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Formation of PZT crack-free thick films by electrohydrodynamic atomization deposition

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Abstract

In this work, electrohydrodynamic atomization was used to spray deposit lead zirconate titanate (PZT) thick films using a PZT composite sol–gel slurry. During atomization splats and clusters were generated from jet break-up. The influence of atomization–substrate distance on the characteristics of splats and clusters was analysed. At a greater distance dried clusters were predominant, which led to the formation of porous films; conversely, at a smaller distance wet splats dominated, which generated dense films. A distance of 10 mm was found to be the optimum deposition distance for this slurry to produce dense films. 28 μm thick PZT crack-free films were produced by depositing 60 layers of slurry using this technique. The resulting films had a homogenous microstructure and exhibited a relative permittivity of ∼ 220 and $d_{33,\mathrm{f}}$ of ∼71 pC N^{-1}.

Keywords: PZT; Films; Suspensions; Electrohydrodynamic atomization

1. Introduction

It is well known that piezoelectric materials are able to transform signals between electrical and mechanical impulses via the piezoelectric effect, which has been widely used in applications such as sensors, actuators, transformers and transducers.[1–4] Lead zirconate titanate (PZT) is one of the most important piezoelectric materials due to its high piezoelectric constant, relative permittivity and electromechanical coupling coefficient.[5] PZT thick films between 10 and 100 μm thick are of great interest in micro-electromechanical system (MEMS) due to the drive for miniaturisation, high power/sensitivity and system integration.[6] However, because of the limitation of low deposition rates and propensity for stress generation during processing, thin film fabrication methods, such as physical vapour deposition (PVD) [e.g. sputtering and pulsed laser deposition (PLD)], chemical vapour deposition (CVD), present significant technical challenges for producing PZT thick films in this thickness range.[7] The use of conventional bulk ceramic processing with subsequent machining and bonding is wasteful of material and time consuming.[8] Other thick film fabrication techniques based on sintering of oxide ceramic particles, such as screen printing, require temperatures normally above 1200 °C, which are likely to damage substrates and electrodes.[9]

Using a combination of conventional sol–gel processing and PZT powder processing, referred to as composite film (ComFi) technology, thick films of 2–30 μm can be fabricated using spin-coating methods at lower temperatures.[10,11] However, cracking and out of plane bending are likely to be generated due to the high stresses produced during the infiltration process, which is needed to improve the density and piezoelectric property of the films.[12]

Electrohydrodynamic atomization (EHDA) deposition provides a new way for forming PZT thick films. EHDA makes use of electrical and mechanical forces to form a liquid jet and its further disintegration into droplets[13] and was first reported by Zeleny in 1914.[14] This phenomenon can be explained by the Rayleigh limit,[15] described by $Q_\mathrm{R} = 2\pi(16\gamma\varepsilon_0 r^3)^{1/2}$ where Q_R is the Rayleigh limit charge on a drop, γ is the liquid surface tension, ε_0 is the permittivity of free space, and r is the drop radius. Fission of a highly charged drop takes place when Q_R is exceeded and the surface tension force is overcome. A metal capillary is usually used as an atomizer nozzle, and a plate, ring or point (positioned below the nozzle) serves as

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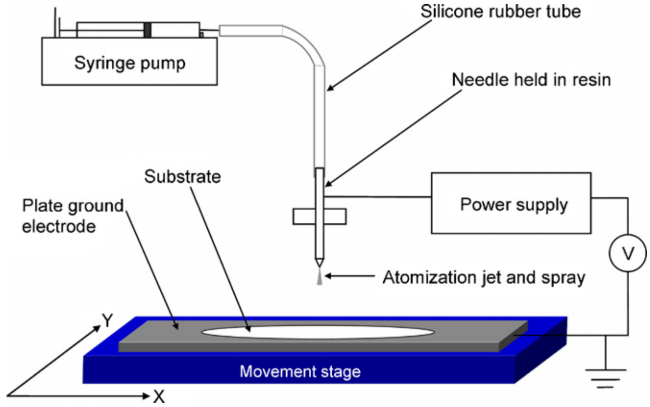

Fig. 1. Schematic representation of EHDA deposition equipment rig.

the ground electrode depending on the requirement of droplets motion.[16,17] According to the geometry of the jet and droplet, the resulting atomization modes can be mainly classified as dripping, microdripping, spindle, multi-spindle, cone-jet and multi-jet.[18] Among these the stable cone-jet mode is the most interesting functioning mode due to the production of small and uniform droplets. The investigations of EHDA using liquids are comprehensive,[19–21] but the use of suspensions is a more recent development.[16] The major advantage of this technique is its capability of forming small droplets.[22] The use of a suspension with this technique offers two distinct advantages: (a) fine deposition product and (b) less risk of nozzle blockage during processing as frequently observed with other droplet forming routes such as piezo-head drive ink-jet printing.[23] In this work a PZT composite sol–gel slurry was used with the EHDA technique enabling the formation of a wide range of PZT thick films for MEMS devices.

2. Experimental details

2.1. PZT sol

The PZT sol was prepared from the precursors lead acetate, titanium isopropoxide and zirconium propoxide. 3.55 g of titanium(IV) isopropoxide (99.99 wt.% purity) was added to 5.39 g of zirconium(IV) propoxide (76 wt.% in 1-propanol) prior to the addition of the solvents 1-propanol (99.7 wt.% purity, 5 ml) and glacial acetic acid (99.8 wt.% purity, 10 ml). An excess (9.95 g) of lead(II) acetate trihydrate was then added to the solution and the system was refluxed at a low heat for 30 min. The sol concentration was adjusted to 0.42 M by adding 13.2 ml of 1-propanol and 12 ml of acetic acid. The chemical stoichiometric ratio of the metal ions in the PZT sol was Pb 1.10:Zr 0.48: Ti 0.52.

2.2. PZT slurry

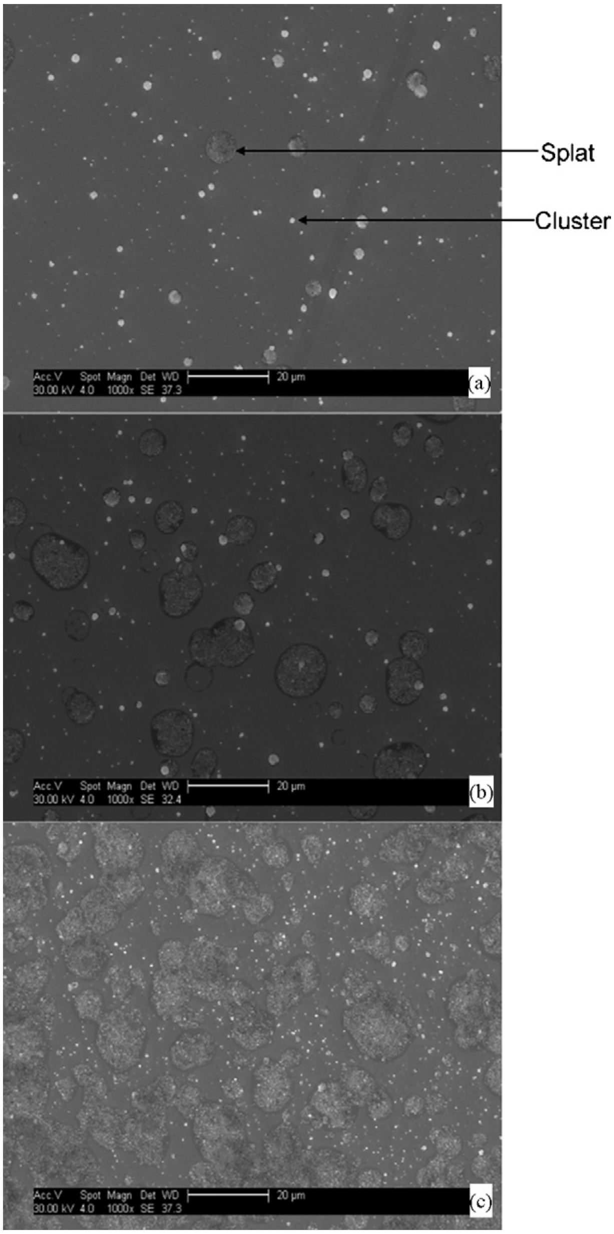

Fig. 2. Scanning electron microscope micrographs showing the one path deposition of PZT slurry at a flow rate of $2.2 \times 10^{-10}\,\mathrm{m^3\,s^{-1}}$ and different working distances and applied voltages: (a) 20 mm and 7.5 kV, (b) 15 mm and 6.5 kV and (c) 10 mm and 5.5 kV.

The composition of the PZT slurry is shown in Table 1. All the components were mixed in a nitrogen environment, then ball-mixed on a roller for 24 h. The PZT powder (PZ 26, Ferroperm, Denmark) has a mean particle size of ∼0.6 µm. 2 wt.% of a dispersant KR 55 (Ken-React Lica 38, KenRich) was added to stabilize the slurry. The addition of 4.7 wt.% of Cu_2O–PbO sintering aid, with respect to the PZT powder, helps to increase the density and piezoelectric properties of the sintered PZT film.[24] This PZT slurry has the advantage of forming thick films at a low

Table 1
Composition of the PZT slurry using in the EHDA deposition process

PZT powder	10 g
PZT sol	14.2 ml
Sintering aid Cu_2O/PbO	0.069/0.428 g
Dispersant KR55	0.2 g
Zirconia ball-milling media	100 g