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Novel forming of columnar lead zirconate titanate structures

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Abstract

The present study is focused on the processing of columnar lead zirconate titanate (PZT) structures on Ti/Pt-coated silicon substrates using electrohydrodynamic deposition. It was found that the as-deposited PZT structure is highly dependent on the concentration of the sprayed precursor, which is believed to be the characteristic of electrohydrodynamic deposition. 0.01, 0.03, 0.06, 0.12, 0.3 and 0.6 M PZT sols were used to prepare as-deposited structures. Columnar PZT structures, which are important for the processing of 1-3 composites, were obtained with the 0.6 M sol. As-deposited and heat-treated columnar PZT structures were investigated using scanning electron microscopy and X-ray diffraction. The development of the PZT columns was studied by observing the cross-section of the structures deposited over different time sprays, revealing a three-stage growth process for these structures. The affect of substrate temperature on the columnar structure was also analysed by studying the density of the columns. Finally, a 1-3 composite was produced by infiltrating photoresists into the columnar PZT structures and the relative permittivity and dissipation factor of such composite were measured as 105 and 0.021. Modelling the structures as a PZT and a polymer capacitor connected in parallel in the PZT/polymer composite suggests that the relative permittivity of PZT columnar material is approximately 154.

Keywords: Electrospray; Microstructure; Dielectric properties; PZT; Functional applications

1. Introduction

Lead zirconate titanate (PZT) has attracted much attention due to its excellent ferroelectric, piezoelectric, dielectric and pyroelectric properties.[1,2] In the form of thin/thick films PZT has a wide range of applications in non-volatile random access memories for computers,[3] piezoelectric micro-sensors[4,5] and intergraded capacitors.[6,7] Various processing methods have been used to fabricate thin/thick film PZT, which include chemical vapour deposition,[8] physical vapour deposition[9] and sol–gel methods.[10] Apart from those, a novel processing method called electrohydrodynamic deposition, has recently generated attention for the preparation of bio-materials,[11] functional ceramics[12,13] and polymeric fibers.[14]

Electrohydrodynamic deposition is a well-established technique, which can effectively combine the patterned deposition of advanced materials from precursors.[15] The precursor is ejected using a pump, and passes through a needle that is at a high electric potential relative to the substrate. The liquid near the needle can be made to form a stable cone under certain flow rate and applied electric field conditions,[16] and deforms to an elongated jet and consequently breaks-up into droplets.[17,18] The droplets transfer through the air and then deposit on the substrate that is connected to the ground potential. The deposition process is completed by the necessary heat treatment. In previous work, the authors have sprayed 0.6 M PZT sol onto metallic substrates successfully, and nano-structured PZT was obtained after heat treating at 650 °C.[19]

It has been reported that in electrospraying the droplet transportation and spreading on the substrate plays an important role in the evolution of the as-deposited structures.[20,21] During droplet transportation, evaporation occurs and this determines the solvent content in the droplets[22,23] when they arrive at the substrate, thus controlling the wetting and spreading of the droplets on the surface: particles in solvent are able to form continuous layers easily[24] whereas solvent-depleted particles tend to form a ‘powdery’ deposit and are exceedingly agglomerated due to their lower mobility. The agglomerations generated

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by dry particles will grow with the deposition time and ultimately a number of isolated columns will be formed. In our recent work it was shown that this feature is closely related to the concentration of the precursor during electrohydrodynamic deposition. A continues film can be formed when using a low concentration precursor whilst a columnar PZT structure can be generated when using high concentration precursors. In this work we have investigated the reasons for this phenomenon in terms of the diameter of the droplets and their evaporation.

It is well known that the columnar PZT structures are of interest when fabricated as 1-3 composites[25] with polymers. Such structures are commonly used, e.g. in sonar,[26,27] medical imaging technologies[28] and non-destructive testing.[29] The isolated PZT columns have connectivity with both the top and bottom electrodes. However, they have zero-connectivity with each other by being embedded in a polymer matrix. Since the polymer does not transmit forces to the PZT in the x–y plane, the negative coefficient d_{31} of the structure is reduced. Therefore, a high hydrostatic coefficient d_h (where $d_h = d_{33} - 2d_{31}$) can be obtained by this particular PZT-polymer design. Such piezoelectric composites can be fabricated by many macro-scale methods[30,31] but the authors suggest that electrohydrodynamic deposition is suitable for the formation of the columnar PZT structures for preparing micrometer and sub-micrometer scale 1-3 composites.

In this work, 0.01, 0.03, 0.06, 0.12, 0.3 and 0.6 M PZT sol–gel solutions were used to investigate how the concentration of sprayed precursor affects the as-deposited structures during electrohydrodynamic spraying. The 0.6 M PZT sol was shown to be suitable for the deposition of columnar PZT structures. The as-deposited columnar structure was heat-treated at 650 °C for 1200 s and investigated using X-ray diffraction and scanning electron microscopy. The development of the PZT columns was studied by observing the cross-section of the samples deposited for 10, 20, 40, 60, 180 and 330 s. The effect of substrate temperature (75, 125 and 175 °C) on the formation of the columnar structure was also analysed by studying the density of the columns deposited onto substrates at different temperatures. Finally, the columnar PZT structures were filled using photoresists to produce 1-3 composites and the dielectric properties were then measured and discussed.

2. Experimental

2.1. Sol dilution and characterization

The preparation of PZT sol used in this work has been described in our previous work.[19] Stoichiometric amounts of titanium isopropoxide and zirconium propoxide were mixed prior to the addition of the solvents 1-propanol and glacial acetic acid (2:1 volume ratio). An excess of lead acetate was then added to the solution and the system was subsequently refluxed for 30 min. The prepared sol of 0.6 M (C6) was diluted to obtain 0.3 M (C5), 0.12 M (C4), 0.06 M (C3), 0.03 M (C2) and 0.01 M (C1) sols. The solvents used for diluting were a mixture of glacial acetic acid (Anala R, VWR, UK) and 1-propanol (GPR, VWR, UK). The two solvents were mixed in the volume ratio of 11:10, then sealed and stirred for 24 h. The electrical conductivity of the different sols prepared was measured using a conductivity probe (Hi8733, HANNA Ltd., UK). The probe was calibrated using standard ethanol.

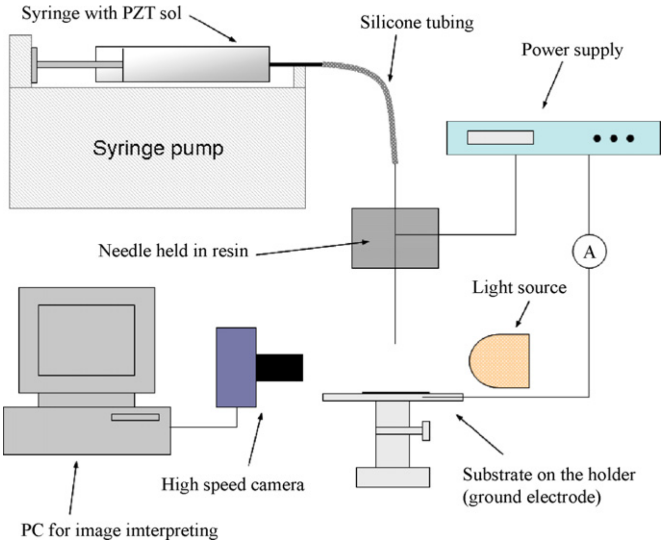


Fig. 1. Schematic diagram of the electrohydrodynamic deposition instruments setup.

2.2. Electrohydrodynamic deposition

The configuration of electrohydrodynamic deposition process is shown in Fig. 1 and is described in detail in the previous work.[19] The flow rate and the applied voltage were set as 2.5×10^{-11} m^3 s^{-1} and 4.2 kV, respectively. Silicon wafer (Si-Mat, Germany) with Ti/Pt (8/100 nm) coated was used as the substrate and the distance between the nozzle and substrate was kept as 10 mm.

Samples for examining the effect of sol concentration (C1 to C6) were electrosprayed for 60 s and then dried on the hot plate for 120 s at 200 °C. For columnar PZT forming, C6 was used with the process parameters set as above. The deposits were collected at different time intervals of 10 s (T1), 20 s (T2), 40 s (T3), 60 s (T4), 180 s (T5) and 330 s (T6), respectively, followed by a heat treatment at 650 °C for 1200 s, which has previously been shown to be the lowest temperature at which the perovskite phase can be formed with this PZT sol.[19] The study of how substrate temperature affected the columnar PZT structure was realized by placing a hot plate directly under the substrate. The deposition parameters were similar to that used for T6 and the temperature was varied to prepare samples at 75 °C (H1), 125 °C (H2), and 175 °C (H3).

2.3. Structure characterization

The microstructures of all the samples were studied using field emission scanning electron microscope (SEM, JEOL JSM/6310F) after sputter coating with gold. The phases present in the sintered PZT samples were investigated using X-ray

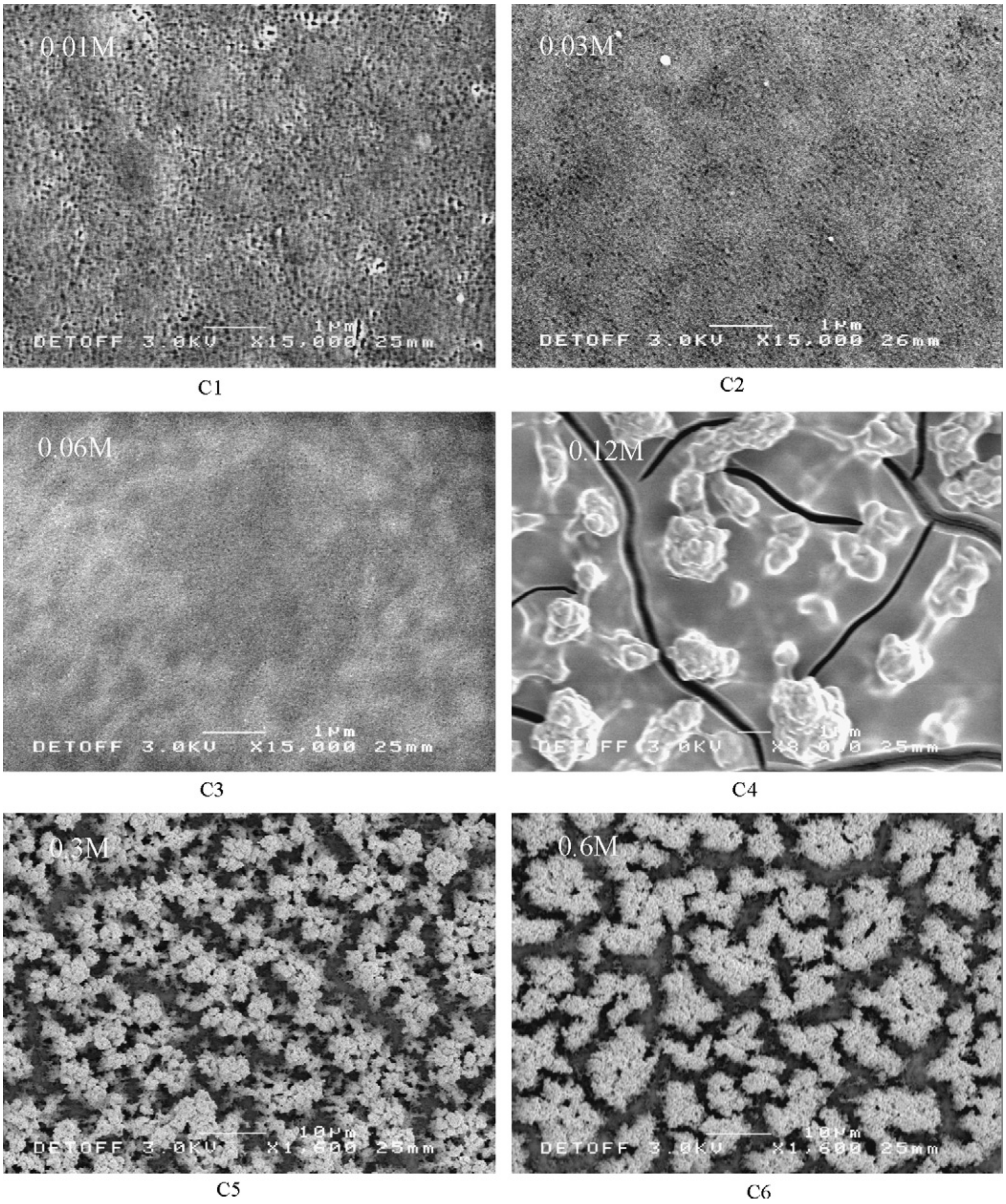


Fig. 2. Scanning electron microscope micrographs of as-deposited structures prepared using different concentrations of PZT sol. C1: 0.01 M, C2: 0.03 M, C3: 0.06 M, C4: 0.12 M, C5: 0.3 M and C6: 0.6 M. The structures were dried on the hotplate at 200 °C for 120 s.

diffraction (XRD, BRUCKER D8 DISCOVER) using Cu Kα radiation.

2.4. Dielectric property

In order to investigate the dielectric properties of columnar PZT, a 1-3 composite was produced by infiltrating a liquid photoresist (AZ9260) into the PZT columns. The photoresists were deposited on top of the PZT columns and left for 300 s to infiltrate into the columns. The material then was placed into an oven (80 °C) for 3 h until the photoresists were entirely dry. Consequently, the top of the composite was polished using grinding paper until the light yellow colour PZT columns were exposed. The average thickness of the composite was measured using a surface profilemeter (Dektak). The material was then coated with gold electrodes using evaporation. A Wayne Kerr 6425 Precision Component Analyser was used to measure the capacitance and dissipation factor of the composite at 50 kHz.

3. Results and discussion

3.1. Effect of precursor concentration

As the concentration of the sol–gel solution is increased, heterogeneities in the deposited film become pronounced as shown in Fig. 2. There are two different kinds of structures evident as can be observed in the micrographs. For low concentration samples (C1, C2 and C3) it is clear that the deposited film is a continuous, non-agglomerated layer, while for high concentrations (C4, C5 and C6) highly agglomerated structures were

Table 1
Variation in conductivities of the precursor sols as a function of concentration

	Sample ID					
	C1	C2	C3	C4	C5	C6
Concentration of sol (M)	0.01	0.03	0.06	0.12	0.3	0.6
Conductivity (μS/cm)	8.3	11.8	16.8	27.8	36.6	44.4

observed. It has been reported that the diameter d of the droplets produced by electrohydrodynamic deposition is related to the fluid and processing parameters as shown in the following equations:

$$d \propto \varepsilon_r^{1/6}\left(\frac{Q}{\kappa}\right)^{1/3} \tag{1}$$

where ε_r is the relative permittivity of the solution, Q is the flow rate and κ is the electrical conductivity.[32] In our case, as the concentration of the PZT sol was changed, the flow rate and the relative permittivity of the system remained constant. Flow rate (Q) was controlled by the pumping rate and was set as a constant value for the entire process. The relative permittivity of the solution (ε_r) could also be assumed as a constant with the following reasons. Firstly, the dielectric property of the PZT sol is based on the atomic, electronic and dipolar polarization, within which the dipolar polarization of the solvents is the dominating factor. In the PZT sol, the dipolar polarization in the Pb^{2+}–Ti^{4+}–Zr^{4+}–O^{2-} system is rather insignificant when compared with that in the 1-proponal solvent (H–O in C_3H_6OH). Secondly, it can be calculated that even in the 0.6 M PZT sol, the volume of the metal–organic molecules is still 20 times less than that of the solvent molecules. Therefore, when the concentration of the solution is changed, the change in the relative permittivity contribution of the metal–organic molecules is insignificant and can be neglected. Thus according to Eq. (1), the diameter of the droplets in our experiments can be considered as inversely proportional to the cubed root of the conductivity of the precursor. The electrical conductivities of the precursors with different concentrations were measured and their changing relationships are shown in Table 1.

The values in Table 1 demonstrate that the electrical conductivity increased when the concentration of the PZT sol increased. Considering the inversely proportional relationship of the conductivity with the droplet diameter, the diameter of the sprayed droplets is then expected to also be inversely proportional to the concentration of the PZT solution.

During electrohydrodynamic deposition, the droplets will be produced in the cone-jet mode, followed by four stages before deposition completes: droplet generation after jet break-up; transportation through the environment; impact and spreading on the substrate; drying and decomposition. The droplet transportation plays an important role due to solvent evaporation during this stage which will determine whether the particles are dry or wet when they impact on the substrate. When large droplets (produced from low concentration sol) are transported between the nozzle and the substrate, evaporation will be less because of the larger amount of solvent contained within the droplets and smaller volume specific surface area (surface area/volume), which will help to maintain the droplets in a viscous liquid state. Conversely, when small droplets (produced from high concentration sol) are transported, they will promptly dry to become solid particles after evaporation of the solvent which is present in a smaller amount when compared with that of low concentration sol. The wet relics have a high mobility and can easily spread on the substrate surface, forming an interconnected three-dimensional structure which is necessary for continuous film formation. On the other hand, the dry solid particles cannot move when they are deposited on the surface, leaving only agglomeration and accumulation. As a result, the configuration of the as-deposit structures varies significantly when the concentration of the sprayed sol is changed.

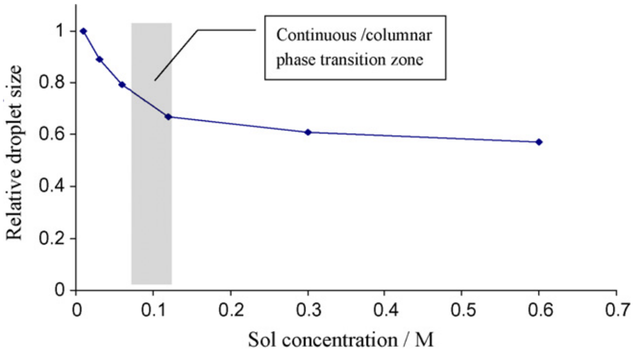


Fig. 3. The relationship between the concentration of the sprayed sol and the relative droplet diameter deduced from Eq. (1). The bar represents the proposed continuous film to columnar structure phase transition region.

The relative diameter of the droplets produced from the sprayed PZT precursors with different concentrations can be deduced from Eq. (1) and is shown in Fig. 3. It exhibits a trend where the diameter decreases rapidly as the concentration is increased up to 0.1 M. Above 0.1 M it shows a nearly flat curve up to 0.6 M without appreciable change in the relative droplet diameter. According to this, any transition between continuous film and agglomerated columnar structure would be most likely expected to exist in the zone of rapid size change (e.g. around 0.1 M). To the left of this demarcation (low concentration), a continuous film is obtained while to the right of it (high concentration), a columnar structure can be obtained. This expectation correlates with the observation of the structures shown in Fig. 2.

As observed in Fig. 2 C3, the 0.06 M precursor was sprayed as a dense, non-agglomerated layer. In C4, when the concentration increased to 0.12 M, the structure seems to comprise of a continuous layer in which some agglomerated particles are trapped. It is believed that this structure is the transition structure between continuous films and agglomerated columnar structures, in that layers are still three-dimensionally interconnected but the agglomerate particles could also be detected. Dramatically different from the previous ones, a columnar structure can be observed in C5 and C6. As stated previously, it is thought that at high concentration (above 0.3 M), the droplets produced are so small that a large amount of the solvent is evaporated, forming a high concentration of low mobility particles when they arrive at the surface. The dried particles easily agglomerate and form an isolated columnar structure. In addition, the whole procedure occurs in a high electrical field in which the particles are charged. The charged particles will have a tendency to travel along the electric field and are therefore attracted more towards the curved/protruding areas, which will lead to preferential landing sites.[33] Therefore, once the initial particles have been deposited to produce protrusions, subsequently arriving particles will be more likely to deposit on these agglomerated sections rather than on the smooth surface. As the deposition continues, the agglomerations grow higher and larger, further intensifying the preferred deposition, and thus the columns are obtained. There is not a significant difference between the structures in C5 and C6. The reason can be deduced from Fig. 3. In the high concentration region, the relative droplet diameters are not considerably different, of which the ratio between C5 and C6 is calculated as 1.08. Therefore, the droplets are of comparable size and will behave similarly, so that the configurations of the columnar structures are nearly identical.

When the sol concentration is too low, the dense structure is interrupted and there are some holes present, with an average size of approximately 50 nm, which are distributed across the whole layer and can be observed in Fig. 2, C1 and C2, with a higher hole-distribution in C1. It is speculated that when the concentration becomes too low, the ratio of solute and solvent will be too small, and each droplet will contain insufficient material to form a continuous film. Therefore, smaller amounts of PZT will be obtained compared with those with higher concentrations at a defined spraying time.

The distance between the needle and substrate (spray distance) may also affect the as-deposited structures during the electrohydrodynamic deposition process. It is believed that the sprayed droplets may experience more evaporation when they are delivered over a longer distance, which may result them to be in a more powdery state rather than in a viscous liquid state. Thus for a sol solution of a certain concentration, a transition from a continuous layer to an agglomerated deposition is expected when the sprayed distance increases during the electrohydrodynamic deposition process.

3.2. Columnar PZT growth

Amongst the investigated solutions, 0.6 M sol is well suited for processing of the columnar PZT structures. To investigate the formation of these columnar structures, further sol was deposited on a Ti/Pt-coated silicon wafer by means of electrohydrodynamic force, followed by heat treatment at 650 °C for 1200 s which is necessary to obtain dense crystalline PZT columns. Fig. 4 shows the XRD pattern of the PZT columns after heat treatment. Apart from very small volume of pyrochlore, perovskite PZT was obtained, which means 650 °C can be used for the heat treatment of columnar PZT. This result corresponds well with our previous works.[19,34]

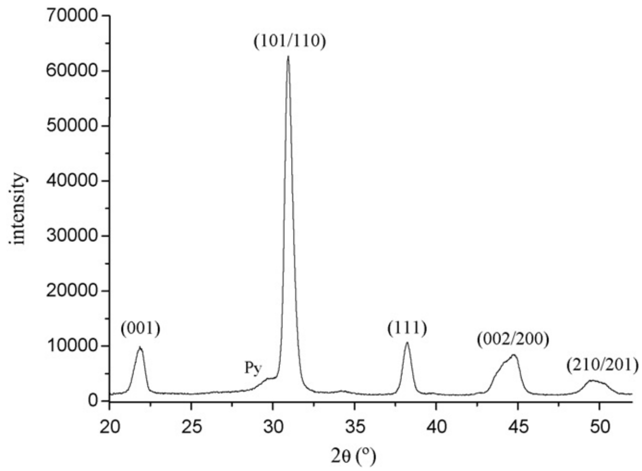


Fig. 4. X-ray diffraction pattern of the PZT columns after heat treatment at 650 °C. The very small amount of second-phase pyrochlore is indicated as Py.

To verify the growth mechanism of the column, samples were studied by observing their cross-sectional structures using SEM at deposition times of 10, 20, 40, 60, 180 and 330 s. These are shown in Fig. 5, T1–T6, respectively. The inset images show the surface morphologies of the columns when viewed at 45°. In T1 relatively dry particles have landed on the substrate with a low distribution density. After that, from 20 to 40 s (T2–T3), further particles arrive and deposit on the previously deposited particles and build up. It is evident that particles are not deposited in the spaces between columns, supporting the theorized growth mechanism given earlier. The area and height of the agglomerates increase slightly in this duration, although the area density of the columns is still small. When sprayed for 60 s (T4), a more defined columnar structure is observed with the area and height of the columns increasing. After 180 s of spraying, the area of the columns becomes stable and only the height of the columns increases with longer spraying times (T5). Finally, columns with a height of approximately 35 μm were obtained after spraying for 330 s (T6).

The observations in Fig. 5, T1–T6, correlate with the results in Fig. 2, sample C6 where the relatively dry particles obtained from the high concentration sol impact on the substrate (deposited for 60 s). The solid particles increase the roughness of the surface which will attract further particles that agglomerate on them under the electrical field, referring to preferential landing. Lengthening deposition time will favour the build up of larger and higher columns due to the same mechanism. Therefore the growth of columnar structure with increased deposition time is reasonable. The small increase in area section at the early stages is due to the slight widening of the features as the preferential landing can still occur at the edges of the columns as well as on their tops.

A deposition model for the columnar PZT growth is represented by the schematic diagram shown in Fig. 6. The dots represent the droplets and the pillar structures represent the PZT columns. Three stages are defined as: the initial stage (Fig. 6a) where the droplets (dry particles) land on the substrate; the growing stage (Fig. 6b) where the subsequently deposited particles are highly attracted to the initial ones so that the area and height of the columns increase; and the sustained stage (Fig. 6c) where the columnar structure is formed and the height of it increases with time. Fig. 7 shows the variation in the thickness of the

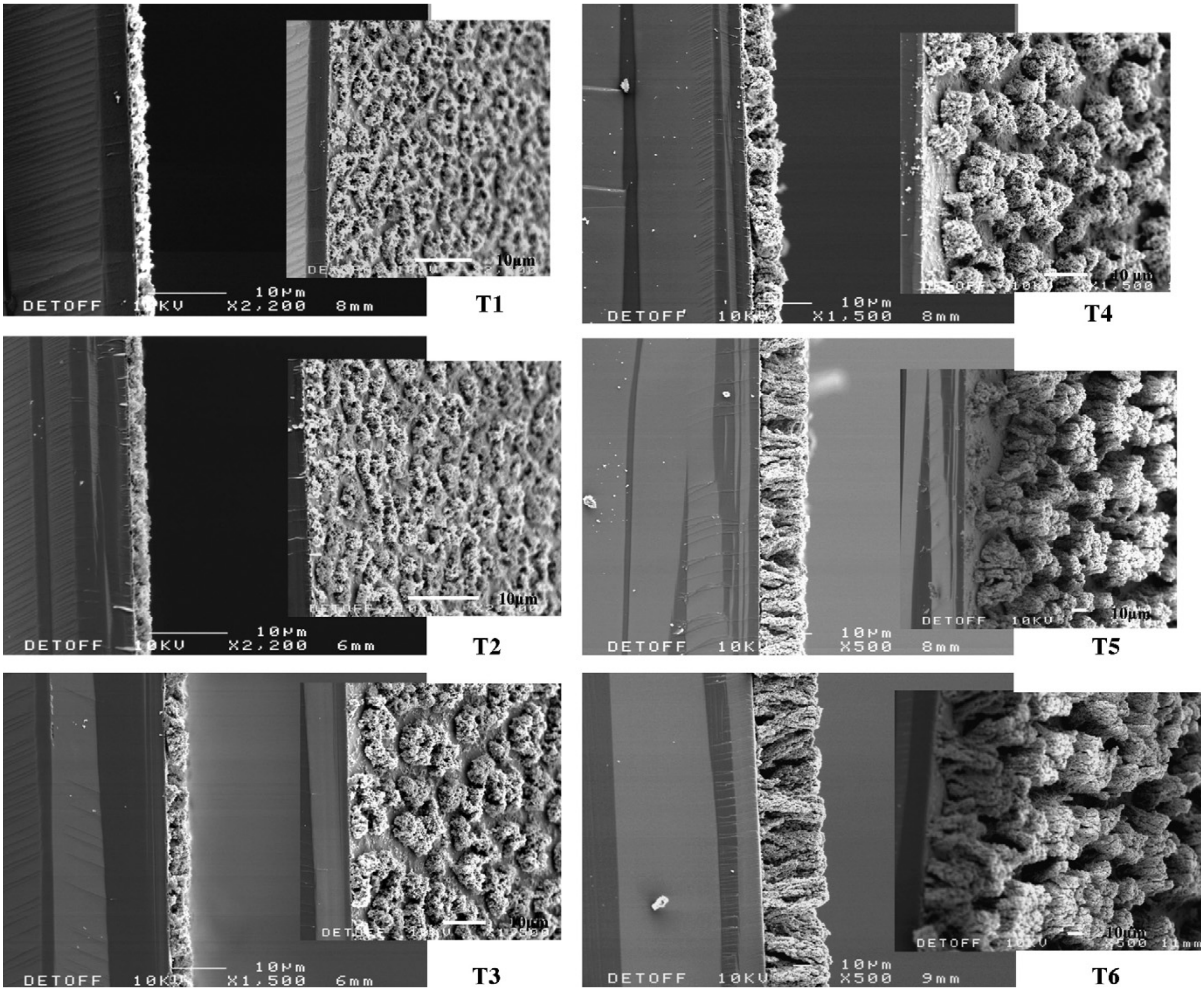


Fig. 5. Scanning electron micrographs of 650 °C-sintered columnar structures obtained at different deposition times. T1: 10 s, T2: 20 s, T3: 40 s, T4: 60 s, T5: 180 s and T6: 330 s. The inset images show the surface morphologies of each sample when viewed with a tilt of 45°.

structures as a function of time. Three different stages according to Fig. 6 are identified throughout the whole process, in which the deposition follows a ‘slow-fast’ sequence. The slope is relatively small in the initial stage, in which the droplets are landing on the surface. In this stage, it is easy for the landing particles to be distributed rather than for agglomeration to occur, which means that cluster growth is more possible in the x–y plane and the thickness increases slowly. Once the initial layer is formed by the first batch of particles, the ones following are more likely to build on the former ones, which is the growing stage. In this stage, the column grows in both the x–y plane and the z-direction by agglomeration and accumulation of dry particles. As the deposition goes on, the area of the columns becomes stable and the height of the layer increases with deposition time, which is the sustained stage. The assumed trend for this stage is marked by dotted lines, of which the slope is greater than the first two stages. However, a large deviation can be observed in the graph at longer deposition time, which is possibly because the data scatter increases as the thickness increases.

3.3. *Effect of substrate temperature*

Fig. 8 shows micrographs of the columnar PZT structure sprayed on the substrate at different temperatures and sintered at 650 °C. It is clear that different columnar structures are obtained with the increase in substrate temperature. At 75 °C, the area density of the columns is small, leaving a large void area where the silicon substrate is exposed. At 125 °C, the area density of the columns increases, leaving fine gaps between the columns. At 175 °C, the structure becomes denser and some of the columns start to interconnect in the x–y plane. These observations may be explained as follows.

First, it is believed that although 0.6 M solution yields small droplets which have undergone significant evaporation, the incoming droplets are not completely dry when they are transported to the substrate at the ambient temperature. When the substrate temperature increases, the radiative and convective heat transfer from substrate to the droplets should be taken into account since the spatial temperature between the needle and

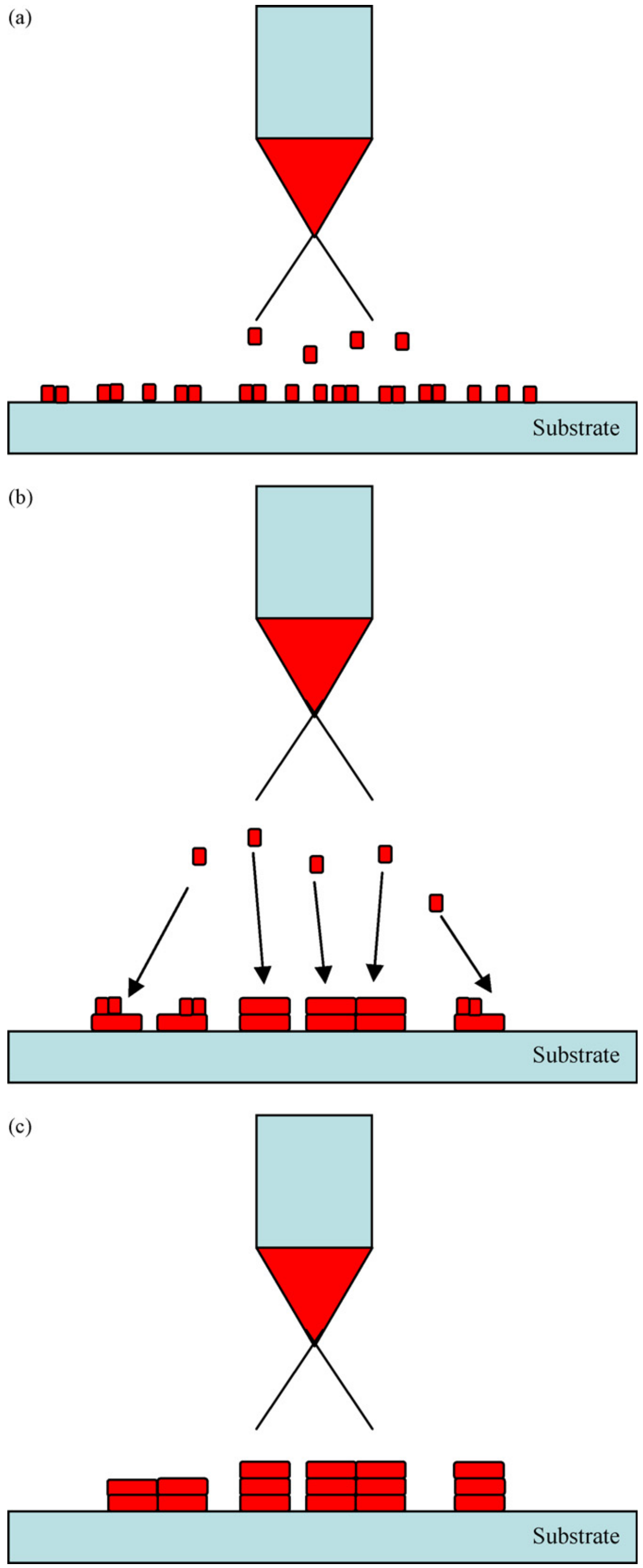


Fig. 6. Schematic representations of the different stages of growth of PZT columns by electrohydrodynamic deposition in the cone-jet mode: (a) initial stage, (b) growing stage and (c) sustained stage. The small dots represent the droplet. The pillar structures represent PZT columns.

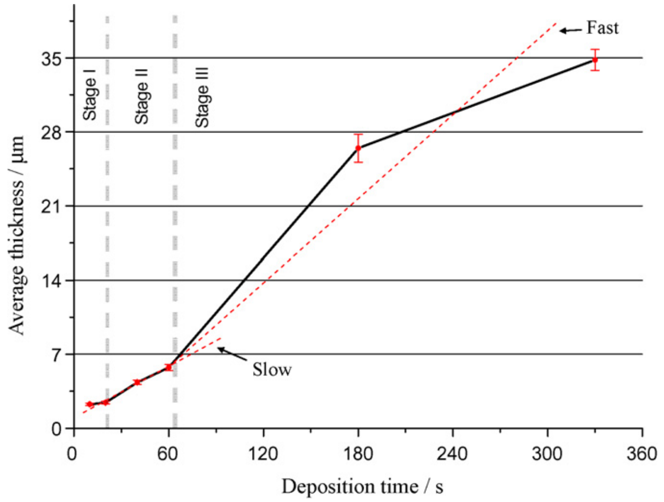
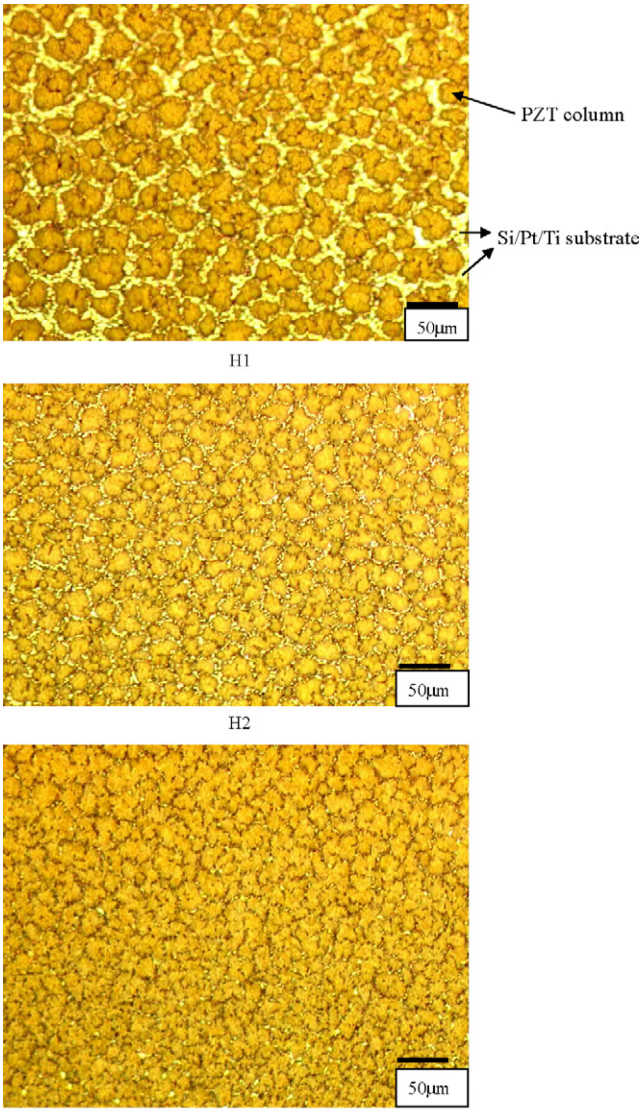


Fig. 7. Variation of the thickness of PZT columnar structure heat-treated at 650 °C as a function of time. Stage I, II and III are initial stage, growing stage and sustained stage, respectively.

substrate is also increased. Therefore the substrate temperature is a key factor when the droplets are transported to the surface. At lower substrate temperature, the incoming particles are relatively wet and still containing significant amounts of organic solvent and their reacted resultants.[19] These “wet” particles are deposited as wet columns, which are believed to be of high conductivity due to the residual solvent in them. These conductive columns connect with the ground resulting in a change of the effective profile of the ground electrode from planar to spiked. After a certain deposition time, the scale of the columns becomes large enough to disturb the electric field between the needle and the substrate. Because of the preferential landing, it is rather difficult for the particles following to deposit in the space between the columns but highly attracted to the surface of the column. However, when the substrate temperature is increased, the deposited columns are drier than those on the corresponding lower temperature substrates. These drier columns are less conductive so they will not act as such an effective extension to the ground electrode, reducing the effect on the electric field even when they present on a large scale. Therefore, the particles will have less of a tendency to deposit at the sites of perturbations leading to a finer columnar structure. Also, due to the lower conductivity, it is difficult for the electrical charges in the column to dissipate which then accumulate on the surface of the column. Thus the particles following, which contain the charges with the same polarity, will be repelled away from the column. Accordingly, it is believed that it is easier for the particles to deposit in the void area between columns due to the lower conductivity of the dry columns, resulting in the formation of interconnected structures. Additionally, the shrinkage of the deposited structure could also be considered as a contribution to this phenomenon. The columns on the lower temperature substrate are wetter and will lose more weight due to the further decomposition at higher temperature, thus incurring a large volume reduction. When the substrate temperature is increased, the columns are drier when deposited, undergoing less shrinkage at the higher temperature; this could help to explain why a



H1

H2

H3

Fig. 8. Light micrographs of columnar PZT structures sprayed at different substrate temperatures followed by heat treatment at 650 °C. H1: 75 °C, H2: 125 °C and H3: 175 °C.

denser structure can be obtained at a higher substrate temperature.

3.4. Dielectric properties

The capacitance and dissipation factor of the PZT/polymer composite at 50 kHz was 15.4 pF and 0.021, respectively. The structure was approximately 25 µm thick with circular electrodes of 740 µm in diameter. Therefore the relative permittivity of the composite ε_m is calculated as 105.

In the current model, the composite can be considered as a PZT and polymer capacitor connected in parallel. As a result:

$$C_m = C_{PZT} + C_{polymer} \tag{2}$$

where C_m is the capacitance of the mixed composite, C_{pzt} is the capacitance of the PZT columns and $C_{polymer}$ is the capacitance of the polymer phase. If the area of the tested composite is A, and the areas of the PZT columns and the polymer phases are A_{pzt} and $A_{polymer}$, respectively, Eq. (2) gives:

$$\varepsilon_m = \frac{\varepsilon_{PZT} A_{PZT}}{A} + \frac{\varepsilon_{polymer} A_{polymer}}{A} \tag{3}$$

where ε_{PZT} and $\varepsilon_{polymer}$ are the relative permittivity of the PZT columns and the polymer phase, respectively. From analysis of the image showing the columnar structures processed at the ambient temperature, the area fraction of PZT column and polymer is 0.678 and 0.322 at this temperature. As a result, Eq. (3) gives $\varepsilon_m = \varepsilon_{PZT}\cdot 0.678 + \varepsilon_{polymer}\cdot 0.322$. The relative permittivity of the photoresist is approximately 3, thus the relative permittivity of the columnar PZT material ε_{PZT} can be calculated as 154.

Compared with homogeneous PZT films produced by spin coating ($\varepsilon_{PZT} = 400$), the relative permittivity of the columnar PZT material is lower. It is believed that this is due to a number of factors. Firstly, the slight presence of second-phase pyrochlore due to the increased loss of lead during heat treatment as a result of the high surface area may be one of the reasons. Secondly, the different crystallographic crystallization of columnar PZT with respect to planar PZT is also expected to result in a change in relative permittivity. Thirdly, the porosity within the column is higher than desired due to the preferential landing of the particles during deposition, leaving air filled pores within the structure; this is possibly another reason for the low relative permittivity. Moreover, the poor connectivity between the polymer and the PZT columns may also leave to small voids, which may increase the porosity in the matrix too. The measured value of dissipation factor is reasonable for a PZT composite. However, there is a possibility that the higher porosity may also increase the dissipation factor due to a large amount of charges accumulated near the boundary of different phases (PZT/polymer/air), which may induce conduction. For a given film, the density of the films can be increased further through infiltration of liquid sol followed by thermal cycling to convert the sol into the ceramic phase as has been demonstrated with porous powder based PZT films.[35] Alternatively, as has been demonstrated here, changing the sol concentration and deposition temperature can yield significant changes in film density.

4. Conclusions

Electrohydrodynamic deposition is a novel processing method that can be used for forming columnar PZT structures. The concentration of precursor affects the as-deposited structures to a large degree, which is due to the different size of the droplets formed during electrospraying and the evaporation of the droplets during their transportation to the substrate. The preferential landing of charged particles is also a factor affecting the as-deposited structures. By changing the concentration from 0.06 to 0.6 M, structures ranging from continuous dense layers to columnar structures can be obtained. It is concluded that 0.6 M sol is well suited for the fabrication of columnar PZT by this technique. A three-stage growth process can be observed in the columnar PZT structure of which a thickness of 35 µm can be obtained after 330 s of electrospray deposition. Heat treatment at 650 °C is necessary for crystallizing the columnar PZT. Substrate temperature has a significant effect on the columnar structure produced during deposition; the structure becomes smaller and denser when the substrate temperature increases due to the changes in the conductivity of the columnar structures during deposition. A PZT/polymer composite can be produced by infiltrating a liquid polymer among the PZT columns. The relative permittivity and the dissipation factor of such a composite is 105 and 0.021, respectively. Modelling the structures as two parallel capacitors in the composite allows the calculation of the relative permittivity of PZT column as approximately 154. A certain amount of voids are distributed throughout the PZT columns and these and the boundaries with the polymer may reduce the relative permittivity and increase the dissipation factor.

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