Ceramics International 30 (2004) 1925–1927

CERAMICS INTERNATIONAL

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Microstructure and properties of PZT53/47 thick films derived from sols with submicron-sized PZT particle

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Received 4 December 2003; received in revised form 18 December 2003; accepted 22 December 2003

Available online 15 July 2004

Abstract

A hybrid sol–gel process technology has been developed for the fabrication of thick films of lead zirconate titanate (PZT) thick films. In this paper, submicron-sized PZT powder was dispersed into a 2-methoxyethanol (MOE) diluted PZT sol solution uniformly to obtain a suspension/slurry for spin-coating purpose. Thick films on platinized silicon substrate with thickness of 10 μm were obtained after annealing at 650 °C for 30 min. A higher sol solution concentration had larger single layer thickness, but a smaller one resulted in a more uniform surface. The resultant films have a composite microstructure. Dielectric and ferroelectric properties were investigated for all samples made from such process. Ferroelectric *P–E* hysteresis loop were obtained for most of them and the dielectric constant, remanent polarization, and coercive field for sample 3023 were 884, 20 μC/cm^2, and 95 kV/cm, which was comparable with bulk PZT ceramic.

Keywords: A. Film; D. PZT; Sol–gel

1. Introduction

Lead zirconate titanate (PZT) piezoelectric film integrated on silicon substrate has been the subject of considerable attention in recent years for its potential application in microelectromechanical systems (MEMS). Combining silicon micromachining techniques with PZT piezoelectric films has resulted in novel micro-devices including micro-sensors and micro-actuators [1]. The primary and simplest structure for these applications is a multilayer diaphragm with piezoelectric actuating layer on an elastic membrane. The piezoelectric actuating layer is often employed as dense micro-patterned films with a thickness of 1–50 μm and geometry of mm^2 in order to produce large displacement and generative force. Therefore, during the fabrication of this piezoelectric diaphragm, deposition of the piezoelectric films and patterning of the actuating element are two key points. One of the challenges in the research on PZT piezoelectric films deposition is to obtain crack-free, dense and uniform films with certain thickness at a temperature compatible with silicon process.

Sol–gel processing technology has successfully been developed to be a 0–3 composite method to deposit PZT thick films on Pt/Si substrate. In this method, a mixed suspension of PZT powder and PZT sol–gel precursor solution is employed to deposit PZT thick films on various substrates by spin-coating [2,3]. PZT films fabricated by this modified sol–gel process have poor mechanical quality because of its porous microstructure. Therefore, by a hybrid sol–gel processing technology, we further improved the quality of the thick films via reducing the size of PZT powders and also increasing the dispersibility of the nano-sized powders in the matrix solution [4,5]. However, although the use of the nano-sized powder is of great benefit to the uniformity of the microstructure, too small a grain size would be detrimental for the ferroelectric properties of the films. Therefore, optimizing the loaded particle size may be necessary to balance microstructure and ferroelectric properties of the deposited PZT thick films. Xerogel solution loaded with submicron-sized powder has been employed to deposit PZT composite thick films. Microstructure and electrical properties of derived PZT thick films are evaluated in this paper.

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0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.040

2. Experimental

Details of the hybrid processing technology used to deposit PZT composite thick film have been described elsewhere [6]. Submicron-sized PZT powder which was in order of 200–500 nm was obtained and then dispersed into xerogel solution using high-energy ball milling. The xerogel solution was fabricated through dissolving PZT xerogel precursor into 2-methoxyethanol (MOE) at two different concentration of 30 and 40 wt.%. The mass ratio of powder to xerogel solution is 2:3, 1:2, and 2:5, respectively. Five wight percent organic vehicle was used as dispersant to get uniform and stable slurry for film deposition. After deposited on Pt/Si substrate by spin-coating method, the PZT composite thick films were annealed at 650 °C for 30 min.

The micro-structure and the thickness of the deposited films were investigated using JEOL filed-emission scanning electron microscopy (FESEM). After coating films of Ti (5 nm) and Pt (250 nm) as top electrode, the dielectric and ferroelectric properties were measured using a HP 4284 LCR meter and RT66A ferroelectric tester.

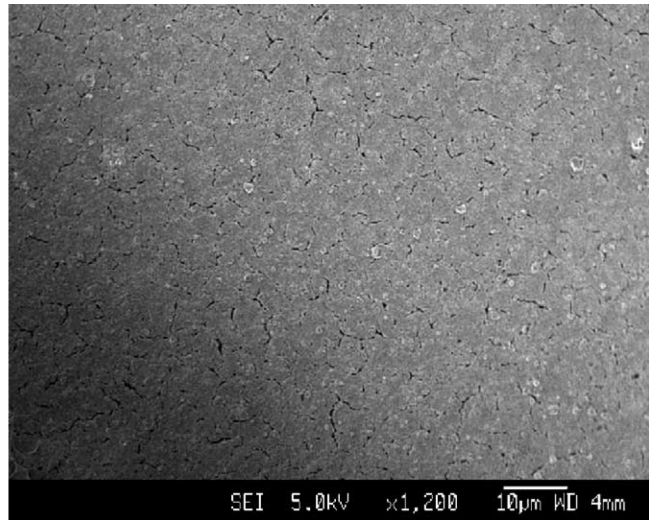


Fig. 2. Surface morphology of PZT composite thick film derived from slurry using submicron-sized powders.

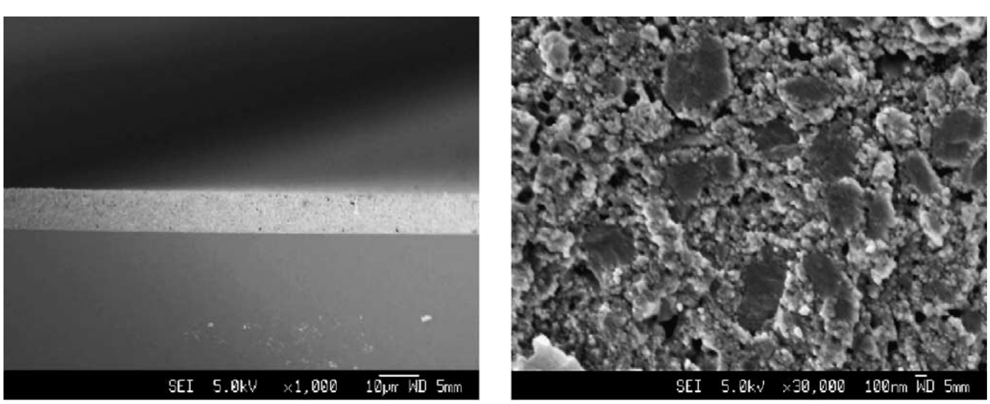
3. Results and discussion

It is clearly shown in the FESEM images that PZT thick films derived from a higher xerogel solution concentration (40 wt.%) have a larger average single coating thickness. Films derived from a smaller xerogel solution, however, have a much more uniform surface. All of the samples derived from 30 wt.% xerogel solution have an even thickness throughout the view field in the cross-section images. There difference might be contributed to the difference in viscosity between them.

Fig. 1 shows FESEM images of the cross-section of the resultant PZT composite thick films. It is shown that all the PZT composite thick films derived from slurry loaded with submicron-sized powder have a relative dense and uniform microstructure, although it is a bit coarse in comparison with that of loaded with nano-sized powders. With optimized xerogel solution and powder solution ratio, a comparable microstructure could be achieved. Moreover, as shown in Fig. 2, the as-sintered surface is reasonably smooth so that it is not necessary to polish it prior to device application.

Moreover, as shown in Fig. 1(a), there are two kinds of grain observed in the films. One has irregular shape and larger grain size in order of 300–600 nm; another one is granular and has a smaller grain size about 50 nm. The former one might origin from the particle loaded in slurry, and the latter one might crystallize and grow from the xerogel solution. Thus, a composite island structure formed where the larger grains were surrounded by the smaller grains. This kind of microstructure was a compromise result of the microstructure and the overall dielectric/ferroelectric properties, and thus, will meet the requirement of both mechanical and electrical properties.

Ferroelectric hysteresis loops shown in Fig. 3 indicate that the PZT composite thick films derived from slurry loaded



(a) (b)

Fig. 1. Cross-section of PZT composite thick film derived from slurry using submicron-sized powders: dense and uniform microstructure in the films (a), and composite structure observed in the films (b).

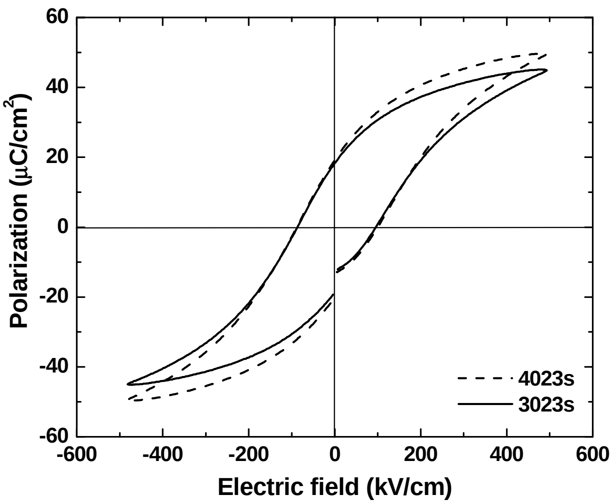


Fig. 3. *P–E* hysteresis loops of PZT composite thick films derived from slurries loaded with submicron-sized powder, and annealed at 650 °C.

with submicron-sized powder exhibit a comparative ferroelectric properties. The dielectric constant (ε_r), remanent polarization (P_r), and coercive field (E_c) for a typical PZT thick film sample 3023 are 884, 20 μC/cm^2, and 95 kV/cm, respectively. It is much higher than that of thick film using nano-sized powder and is comparable with that of bulk materials.

4. Summary

A hybrid sol–gel based process using submicron-sized powder loaded in xerogel solution has been developed to deposit crack-free, uniform, and dense PZT composite thick films on platinum coated silicon substrate. A higher sol solution concentration has larger single layer thickness, but a smaller one resulted in a more uniform surface. The resultant films have a composite microstructure, which there are two kinds of grain with different size and shape observed. Dielectric and ferroelectric properties were investigated for all samples made from such process and comparable with those of bulk PZT ceramic.

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