Applied Surface Science 314 (2014) 711–719

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis and characterization of thick PZT films via sol–gel dip coating method

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ARTICLE INFO

Article history:
Received 14 February 2014
Received in revised form 28 June 2014
Accepted 7 July 2014
Available online 22 July 2014

Keywords:
PZT
Sol–gel
Dip coating
Thick film
Diethanolamine

ABSTRACT

Thick films of lead zirconate titanate (PZT) offer possibilities for micro-electro-mechanical systems such as high frequency ultrasonic transducers. In this paper, crack-free thick films of PZT have been prepared up to 45 μm thickness via modified sol–gel dip coating method. In this procedure, acetic acid–alcoholic based sol is used by applying diethanolamine (DEA) and deionized water as additives. The effects of DEA and water on the crystal structure and surface morphology of the films are investigated. The mechanisms of acetic acid and DEA complexations are introduced by using FTIR spectrometer which illustrates suitable substitution of complexing agents with alkoxide groups. DEA/(Ti + Zr) = 0.5 or water/(Ti + Zr) = 0.5 are determined as the optimum molar ratio of additives, which lead to the formation of almost pure perovskite phase with the tetragonal lattice parameters of c_t = 4.16 Å and a_t = 4.02 Å and a distortion of 2%. Values of remanent polarization and dielectric constant of 7.8 μC cm^{-2} and 1630 were obtained for 45 μm thick films, respectively.

1. Introduction

Crack-free piezoelectric thick films (>10 μm) have been investigated for a variety of device applications including micro electromechanical systems (MEMS), microactuators with relatively large generative force, ultrasonic transducers at frequency larger than 50 MHz, micropumps, pyroelectric infrared detectors, and bulk acoustic wave bandpass filters [1–3]. Morphotropic composition of lead zirconate titanate solid solution $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) has been subject of interest in the area of MEMS because of its remarkable dielectric, piezoelectric, and ferroelectric properties [4].

Fabricating piezoelectric ceramic thick films in the thickness range of 20–60 μm presents a considerable technological challenge. Researchers adopted different methods, such as screen printing [5,6], aerosol deposition [7], arc-discharged reactive ion-plating [8], and sol–gel technique [9] in order to prepare dense crack-free thick films. Most of the PZT thick films prepared by screen printing method need to be heat treated at high temperature (>850 °C) [10]. Also, these films have low density and should be infiltrated, which is a time consuming process. Gas deposition methods are suitable for fabricating thick films, but they usually require developed and prohibitively expensive apparatus [11,12].

Sol–gel technique offers some important advantages such as the ability to accurately control the sol composition at the molecular level, the ability to precisely control the microstructure of the deposited film, together with a considerable simplicity, versatility, and cost effectiveness [13–17]. There are two types of sol–gel routes, which are generally used to synthesize PZT films: typical sol–gel method and composite sol–gel method. Synthesizing a crack-free PZT thick film by typical sol–gel method was difficult due to the residual stresses induced by different shrinkage in surface and bulk of the layers during drying. Typical sol–gel synthesized PZT films crack in thicknesses of higher than 1–3 μm. However, there are few reports of PZT films with a thickness of 8–10 μm, which are obviously not thick enough for several devices such as high frequency ultrasonic transducers, micropumps, and microactuator [18]. Composite sol–gel process, which uses the suspension of PZT powder in PZT sol–gel solution, is an alternative way to get crack-free films of high thickness on coated silicon or other substrates [19]. The powders decrease the solvent volume and hence reduce the shrinkage. Also, strong bonding between the PZT particles and sol or subsequent gel reduces the tendency of film cracking [20]. However, these films have porous microstructure, which results in inappropriate mechanical quality and low

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http://dx.doi.org/10.1016/j.apsusc.2014.07.087
0169-4332/

dielectric constant value [21]. In addition, producing PZT powders and ball milling processes are time consuming. Moreover, ball milling process brings in many impurities and imperfections in the structure of the film [22].

In this article, a new acetic acid/alcoholic based sol–gel method is presented that can be used to fabricate up to 45 μm crack-free PZT thick film. Moreover, using diethanolamine (DEA) and deionized water additives in the sol–gel process result in improvement of PZT films dielectric and ferroelectric properties. In this method, the necessities for pyrolysis treatment at high temperature (400–600 °C) for each layer or rapid thermal annealing process are completely eliminated. Furthermore, the PZT thick films with morphotropic composition (53:47) were deposited on stainless steel substrates. Currently, most PZT thin films are deposited on platinized silicon ($Pt/Ti/SiO_2/Si$) wafers due to compatibility with integrated circuit technology [23]. The integrability of the film in engineering systems such as high performance sensors and actuators would be significantly improved by depositing PZT layers on a common metal substrate, such as stainless steel. Moreover, no further process would be required to provide a bottom electrode and the metal substrate could act as an electrode.

2. Materials and methods

2.1. Materials

Zirconium *n*-propoxide ($Zr(OCH_2CH_2CH_3)_4$, 70% in 1-propanol, Sigma–Aldrich), titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$, Merck), lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$, Merck), glacial acetic acid (CH_3COOH, Merck), *n*-butanol (C_4H_9OH, Merck), methanol (CH_3OH, Merck), diethanol amine (DEA, $HN(CH_2CH_2OH)_2$, Merck), deionized water (18.2 MΩ) were all in reagent grade and used as received. Commercial polished stainless steel (grade 304) with the thickness of 0.7 mm was used as a substrate for the deposition procedure.

2.2. Sol preparation

The sol preparation process of PZT thick films is as follows. First, stoichiometric amounts of titanium and zirconium alkoxides were dissolved in acetic acid. After formation of clear alkoxide solution, lead precursor (8% excess) together with methanol and *n*-butanol were added to the solution and stirred for 5 min in 85 °C. This was followed by the addition of DEA with the molar ratio (DEA/(Ti + Zr)) of 0.5 as the complexing agent and stirred for another 5 min at the same temperature. Next, the sol was mixed by deionized water with the molar ratio (water/(Ti + Zr)) of 0.5, methanol, and *n*-butanol to obtain 1 M stable PZT sol. It should be mentioned that in order to investigate the effects of DEA and water additives, various molar ratios of DEA equal to 0, 0.25, and 0.5, and molar ratios of water equal to 0, 0.5, and 2 were considered.

2.3. Film preparation

The substrates were ultrasonically cleaned in alcohol prior to use. Then, PZT sol was dip-coated onto the substrates in 10 steps, using a withdrawal speed of 30 mm/min. In each step, the films were dried on a hot plate at ~220 °C for 5 min. Drying condition for preparation of PZT thick film is optimized to prevent high amount of Pb-loss as well as incomplete elimination of organic compounds. Finally, the films were calcined at 700 °C for 1 h. The processes of sol preparation and film deposition were schematically shown in Fig. 1.

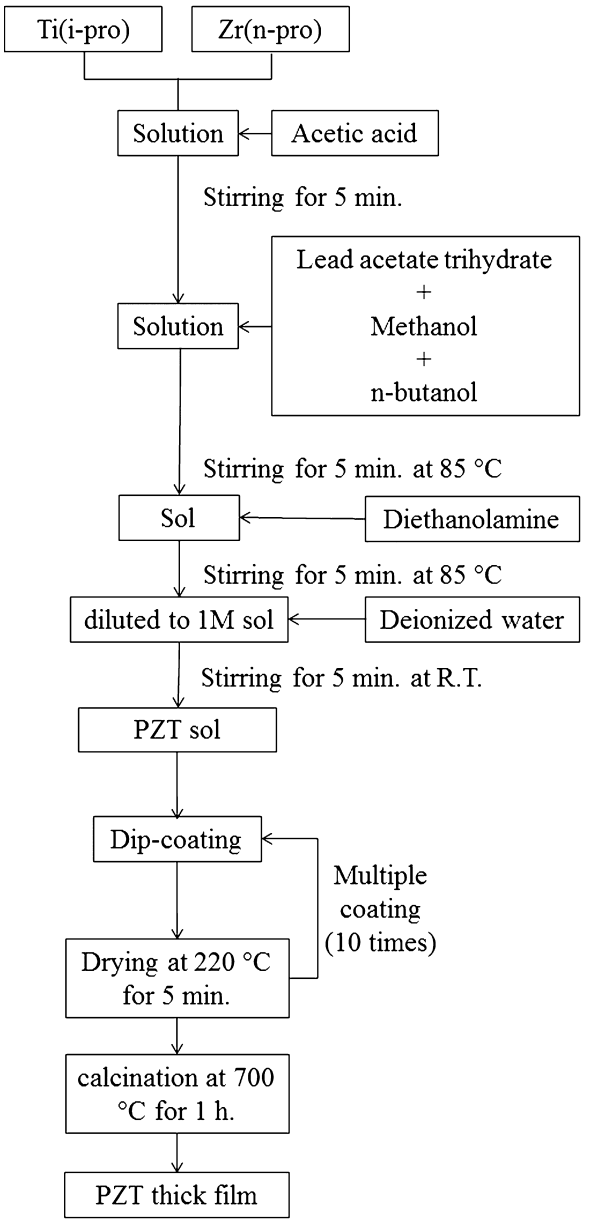

Fig. 1. Flow chart of preparing PZT thick film on a stainless steel substrate.

2.4. Characterization

X-ray diffractometer (XRD), Philips DW 1730, was utilized to examine the phase structure of PZT thick films using Cu Kα radiation. The surface morphology and the thickness of the films were examined by field emission scanning electron microscopy (FE-SEM), Hitachi S4160. A Fourier transform infrared (FTIR) spectrometer, NEXU670, was utilized to study the sol reactions. For electrical measurement, the top electrode of Au was deposited on the PZT films by means of sputtering. The size of the electrode can be as large as 10 mm × 10 mm without short-circuiting the PZT film. Ferroelectric hysteresis loop characteristics were assessed by means of a Sawyer–Tower circuit in conjunction with a TNM DS20000 oscilloscope, which applied a sinusoidal voltage waveform of 20 V at a frequency of 50 Hz. LCR meter, Gw Instek LCR-821, was used to determine the relative permittivity and dissipation factor of the films.