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Crystallization kinetics of amorphous lead zirconate titanate thin films in a microwave magnetic field

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Abstract

We investigated the crystallization process and kinetics of lead zirconate titanate (PZT) thin films fabricated in the magnetic field of microwave irradiation. The PZT thin films were prepared by the sol–gel method and crystallized by microwave irradiation at 2.45 GHz. X-ray diffraction was used to identify the phases and to determine the volume fraction of the perovskite phase transformed during crystallization. Transmission electron microscopy gave information on nucleation, growth and grain structure. We also discussed how the crystallization and phase transformations correlated to the ferroelectric properties of the resultant films. We found that an intermediate phase formed during initial crystallization; it had a perovskite-like crystal structure, but it had a smaller lattice constant than perovskite PZT and contained more Ti. This intermediate phase acted as a nucleation site for the perovskite PZT, which grew with a columnar grain structure into the pyrochlore matrix throughout the film. Using Avrami's model, we found the effective activation energy for crystallization of the PZT films by microwave irradiation to be ~214 kJ mol^{-1}, lower than the activation energy for crystallization by conventional thermal processes. These results show that microwave irradiation indeed affected the crystallization of amorphous PZT thin films differently than conventional annealing.

Keywords: PZT thin film; Sol–gel; Microwave irradiation; Crystallization; Kinetics

1. Introduction

Lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$; PZT) thin films have attracted interest for many applications in non-volatile ferroelectric random-access memory [1] and micro-electromechanical systems (MEMS) [2], such as atomic force microscopy cantilevers [3] and MEMS shunt switches [4]. Many techniques for depositing ferroelectric PZT thin films have been studied, including physical methods, such as magnetron sputtering [5] and pulsed laser deposition [6], as well as chemical methods, such as metalorganic chemical vapor deposition [7] and sol–gel methods [8,9]. To fabricate well-crystallized PZT films with compositions close to the morphotropic phase boundary (Zr/Ti = 52/48), substrate temperatures or post-deposition annealing temperatures of 600–750 °C are often required. However, treatment at such high temperatures causes many adverse effects, including interdiffusion between the films and substrate as well as evaporation of lead and lead oxide from the surface, changing the stoichiometry [10,11]. Thus, fabricating PZT films at lower treatment temperatures and times would be beneficial.

The sol–gel method is an effective chemical technique for fabricating PZT thin films and has been widely studied to achieve lower processing temperatures. This method typically involves introducing a seed layer or template layer and modulating the Zr/Ti ratio and Pb excess in the precursor solution. For example, by using a seed layer of lead titanate ($PbTiO_3$), Kwok and Desu decreased the

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crystallization temperature needed to produce perovskite PZT (Zr/Ti = 53/47) films to 550 °C for 15 min [12]. Huang et al. [13] reported crystallization of PZT (30/70) films at 440 °C for 100 min, attributing the lower temperature to the formation of a Pt_xPb interlayer. Suzuki et al. reported crystallization of pure perovskite PZT (53/47) films on Pt/Ti/SiO_2/Si at 500 °C for 2 h by using a $PbTiO_3$ seeding layer with 50 mol.% excess PbO [14]. Then, by using seeded diphasic sol–gel precursors, Wu et al. reported crystallization of pure perovskite PZT (52/48) films at 410 °C for 30 h and at 550 °C for 30 min [15]. More recently, by using a low pyrolysis temperature (210 °C) to circumvent the formation of a pyrochlore phase, Li et al. reported crystallization of device-quality PZT (30/70) films at 450 °C for 1 h [16]. These reports clearly show that perovskite PZT films can be crystallized at low temperatures by introducing a seed layer and modulating the Zr/Ti ratio and Pb excess in the precursor solution; however, this process requires a long annealing time. Another way to lower the processing temperature is by annealing PZT films with special methods, including laser irradiation or laser annealing [17–19] as well as microwave irradiation or microwave annealing [20–25].

Recently, microwave heating techniques have attracted considerable attention as a new way to anneal sol–gel-derived PZT films because they offer many advantages such as low energy cost, fine resultant microstructure, short processing time and low processing temperature. For example, Wang et al. crystallized perovskite PZT (52/48) films with good electrical properties by using multimode microwave irradiation with a frequency of 28 GHz at 480 °C for only 5 min without needing to modify the precursors [20]. In single-mode microwave irradiation, the electric and magnetic fields of the microwave can be spatially separated, exposing the sample being treated to a reasonably pure electric or magnetic field. Bhaskar et al. reported crystallizing perovskite PZT films at 450 °C for 30 min in a microwave electric field generated by a single-mode 2.45 GHz microwave heating system with SiC rods acting as susceptors to absorb the microwave energy and transfer the heat generated to the film [21,22]. By using the magnetic field of single-mode microwave irradiation instead of the electric field, we crystallized PZT films similar to those of Bhaskar et al. at the same temperature and time without needing to use SiC rods as susceptors [23–25]. In one of our previous studies, we also found that the pyrochlore phase transforms into the perovskite phase via an intermediate pseudo-perovskite phase, which may be induced by microwave energy [25]. These results suggest that the nucleation and growth of perovskite grains in PZT films crystallized by microwave irradiation may be different from those processes in PZT films crystallized by conventional thermal processing. However, the mechanism by which microwave irradiation induces amorphous PZT to transform into perovskite PZT in thin films is not yet fully understood. Studying the kinetics of the formation of the perovskite phase, including its nucleation and growth, is fundamental to optimizing the processing conditions of crystallizing PZT, specifically reducing its processing temperature and time. Additionally, understanding how microwave irradiation affects the crystallization of amorphous PZT thin films in ways different from conventional thermal annealing will improve treatments of other functional thin films using microwave irradiation.

In this study, we evaluated the transformation from amorphous to perovskite in sol–gel-derived PZT films induced by microwave irradiation. Using X-ray diffraction (XRD), we determined the volume fraction of the perovskite phase transformed during this process. The nucleation site, crystal structure and grain growth were identified by transmission electron microscopy (TEM). We correlated the phase information to the ferroelectric properties of the film, assessed the nucleation and growth kinetics and discussed the mechanism by which the microwave irradiation affected the phase transformation.

2. Experimental procedure

A B-doped Si wafer with an electrical resistivity of 4–7 Ω cm was used as the substrate. To prepare the Pt/Ti/SiO_2/Si stack, the Si wafer was oxidized to produce 500 nm of SiO_2, and then Pt (200 nm)/Ti (50 nm) stacks were sputtered. The amorphous PZT films were deposited on the Pt/Ti/SiO_2/Si stacks using a sol–gel method. The precursor solution was prepared from lead acetate ($Pb(CH_3COO)_2$), zirconium-n-propoxide ($Zr(OCH_2CH_2CH_3)_4$) and titanium tetraisopropoxide ($Ti((CH_3)_2CHO)_4$). 2-propanol [$(CH_3)_2CHOH$] was used as the solvent. The final concentration of the solution was adjusted to 0.4 M with the atomic ratio of Pb:Zr:Ti = 1.1:0.52:0.48. We coated the substrate with precursor using a spin coater, operated at 1500 rpm for 10 s and then at 4000 rpm for 40 s. The coated films were dried at 120 °C for 5 min and then pyrolyzed at 250 °C for 5 min. This coating, drying and pyrolizing process was repeated once more to obtain 300 nm thick amorphous PZT films for microwave irradiation.

To produce the microwave irradiation, we used a single-mode microwave (frequency = 2.45 GHz) generator with a waveguide in TE103 mode; the wavelength (λg) of the standing wave formed in this cavity was 12.24 cm. By moving a plunger at the end of the waveguide, the electric and magnetic fields could be maximized at a specific position. Each sample ($10 \times 10\ mm^2$) was irradiated by placing it at the center of the highest magnetic field. The temperature of the samples was measured during microwave irradiation by using an infrared thermometer (CTLaser2 M; Optris, Berlin, Germany). This sensor could not measure sample temperatures below 300 °C. We measured the accuracy of the infrared pyrometer over the temperature range of 400–700 °C by using Zn and Al films with known melting point of 419.5 °C and 660.4 °C, respectively; all temperatures reported in this paper are accurate to within 5 °C. The amorphous PZT films coated on the substrates were