Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 185–193

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Sol–gel derived lead zirconate titanate: Processing, micrometer and nanometer scale patterning and characterization

Sajid Ullah Khan*, Abdul Mateen, Ibrahim Qazi

Faculty of Materials Science and Engineering, Institute of Space Technology, P.O. Box 2750, Islamabad 44000, Pakistan

Received 31 July 2015; received in revised form 12 August 2015; accepted 14 August 2015
Available online 22 August 2015

Abstract

To produce good quality films and patterns with high fidelity, the fabrication of PZT by sol–gel process was investigated, and various processing steps were studied. Sol–gel based PZT solutions were prepared and converted into thin films and patterns with spin coating and soft lithographic techniques, respectively. Structural and compositional analysis of the films and patterns was performed with XRD, and surface and topography were studied with HRSEM and AFM. Electrode deposition on the thin films and patterns were done with FIB, PLD and sputtering. The ferroelectric and dielectric properties of the film derived were also investigated.

Keywords: Soft-lithography; MIMIC; μTM; Ferroelectric materials; Oxides

1. Introduction

Lead zirconate titanate (PZT) is a perovskite-type ferroelectric material. Ferroelectrics are characterized by their spontaneous polarization, the direction of which can be reversed by external electric field. These properties actually stem from the non-centrosymmetric crystal structure. The high piezoelectric and pyroelectric coefficients of PZT made it a good candidate for commercial applications. These applications include, for example, infrared (IR) sensors, high frequency piezoelectric transducers and surface acoustic wave devices [1–4]. Because of the high dielectric constant, and polarization hysteresis, it is considered as a good candidate for non-volatile random-access memory (NVRAM) devices [5,6]. Films of PZT can be derived from both physical and chemical methods. The chemical solution deposition (CSD) methods consist of sol–gel and metal organic deposition (MOD) [7–10]. The advantages of using these methods are many fold; e.g. good control over composition, low capital cost, and ease of process integration with semiconductor technology. Most commonly precursor solutions are deposited as thin films, which are then transformed from amorphous into crystalline phase by thermal treatment.

However, the reproducibility of high quality PZT films in terms of microstructure, composition and properties is complicated. It has been reported that the solution preparation conditions have significant influence on the microstructure, orientation and electrical properties, and substantial research has been dedicated to investigate the factors affecting the processing of PZT films [11–16]. Another important area is the integration of PZT films in electric devices such as dielectrics, transducers, capacitors, and micro-electromechanical systems (MEMS). Conventional photolithography is generally not compatible with ceramic materials. The use of various subtractive steps such as wet etching with HF limits the use of materials such as PZT. Alternative techniques that are simple, cheap, and may have high throughput, and most importantly, are compatible with such materials should be adopted. Ferroelectric PZT has been patterned with soft-lithographic techniques on different length scales [17–20]. The present work on PZT has three main objectives: (1) preparation of highly reproducible solutions, (2) patterning with soft-lithographic molding techniques, and

*Corresponding author.
E-mail address: sajid.ullah@ist.edu.pk (S.U. Khan).

http://dx.doi.org/10.1016/j.ceramint.2015.08.077
0272-8842/

comparison of the resulting structures, and (3) electrical characterization of derived films and patterns. Furthermore, evolution of the shapes of patterns, effect of shrinkage, and cracking phenomena related to the evolution of the PZT phase will also be discussed.

2. Experimental

2.1. Chemicals and reagents

All chemicals were used as received, unless otherwise stated. Metal alkoxides were stored and mixed in a glove box (MBRAUN, Siemens) with water and oxygen concentrations below 1 ppm. Lead(II) acetate trihydrate (99%), titanium (IV) isopropoxide (99.99%), 2-methoxyethanol (> 99.3%), poly(ethylene glycol) (M.W. 600) were all purchased from Aldrich. Zirconium(IV) n-propoxide (70% w/w in n-propanol) and ethylene glycol (99%) were purchased from Alfa Aesar. Glacial acetic acid (99.8%), acetyl acetone (> 99%) were obtained from Merck.

2.2. Substrate and molding materials

The substrates used were Si(100), oxidized Si, and platinized Si (Pt/Si). The PDMS line molds/masters used in this work were of 4 µm, 6 µm, 8 µm, 10 µm and 12 µm widths having aspect ratios of 1, 1.5, 2, 2.5, and 3 respectively.

2.3. Solution synthesis: state of the art

A number of chemical solution processing methodologies for the fabrication of lead zirconate titanate (PZT) solution have been reported in literature [7–10]. Most common techniques make use of a lead salt and zirconium/titanium alkoxide precursors. The preparation procedure adopted in the present work will be explained below. In all cases the molar ratio of Zr/Ti was kept at 52:48 and the final concentration of the PZT solution was 0.6 M.

2.3.1. Solution A

This solution was prepared according to Yi et al. [21]. The recipe is based on the use of acetic acid and water and is the most widely adopted method for the preparation of PZT thin films. First of all, lead acetate trihydrate was dissolved in acetic acid at 80 °C for 15 min and then refluxed at 105 °C for 3 h. To this solution stoichiometric amounts of Zr-n-propoxide and then Ti-isopropoxide with the right molar ratios were added and stirred for 30 min. Finally to the solution water was added such that the final concentration of the PZT sol was 0.6 M.

2.3.2. Solution B

This solution was prepared according to the method of Schwartz et al. It is known as the inverted mixing order (IMO) process [22,23]. Here the order of mixing is slightly reversed. Firstly a Ti-alkoxide solution was added to Zr-alkoxide upon which an exothermic reaction took place. To this acetic acid was added and ultrasonicated, followed by addition of a solution of lead acetate in methanol refluxed at 105 °C. Finally, methanol and water were added.

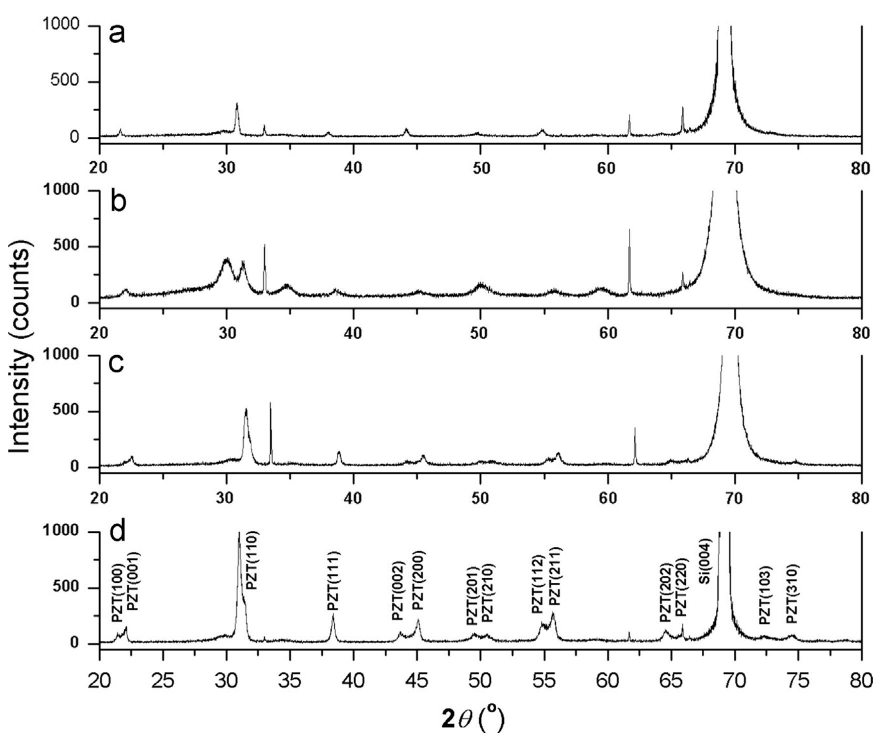

Fig. 1. XRD graphs of PZT thin films obtained from solutions A (a), B (b), C (c) and D (d). Four layers were spin coated at 4000 rpm on a Si(100) substrate, pyrolyzed on a hot plate at 280–300 °C, and finally annealed at 650 °C for 30 min.