurry were described in our previous work.[21]

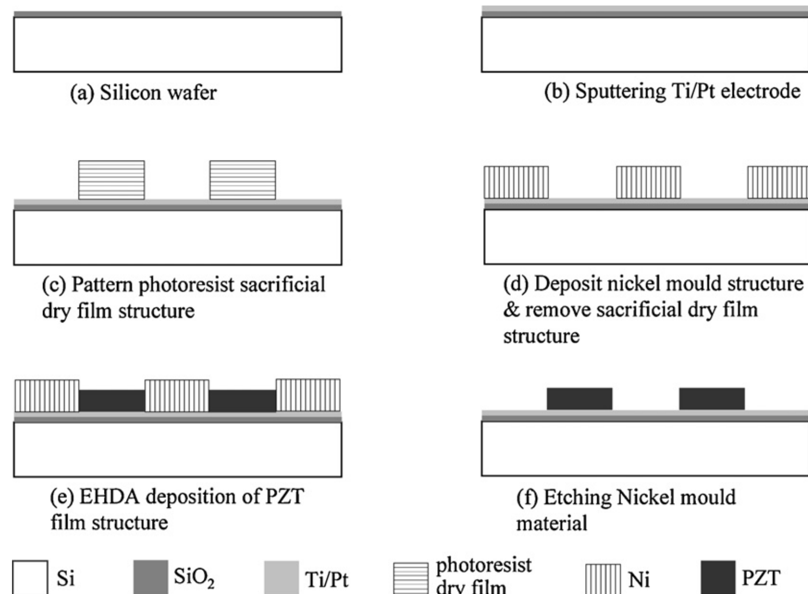

Fig. 1. Schematic illustrating the PZT micromoulding route using EHDA deposition and nickel micromoulds.

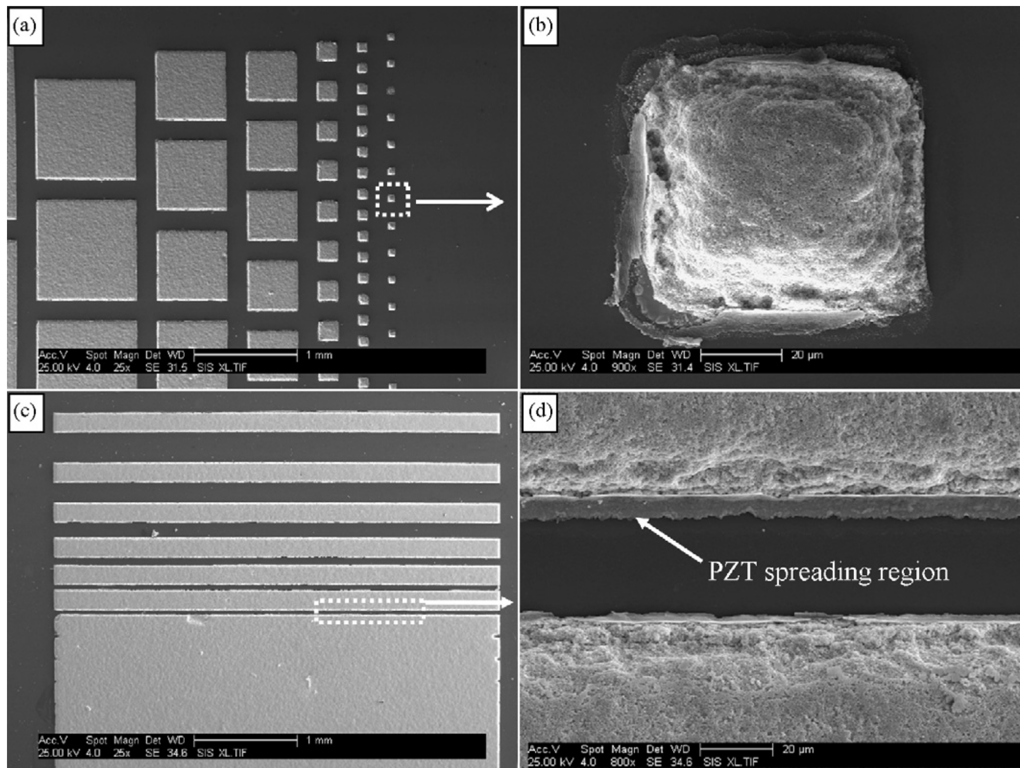

Fig. 2. Scanning electron micrographs showing the sintered patterned PZT film structures after depositing 50 EHDA layers: (a) overview of the squares of different sizes, (b) overview of the 200 μm wide rectangles separated by gaps of varying widths, (c) a 78 μm wide square and (d) the smallest gap resolvable.

Dispersant KR 55 was used to stabilize the slurry, Cu_2O/PbO sintering aid was used to increase the density and piezoelectric properties of the sintered PZT film.

The EHDA deposition device consists of an electrohydrodynamic needle, a high voltage power supply, a syringe pump and a computer controlled X–Y movement stage.[21] The needle (inner/outer diameter of 0.85/1.3 mm) was connected to the high voltage power supply (Glassman High Voltage Inc., NJ, USA) and its inlet was connected to the syringe pump (KD Scientific Inc., MA, USA) using a silicone rubber tube. The high voltage power supply was used to apply an electric field between the needle and the ground electrode. The syringe pump was employed to provide the hydrodynamic force to push the PZT composite slurry up to the outlet of the needle. A thin aluminium plate was placed directly on the X–Y movement stage and connected to earth potential, which was served as the ground electrode during EHDA deposition. The nickel micromould wafer was placed on the aluminium plate ground electrode at a fixed distance of 10 mm below the needle exit throughout EHDA deposition. The flow rate and the applied voltage were kept constant at $2.2 \times 10^{-10}\,m^3\,s^{-1}$ and 5.5 kV during deposition to ensure the stable cone-jet mode deposition. During the EHDA deposition the nickel micromould wafer was alternately rastered with scan in the *X* and *Y* directions individually for every layer at a speed of $28\,mm\,s^{-1}$. A distance of 3.4 mm between two neighbouring parallel paths of deposition was set to ensure a degree of overlap between deposited materials. 26 μm thick PZT film was built up by depositing 50 layers over the nickel micromould. After every two intermediate layer depositions the PZT film was dried at 200 °C for 60 s and pyrolysed at 350 °C for 60 s to remove all the organic components.

2.3. PZT structure evaluation

After the EHDA deposition of PZT composite sol–gel slurry the nickel micromould with PZT thick film structures was initially heat treated at 600 °C for 10 min in a muffle furnace to increase the bonding strength between PZT sol and PZT powders, as the $FeCl_3$ etching solution is likely damage the PZT structures during the subsequent nickel removal process. The reason for treating the film at 600 °C is that the interdiffusion of Ni and Si can lead to the formation of silicide high temperatures.[23] The PZT film structures were obtained by removing the nickel in a 3.03 M $FeCl_3$ etching solution at 45 °C for 2.5 h. The final PZT film structures were sintered at 720 °C for 20 min in a muffle furnace to obtain the perovskite phase structure. Chromium/gold circular top electrodes with a thickness of 15/100 nm and a diameter of 770 μm were deposited on the PZT film structure surface by vacuum evaporation (Edwards Evaporator E480) to evaluate the electrical characteristics of the PZT.

3. Results and discussion

3.1. Feature of PZT structures

After EHDA deposition of the PZT slurry, the nickel micromould presented an orderly structure and uniform coating

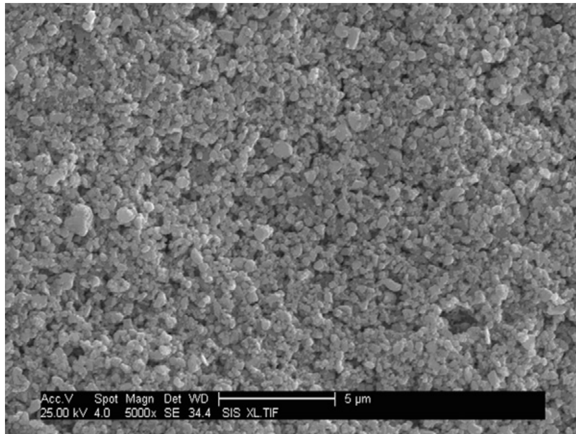

Fig. 3. Scanning electron micrograph showing the surface microstructure of the patterned PZT film structure after 60 EHDA deposition layers.

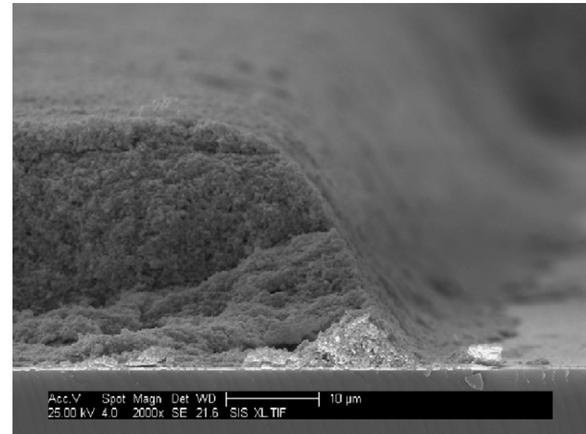

Fig. 4. Scanning electron micrographs showing a typical edge fracture cross-section of the patterned 200 μm wide rectangle PZT film structure.

behaviour with no observable damage following the heat treatment during the drying process compared to the cracking and deformation of the photoresist moulds observed in our previous work.[22]

Fig. 2 shows the sintered patterned PZT structures consisting of rectangles and squares of different sizes and separations obtained after depositing 50 EHDA layers and the removal of the nickel micromoulds. The features exhibit more regular features compared with those produced from polymeric moulds.[22] Fig. 3 presents the surface microstructure of the patterned PZT film structure after sintering, which exhibits a well-packed and crack-free film. There is a high level of evenly distributed small size pores evident in the structure.

In comparing the design size with that achieved it was observed that the sintered and patterned PZT structures were enlarged by approximately 8 μm relative to their design, which resulted in a corresponding 8 μm reduction of the gap between the structures. The smallest PZT square structure produced was 78 μm in width (Fig. 2c) which corresponded to the smallest nickel micromould cavity obtainable. The minimum resolvable gap between two neighbouring PZT rectangles and squares obtained was 31 μm (Fig. 2d). It was not possible to produce smaller separations due to the limitation of the resolution of dry film photoresisit photolithography process used to produce the nickel micromoulds. Fig. 4 shows a typical edge fracture cross-section of the patterned 200 μm wide rectangle PZT film structure. A degree of spreading was observed at the base side wall of the PZT structures (Figs. 2c, d and 4). This is due to an edge defect in the nickel micromould wall (Fig. 5a), caused by the shape of the sacrificial dry film structure (Fig. 5b), which is filled during the EHDA deposition process.

It was also observed that the side wall of the PZT structure was not straight, presenting a rounded sloping characteristic and an angle of approximately 45° (Fig. 4). Fig. 6a shows how PZT deposited on the surface of the nickel moulds protrudes over the mouth of the mould cavity and subsequently shields the underlying area leading to the characteristic sloping side wall.

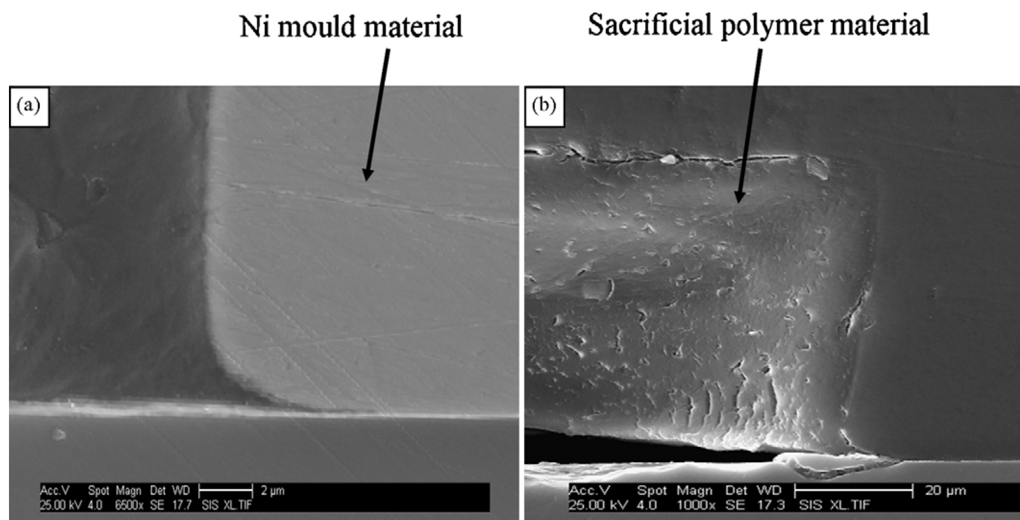

Fig. 5. Scanning electron micrographs showing the cross-section of a typical nickel micromould (a) and dry film mould former (b).

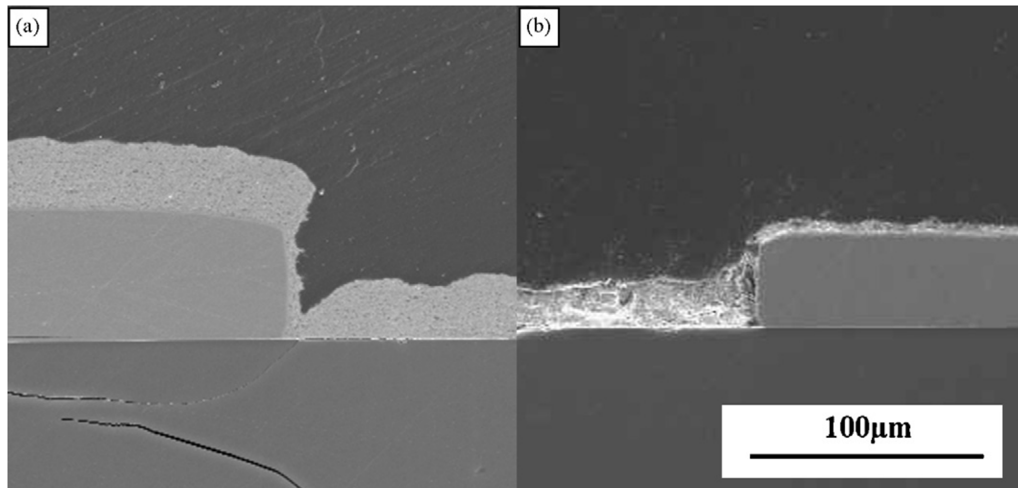

Fig. 6. Scanning electron micrograph showing the cross-section of the PZT film structure after 50 EHDA deposition without release layer (a) and 40 EHDA deposited employing releasing process (b).

3.2. Side wall refinement of PZT structures with the use of PDMS releasing process

In order to eliminate the sloping side wall of the PZT structure, S1818 photoresist applied using the PDMS stamp (SYLGARD 184 Silicone Elastomer, Dow Corning Corp., MI, USA), was used as a releasing agent to remove the residual PZT films stacks deposited on the surface of the nickel micromould. After every 10 layers of PZT deposition the releasing agent, and over coated material, was removed by washing in acetone for 1 min and then cleaned in an ultrasonic bath. Before applying the next layer of photoresist the nickel micromould was dried at 100 °C for 5 min. Due to the presence of the S1818 release material, the PZT/mould structures were dried at 100 °C for 5 min (instead of 200 and 350 used with pure Ni moulds) after every two EHDA deposition stages to remove organic solvent. PZT film structures were built up using 40 layers. It was observed that the PZT film structure produced with the use of the PDMS releasing process exhibited straighter side walls (Fig. 6b) compared with that observed without the PDMS releasing process (Fig. 6a). It was also found that the PZT structure was thicker near the side wall edge, which resulted from the electric field interaction between the nickel micromould side wall and the atomization needle leading the preferential deposition of PZT in this area (Fig. 6). It should be noted that the appropriate sintered and patterned PZT structure was not obtained, after removing nickel micromould, due to the low drying temperatures employed such that the film was no longer able to withstand the nickel etching process. The S1818 photoresist is intolerant to high temperatures, so only low drying temperature of 100 °C was used in order to keep the uniformity of the S1818 photoresist releasing layer during the PZT structure deposition process. A high temperature tolerant releasing agent, or alternative cleaning mechanism, is suggested to improve bonding strength of the PZT structure and obtain the sintered and pattered PZT film structure. Despite the failure to produce sintered PZT structures the work clearly shows the need to remove excess material during processing in order to enhance the side wall angle of the features.

3.3. Electrical characterisation

Fig. 7 shows the ferroelectric hysteresis loops of a PZT film structure at different applied electric fields. The film becomes saturated at the maximum electric field intensity of 35 V μm^{-1}. The relative permittivity (ε_r) of the PZT structures was calculated to be 240(±8) at 50 kHz, and the dielectric loss is less than 0.02. The low value of relative permittivity and remnant polarisation is due to the high level of porosity in the system. It is possible, however, to increase the density, and so relative permittivity, of the films through the use of repeated sol infiltrations.[9,13] The highest film piezoelectric constant ($d_{33,f}$) obtained was 70 pCN^{-1} when poled at 12 V μm^{-1} at 200 °C for 5 min.

The remnant polarisation (P_r), ε_r and $d_{33,f}$ of the PZT film structure produced using nickel micromoulds exhibits similar results to those obtained from structures produced using photoresist micromoulds in our previous work.[22] While, it can be concluded that the drying temperature during the EHDA deposition process has no distinct effect on the electrical properties of the structures it does, however, lead to better shape control. The P_r and ε_r are still lower than the bulk PZT materials, which

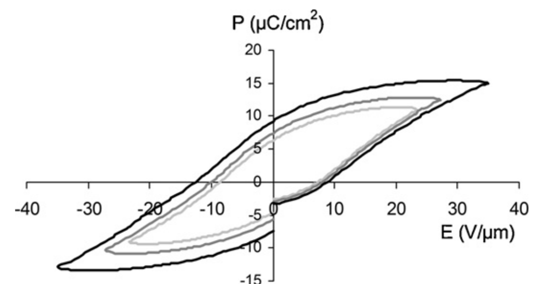

Fig. 7. Ferroelectric hysteresis loop of the PZT structures.

is mainly due to the existence of pores in the films and presence of the rigid substrate constraining the film.

4. Conclusions

Electrohydrodynamic atomization deposition in combination with nickel micromoulding process was introduced to form PZT thick film structures. The drying process induced deformation of the photoresist mould and PZT structure observed in our previous work is absent in this work with the use of nickel micromoulds. The smallest PZT square sizes and separations produced were 78 μm and 31 μm, which correspond to the minimum nickel micromould cavity obtainable with the relevant design of 70 μm and 40 μm, respectively. It was observed that the PZT structure presented a 4 μm PZT thin film expansion along the both side wall edge, which resulted in a 8 μm enlargement of the PZT structures in width and 8 μm reduction of gaps between PZT structures. The sloping side wall behaviour caused by the shielding effect of the stack of the PZT structure on the nickel micromould could be improved by using the PDMS releasing process. The piezoelectric coefficient ($d_{33,f}$) of 70 pCN^{-1}, relative permittivity (ε_r) of 240 and ferroelectric hysteresis loop were obtained for this PZT film structure, which are comparable with those attained in our previous work and for continuous films with similar microstructures reported in literature.

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