Effect of porosity on the ferroelectric properties of sol–gel prepared lead zirconate titanate thin films

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Abstract

Pb(Zr$_{0.3}$Ti$_{0.7}$)O$_3$ (PZT) thin films are of major interest in micro-electro-mechanical systems for their ability to provide electro-mechanical coupling and pyroelectric coupling. In this work, dense, crack-free PZT thin films have been obtained on silicon substrates up to a thickness of 3 μm. Piezoelectric coefficients $d_{33,f}$ and $e_{31,f}$ of sol–gel processed films were investigated as a function of film thickness. Both $d_{33,f}$ ($-50\sim-90$ pC/N) and $e_{31,f}$ (2.5$\sim$4 C/m^2) values have been obtained in the whole thickness range of 1–3 μm. Increasing the thickness of a single layer introduced pores into the films. Up to 700 nm porous, crack-free single layers could be obtained. It was found that the introduction of pores into the thin films decreased the dielectric constant. Therefore, it helps increase the pyroelectric performance. A dense PZT thin film (700 nm) has dielectric constant, F_d and F_v of 372, 1.02×10^{-5} Pa$^{-0.5}$ and 0.022 m^2/C, respectively, while a porous thin film (700 nm) with porosity of 3% has dielectric constant, F_d and F_v of 210, 1.32×10^{-5} Pa$^{-0.5}$ and 0.031 m^2/C, respectively.
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1. Introduction

In recent years, the use of ferroelectric thin films of PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) family for memory, piezoelectric and pyroelectric devices has drawn considerable interest [1]. Deposition of PZT films on silicon substrates has been extensively investigated in thin film form (thickness less than 1 μm) where their advantage over bulk materials is that they can be directly deposited on platinised silicon to allow direct integration with electronics. There is a growing need for thicker PZT films (>1 μm) for applications in micro-actuators in order to produce greater power.

The sol–gel process used to deposit PZT films on substrates has been considered as one of the best methods due to its low processing temperature [2], precise control of composition [3] and low cost. However, one of the drawbacks in the use of the sol–gel process is its limit of single-layer thickness. The thickness of a single sol–gel layer usually falls in the range of less than 0.1 μm. Deposition of thicker layers than this usually results in cracks and/or formation of porosity. The required thickness is achieved by repeating the coating and heat treatment, which produces a sequence of thin layers free from cracking. Such repetitive coating procedures, however, may not be realistic in the industrial production of films. The limited thickness achievable without crack formation is one of the factors that discourage application of the sol–gel technique to the industrial production of functional ceramic coatings. The origins of cracks are widely thought to come from two sources: the shrinkage during the crystallisation anneals in the sol–gel processing, and the thermal mismatch between the film and the substrate.

Many efforts have been made to prepare crack-free, thick, ceramic coating films from gels [4–9]. The largest single-layer thickness has been reported to be 1.7 μm [9]. However, all these thick films contain, more or less, some

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porosity, which will reduce the piezoelectric and ferro-electric properties. The most pyroelectric properties of sol–gel PZT thin films (≤ 1 μm) reported in the literature so far are based on samples with a single-layer thickness of less than 0.1 μm, which tends to produce dense films. Recently, Suyal and Setter [10] added polymer into PZT precursor sol prior to spin coating to prepare porous PZT films where the porosity was in the range of 20–25%. The introduction of pores created a matrix void composite resulting in an increase of the figures-of-merit for pyroelectric applications.

The objects of the work described in the present paper were to investigate the effects of changing the individual (or single) deposited layer thickness on the deposition and microstructures of PZT films and to study the influence of this thickness on the piezoelectric and pyroelectric properties.

2. Experimental details

Pb(OOCCH$_3$)$_2$·3H$_2$O was dissolved in CH$_3$OH with heating. Ti(O^{n}Bu)$_4$ and Zr(O^{n}Pr)$_4$·Pr^{n}OH was mixed together and dissolved in a mixed solution of CH$_3$COOH and MeOH. The molar ratio of Zr/Ti was equal to 30/70. Two solutions were then mixed together and refluxed for 2 h. Pb excess was fixed at 10% extra to compensate for Pb loss during heat treatment. The concentration of the solution was 0.4 M based on Pb. This sol (Sol A) was used for making dense thin films. Thicker films were obtained by repeatedly depositing thin layers on the substrate. A typical thickness of a single layer at 3000 rpm is 70 nm. To obtain a film of 3 μm thick, more than 40 layers are needed. To make films with thicker layers, this solution was then concentrated to 1 M by distillation. A small amount of organic additive (diethanolamine, DEA) was then added to the concentrated solution (the ratio of PZT:DEA, 15:1 v/v) to increase the viscosity and avoid the creation of cracks during the preparation of thick films. Distilled water was added to the PZT precursor solution with the ratio of PZT solution to water, 10:1 v/v. The resultant solution (Sol B) was aged at room temperature for 24 h prior to use. Sol B could be used both for thick layer and thin layer deposition, depending on the spinning rate. In this study, a series of thin films were made using Sol B, each of which had a single layer of different thickness in order to investigate the relation of porosity with the single layer thickness. The thickness variation was obtained through changing the spinning rate. The porosity in the films was analyzed by using UTHSCSA Image Tool for Windows (version 2.00) combining with scanning electron microscopy (SEM) images. The SEM cross-section image of a thin film was then converted into black and white images that represent areas of pores and dense materials, respectively. Therefore, the area fraction of the pores was calculated.

The films were fabricated by applying sols onto Pt(111)/Ti/SiO$_2$/Si(100) substrates (thickness Pt/Ti/SiO$_2$=100/5/500 nm) by spin coating with a photo resist spinner (Model 1-EC101D-R790, Headway Research Inc) at various spin rates depending on the required thickness. Each wet layer went through a drying and annealing cycle.

The orientation of each film was determined by the standard $\theta - 2\theta$ X-ray diffraction (XRD) method on a Siemens D5005 diffractometer using CuK$_\alpha$ radiation and a Goebel mirror. Film cross-sections were prepared by fracture and using a focussed ion beam system (FIB-FEIFIB 200). These were examined using a SEM (Philips SFEG XL30). For the measurement of electrical properties, a set of Au/Cr electrode dots was evaporated onto the film surface either through a photoresist mask obtained by photolithography (for pyroelectric property measurements) or by a stainless steel shadow mask (diameter 2 mm) (for piezo-electric property measurements). The exposed Pt bottom electrode beneath the film provided the counter-electrode. Film thickness was determined from a Dektak surface profilometer, and compared against values taken from the SEM cross-section images. The dielectric constant and loss
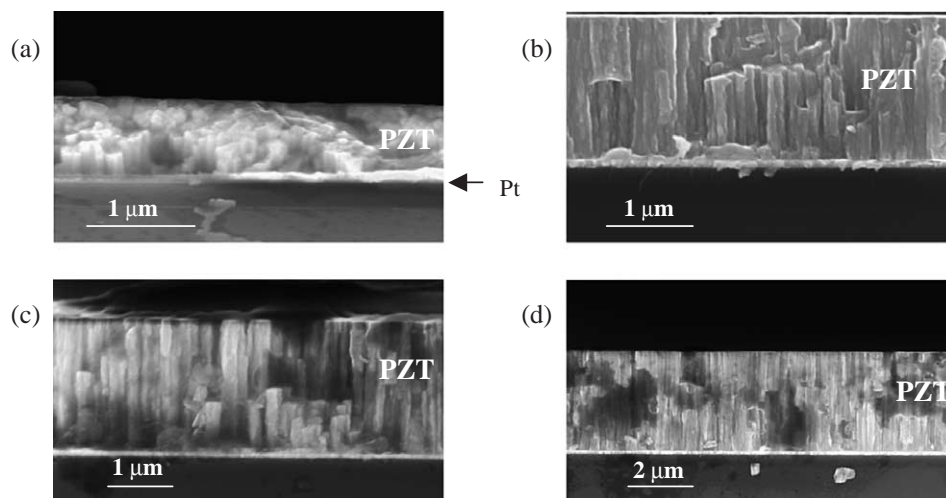

Fig. 1. SEM cross-sectional images of four samples with (a) 1; (b) 1.5; (c) 2; and (d) 3.17 μm thick.