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Ferroelectric PLZT thick films grown by poly(1-vinylpyrrolidone-co-vinyl acetate) (PVP/VA)-modified sol–gel process

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ABSTRACT

We report the growth of ferroelectric $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ (PLZT) thick films using a poly(1-vinylpyrrolidone-co-vinyl acetate) (PVP/VA)-modified sol–gel process. A per-coating thickness of $\approx$0.66 μm has been demonstrated using PVP/VA-modified solution, which is more than doubled that of the PLZT films grown by PVP-modified method, and nearly 6 times the per-coating thickness of films prepared by conventional sol–gel process. PLZT thick films grown on LNO/Ni substrates exhibited denser microstructure, higher remanent polarization (11 $\mu C/cm^2$) and dielectric tunability (45%), lower leakage current density ($\approx 1.2 \times 10^{-8}$ A/cm^2), and higher breakdown strength ($\approx$1.6 MV/cm) than those for the samples grown on PtSi substrates. These results demonstrated great potential of using PVP/VA-modified sol–gel process for high power film capacitor applications.

1. Introduction

Ferroelectric thick films (>1 μm) of lead zirconate titanate (PZT) and lanthanum-doped PZT (PLZT) exhibit promising potentials for applications in actuators, sensors, DC/AC inverters, micro-electro-mechanical systems, and high power capacitors owing to their excellent dielectric, ferroelectric, and piezoelectric properties [1–7]. Sol–gel techniques have been used extensively for the fabrication of high quality ferroelectric films as they allow fast economical processing, easy stoichiometry control, and large coating area [8–10]. However, per-coating thickness that can be achieved by conventional 2-methoxyethanol sol–gel method is generally limited to $\approx$0.1 μm [11,12]. To fabricate thick films, repeated coating and heating processes using low-viscosity solutions are necessary, because thicker single-coating films undergo cracking or delamination on gel-to-ceramic conversion; this is energy and time consuming, and thus unfavorable for industry production.

Several approaches have been proposed to achieve thick per-coating layer while avoiding crack or delamination in ferroelectric films. One is to use propanediol or acetic acid as solvents to increase the solubility and viscosity [10,13,14]. Tu et al. reported the use of propanediol to prepare high concentration PZT precursor solution (1.6 M) for the fabrication of 1 μm single-layer PZT films [13]. However, the high concentration diol solution is unstable in air and can lead to segregation after a few hours. Another approach is to use the composite sol–gel method by dispersing fine ceramic powders into the sol–gel precursor solution [15,16]; however, the ceramic powders resulted in considerable amount of micro-pores in the films and requires intricate filtrations steps to produce dense films [16]. The per-coating thickness could also be increased by adding organic polymers such as polyvinylpyrrolidone (PVP) or polyethylene glycol (PEG) into the sol–gel solutions [17–23]. The addition of PVP could help to achieve the desired viscosity for solutions and act as capping agent for metal precursors [17,18]. The higher viscosity of solutions leads to higher per-coating thickness. The strong hydrogen bonding between the C=O groups of PVP and the OH groups of the metalloxane polymers prevents the films from cracking. By proper control and optimization of processing parameters such as sol concentration, spin coating parameters, heat treatment, and repeat times, thick films with desired thickness and minimum defects can be obtained [24]. In our earlier work, we reported the fabrication of high-quality PLZT films on platinized silicon (PtSi) and $LaNiO_3$-buffred nickel (LNO/Ni) substrates by PVP-modified sol–gel deposition [25,26]. However, the per-coating thickness appears to be limited to $\approx$0.27 μm when PVP with an average molecular weight of 10,000 g/mol is used for making dense crack-free films [26].

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In the present work, we report a modified sol–gel process to fabricate high-quality PLZT thick films by incorporating a new polymer poly(1-vinylpyrrolidone-co-vinyl acetate) (PVP/VA) into the precursor solution. To the authors' knowledge, this is by far the first report of using a PVP/AV-modified sol–gel process for making dense thick films. PVP/VA copolymer has been widely used as hot melt adhesives and photoresist binders [27]. The large molecular weight (≈50000 g/mole) indicates that it will be effective in increasing the solution viscosity. More importantly, both PVP and VA in the monomer of PVP/VA exhibit $C{=}O$ groups. It could be expected that the strong hydrogen bonds between the amide groups of PVP/VA and the hydroxyl groups of the metalloxane polymers could impede the condensation reaction in PLZT films, promote the stress relaxation in the heating-up stage, and thus prevent the formation of cracks in thick films.

2. Experimental

High-purity nickel sheets polished by chemical mechanical planarization (MTI Corp., Richmond, CA) and platinized silicon wafers (Nova Electronic Materials, Flower Mound, TX) were used as substrates. Before being coated, the substrates were wipe-cleaned with acetone and methanol in sequence. Conductive oxide $LaNiO_3$ (LNO) was first deposited on the nickel substrates by a sol–gel process to serve as a buffer layer [12,28,29]. PLZT (La/Zr/Ti = 8/52/48) stock solution of 0.5 M concentration was prepared by a modified diol synthesis route by using following raw materials (all from Sigma-Aldrich): lead acetate trihydrate, lanthanum nitrate hexahydrate, zirconium propoxide, and titanium isopropoxide, as illustrated in Fig. 1. Lead acetate was first dissolved in 1,3-propanediol with a Pb: diol molar ratio of 1:5, and refluxed at 100 °C for 1.5 h. A 20 mol% excess of lead acetate was added to compensate for lead evaporation during the annealing. Zirconium propoxide, titanium isopropoxide, and lanthanum nitrate hexahydrate were then diluted in 2-methoxyethanol in sequence. The lead-diol solution was then added dropwise to the Zr-Ti-La solution and refluxed at 115 °C for 1 h, and then cooled to room temperature. Finally, PVP/VA (with an average molecular weight of 50,000 g/mol, and VP:VA ≈ 1.3:1) was added to the PLZT stock solution at a Pb:PVP/VA molar ratio of 1:1 (PVP/VA is defined by its monomer), and mixed for 1 h at room temperature. The PVP/VA-containing PLZT solution was aged for >12 h before spin coating. The aged PLZT solution was transparent and stable for >3 months.

After being filtered through a 0.2 μm syringe filter (Whatman Inc., Sanford, ME), the PLZT solution was spin coated at 3000 rpm for 30 s onto LNO/Ni and PtSi substrates, respectively. Pyrolysis of the green films was conducted via step-wise preheat treatment [25]. Films were dried at 200 °C for 5 min, then preheated at 300 °C for another 5 min, and finally at 450 °C for 10 min, by pushing the film into separate hot zones with designated temperatures in an electric furnace. After pyrolysis, the films were crystallized at 650 °C for 10 min. The spin coating, pyrolysis, and crystallization steps were repeated to build up thick films with desired thickness. Final crystallization and densification were conducted at 650 °C for 30 min. All the coating and heat treatments were performed in ambient atmosphere.

Microstructures of the PLZT thick films were observed with a field emission scanning electron microscope (SEM, Hitachi S4700). Phase identification was performed on a Bruker D8 AXS diffractometer with general area detector diffraction system. To measure the electrical properties, platinum top electrodes (diameter of 250 μm and thickness of 100 nm) were deposited by electron beam evaporation using a shadow mask. Polarization-field hysteresis loops were measured on a Radiant Technologies' Precision Premier II tester. Dielectric measurements were made with an Agilent E4980A LCR meter using an oscillator level of 0.1 V in conjunction with a Signatone QuieTemp® probe station with hot stage. Current–voltage and the breakdown strength characteristics were measured by a Keithley 237 high-voltage source meter.

3. Results and discussion

Fig. 2 shows X-ray diffraction patterns of the 2 μm thick PLZT films deposited on different substrates using PVP/VA-modified solutions. Well-crystallized, randomly oriented PLZT phases are observed in both samples without any traceable secondary phase. Pt top electrodes are also detected for the PLZT films grown on LNO/Ni substrates. The peaks of PLZT films deposited on PtSi (Fig. 2(b)) shifted to higher 2θ angle when compared to those grown on LNO/Ni substrates (Fig. 2(a)), which can be ascribed to the different strain states in the PLZT films on different substrates [30]. According to Bragg's equation $2d\sin\theta = n\lambda$ (λ is the wavelength of X-ray), a peak shift to higher 2θ angle indicates a

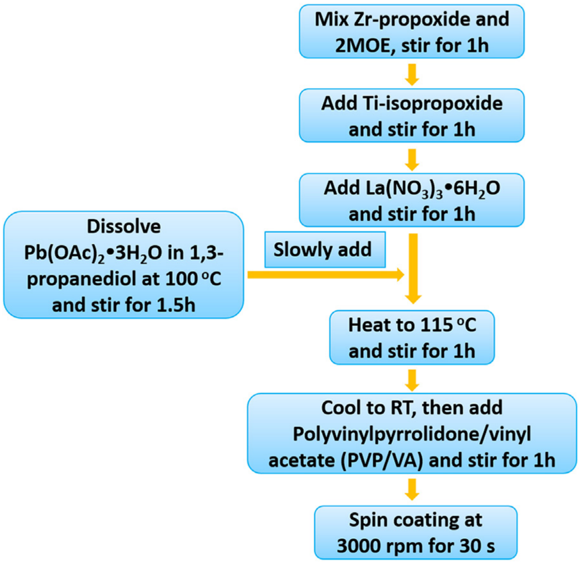

Fig. 1. Preparation of PLZT films via PVP/VA-modified sol–gel process.

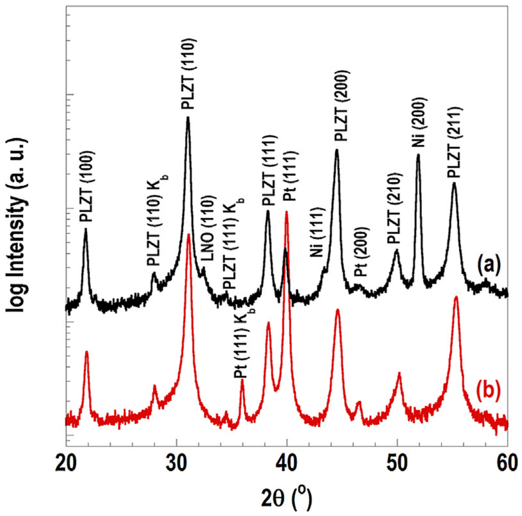

Fig. 2. XRD patterns of 2-μm-thick PLZT films grown on (a) LNO/Ni and (b) PtSi substrates.