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Morphological and electrical investigations of lead zirconium titanate thin films processed at low temperature by a novel sol-gel system

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ABSTRACT

Lead zirconate titanate (PZT) films prepared from a new chelate-based precursor solution were dip-coated onto ITO-coated glass substrates. ITO has been chosen to preserve the transparency necessary for the specific applications. The effects of chemistry and processing conditions are explored in solution-derived morphotropic composition PZT films. The PZT transformed directly from the amorphous phase into perovskite, without going through a pyrochlore intermediate stage. The PZT phase crystallized at significantly low temperature of 450 °C following conventional heat-treatment without necessitating special irradiations, rapid thermal annealing and/or particular substrates. Ferroelectric and dielectric properties were measured and compared for PZT films processed from two sol-gel precursor systems. A remanent polarization, Pr, of 7.5 μC cm^{-2}, coercive field, Ec, of 18.7 kV cm^{-1}, dielectric constant, ε_r, of 739, and loss value, tan(δ), of 0.04 were measured for PZT film post-annealed at 700 °C.

1. Introduction

Lead-zirconate-titanate, $Pb(Zr_xTi_{1-x})O_3$ or (PZT) is considered to be one of the most important and promising functional ceramic materials among the perovskite compounds. Thin films of PZT are widely used for preparing miniaturized electronic devices like non-volatile memories, infrared sensors, optical shutters and modulator, micro-sensors and micro-actuators [1–4]. For these potential applications, the growth of good quality PZT thin films is imperative.

PZT films grown by various fabrication techniques require high temperature (~600°–750 °C) post-deposition annealing for crystallization and post-annealed films often contain both ferroelectric perovskite and non-ferroelectric pyrochlore/fluorite phases [5]. Presence of non-ferroelectric pyrochlore/fluorite phase adversely affects the structure and properties of the Pb-based ferroelectric films [6].

Over the years, efforts have been deployed to enhance the perovskite fraction at the detriment of that of eventual intermediate phases. Several options have been proposed to promote the formation of the perovskite phase at low processing temperature and to minimize microcracks. Applying a seed layer prior to PZT film deposition is considered to be one of the effective approaches for growing high quality PZT film at low processing temperature [7,8]. A suitable seed layer of optimal thickness in between PZT film and substrate not only suppresses the pyrochlore/fluorite phase formation, but also improves the crystalline quality of the PZT films grown on lattice mismatched substrates [9]. Varieties of seed layers have so far been used to develop and to control the crystalline orientation of the perovskite PZT films. As a seed layer, a thin titania (TiO_2) film promotes the crystallization of PZT films by increasing the number of active sites for perovskite phase nucleation and also provides some control over PZT film texture [10,11]. Several research groups have attempted to lower the transition temperature into perovskite phase through the adoption of different other buffer layers between electrodes and PZT, such as $PbTiO_3$ (PT) [12–14], $PbZrO_3$ (PZ) [15], (Pb,La)TiO_3 (PLT) [16], (Ba,Sr)TiO_3 (BST) [17], $SrTiO_3$ (STOII) < [9] and ITO [12]. The use of special substrate configurations such as Pt/Ti/SiO_2/Si with a perfect lattice match with PZT has been often tested. An intermetallic Pt_3Pb [18–20] phase was formed in the early stages of pyrolysis for PZT thin films deposited on Pt/Ti/SiO_2/Si substrate. The formation of this intermetallic phase has a significant role in reducing the nucleation activation energy and thereby the processing temperatures of PZT films have been reduced. Another approach to lowing processing temperature is the direct phase transformation from amorphous to perovskite PZT films by laser [21–23] or microwave irradiations

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[24,25]. The effect of heating mechanism and rate on the formation of the perovskite phase was also attempted. Particularly, rapid thermal annealing where the heating mechanism is due primarily to optical energy absorption was tested. Table 1 summarizes the research outcome regarding PZT thin films processed via sol-gel method.

The change in composition and in particular the level of Pb is reported to have important effects on the microstructure of PZT films. In general, it has been observed that the presence of excess lead in the starting product favors perovskite-phase formation, as would be expected, because of the volatility of lead species. The preferential loss of lead compounds, which occurs during the heat-treatment, may cause stoichiometry deviation. The well-known adverse effect of lead loss during PZT processing is typically circumvented by providing excess lead. Therefore, the measures described above are often accompanied with the use of lead-rich precursor systems. However, excess lead increases the risk of the retention of PbO at grain boundaries or as a second phase [26] and shifts the PZT composition toward the titanium-lean side, because TiO_2 has higher solubility than ZrO_2 in the PbO liquid phase. This may negatively affect the ferroelectric properties of the final product. In addition to concerns about lead toxicity, substantial degassing due to Pb and/or PbO evaporation may leave voids resulting in less dense material [27]. Therefore, for the present study, a series of perovskite PZT (52/48) films was prepared using a stoichiometric starting composition. Deviation from stoichiometry can also result from lead diffusion. Bose et al. reported that compared to Pb-loss by volatilization, Pb-loss from PZT matrix due to diffusion is more pronounced during crystallization of PZT film by conventional furnace annealing [28].

For many of device applications, PZT thin films need to be deposited on top of an underlying transparent semiconductor circuit. Therefore, it is of practical importance to carry out the annealing for the pyrochlore and/or amorphous phase-to-perovskite transformation at the lowest possible temperature (typically <450 °C) and thermal treatment time in order to avoid any thermal and electrical degradation to the underlying layer. In particular, in order to preserve their electro-optical performance and guarantee high thermal stability, transparent conducting oxides (TCO) should not be subjected to temperatures higher than 450 °C under oxidizing atmosphere. The successful deposition of PZT thin films on TCO materials at low temperature will facilitate the integration of both ferroelectric and optoelectronic devices. Therefore, lowering the processing temperature is another challenge that should be realized to prevent inter-diffusion between the elements of the films and the substrate and to prevent the evaporation of lead and lead oxide from the surface of the films. Furthermore, thermal stress developed during the high temperature annealing may affect the long-term reliability of the ferroelectric devices [29].

Various techniques for synthesizing good quality PZT thin films have been developed rapidly over the years like metal oxide deposition (MOD) [30], radio frequency (RF) magnetron sputtering [31,32], sol–gel [33], laser ablation [34], etc. Sol-gel has been widely used as a low-temperature deposition method for multi-oxide thin films, and powders.

In this work we propose a novel, simple, and straightforward system for the deposition of transparent crack-free PZT thin film which only involves mixing of precursors to appropriate stoichiometry and in proper order, at room temperature. Acetoin with appreciably low boiling point is used to simultaneously dissolve the precursors of lead, zirconium, and titanium. This PZT preparation technique will eliminate the time consuming and complicated procedures such as refluxing, and therefore, provide for their low-cost and large-scale production. This article reports the preparation of PZT (0.52/0.48) films formed at temperatures as low as 450 °C, to the best of our knowledge, one of the lowest reported anywhere for sol-gel processed PZT films. We seek to better understand the interplay of the solution chemistry and annealing temperatures, on the crystallographic structure and electrical performance of PZT films.

2. Experimental

2.1. Solution synthesis

The most significant processing issue facing the PZT system is the volatility of the Pb-cation at crystallization temperatures > ≈ 600 °C. In sol-gel processing, DEA and TEA are often used as stabilizing agents. During the firing of the gel films, these stabilizers reduce Pb^{2+} ions to metallic lead, which is highly volatile. Similarly, the reduction of Cd^{2+} ions to the metallic state has been previously observed [35,36] in the case of the gel prepared from the $Cd(OAc)_2$-DEA system. In order to limit the lead volatility, the commonly used ligands have been substituted by acetoin. This compound is tested for the first time in thin PZT film deposition and no excess lead was introduced.

The preparation of the stock solutions followed two formulations. In formulation 1, lead zirconate titanate stock solutions with morphotropic composition were produced by first premixing appropriate amounts of zirconium (IV) butoxide [$Zr(OC_4H_9)_4$] (80 wt.% in 1-butanol, Aldrich) with titanium (IV) isopropoxide

Table 1
Deposition conditions and phase formation of PZT thin films deposited by sol-gel technique.

Composition (Zr/Ti)	Excess Pb	Substrate	Phase transition	Transition temperature into pure perovskite (°C)	Refs.
53/47	0–10 mol%	$Pt/Ti/SiO_2$	Pyro → Perov	600	[5]
52/48	–	$SrTiO_3$/sapphire	Amorphous → Perov	550–700	[9]
53/47	50%	$Pt/Ti/SiO_2/Si$	Pyro → Perov	500	[12]
52/48	10–30 wt%	$Pt/Ti/SiO_2/Si$	Pyro → Perov	650 (Trace pyro remains)	[45]
54/46	5 mol%	Si (100)	Pyro → Perov	650	[48]
50/50	5 mol%	$Pt(1\ 1\ 1)/Ti/SiO_2/Si(100)$	Pyro → Perov	550	[59]
52/48	–	Pt/Si	? → Perov	650–750	[60]
53/47	15%	Pt/GaAs	Pyro → Perov	550–600	[61]
_	–	Sapphire	Pyro → Perov	650	[62]
53/47	0–10 mol%	(111) Pt	Pyro → Perov	650	[63]
53/47	10 mol%	$Pt/TiO_2/Si_3N_4/GaAs$	Pyro → Perov	650	[64]
53/47	10 mol%	$Pt/Ti/SiO_2/Si$	Pyro → Perov	600	[65]
65/35	10 mol%	$Pt(111)/Ti/SiO_2/Si$	Pyro → Perov	700 (partial conversion)	[66]
_	–	$Pt/Ti/SiO_2/Si$	Pyro → Perov	675 (partial conversion)	[67]
52/48	0 mol %	ITO/Glass	Amorphous → Perov	450	This work