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Preparation and Characterization of Sol-Gel Derived Epitaxial and Oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ Thin Films

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Epitaxial and oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films were prepared from nonhydrolyzed polymeric precursors. PZT thin films with a single (001) orientation were prepared on $SrTiO_3$ (100) and MgO (100) substrates by solid-phase epitaxial growth. Crystallization of sol-gel PZT with a (111) preferred orientation was also observed on sapphire (0001) substrates. The guided wave modes were excited by a prism coupling method for PZT thin films crystallized on MgO (100) at 700 °C, and the verified refractive index was as high as 2.561. Dielectric constant and remnant polarization of epitaxial PZT thin films, crystallized on conductive Nb-$SrTiO_3$ (100) substrates at 650 °C, were 448 at 10 kHz and 15 $\mu C/cm^2$, respectively.

KEYWORDS: PZT thin films, sol-gel, $SrTiO_3$, MgO, sapphire, epitaxy, optical waveguide, dielectric constant, polarization

1. Introduction

Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films are promising candidates for a variety of potential device applications such as nonvolatile memory (FRAM), dynamic random access memory (DRAM), and sensors. These potential applications are possible due to superior properties of PZT, including a high dielectric constant, large remnant polarization, and large piezoelectric and pyroelectric coefficients. Busch *et al.* also demonstrated an electrooptic effect in a sol-gel derived PZT planar waveguide on $SrTiO_3$ indicating the possibility for optoelectronic applications.[1] Many of these properties are maximized near the morphotropic phase boundary at a composition corresponding to $x=0.52$. For the device applications, current major concerns in terms of thin film processing are crystallinity (orientation and phase purity) and stoichiometry (lead content) of PZT. In order to resolve these issues, vapor phase growth processes and a sol-gel process were actively investigated. Vapor phase growth processes, including rf sputtering, pulsed laser deposition (PLD), and metalorganic chemical vapor deposition (MOCVD), are generally costly and difficult to compensate for lead loss, although they are advantageous in preparing oriented or epitaxial PZT thin films because the produced species have relatively high mobility to form epitaxial nuclei on substrates. For instance, electrical properties of oriented or epitaxial PZT fabricated by reactive sputtering,[2] PLD,[3,4] and MOCVD[5] have been reported. In contrast, the sol-gel process is useful in processing cost reduction, stoichiometric composition control, and large-area fabrication. However, the sol-gel process has generally been used to prepare polycrystalline ferroelectric thin films since the process involves the crystallization of coated metalorganic materials where homogeneous nucleations are favored.

We have succeeded in sol-gel solid-phase epitaxial growth of $LiNbO_3$ thin films on sapphire substrates.[6,7] It was also established that their change in orientation from epitaxial to oriented or random with an increase in the amount of water contributed to hydrolysis of metal alkoxides. With a similar strategy using nonhydrolyzed metal alkoxide precursors, epitaxial $LiTaO_3$ thin films were obtained on sapphire.[8] For lead titanate-based ferroelectric materials, although sol-gel derived oriented and epitaxial thin films have been reported,[9–12] studies have been few on the preparation and properties of sol-gel derived PZT thin films with near-single-crystal qualities. In the present study, we produced near-single-crystal PZT thin films on $SrTiO_3$ and MgO substrates, and oriented PZT on sapphire substrates through crystallization of amorphous films derived by a sol-gel based method. Optical and electrical properties of these thin films were also examined.

2. Experimental

The precursors were synthesized by reacting lead acetate, zirconium isopropoxide and titanium isopropoxide in 2-methoxyethanol. No excess lead was added, and the composition of the precursors was fixed at the morphotropic composition of Pb:Zr:Ti= 1:0.52:0.48. Through distillation and refluxing of these starting materials in 2-methoxyethanol under dry nitrogen atmosphere, stable polymeric complex precursors were obtained without hydrolysis. Residual lead acetate in the precursor complexes was reduced to less than 10 at.%, and by-products in the precursor solutions were removed by successive vacuum distillations and redilutions. Their structural elucidations were done by ^1H NMR spectroscopy. $SrTiO_3$ (100), Nb-doped conductive $SrTiO_3$ (100), MgO (100), and sapphire (0001) single crystals with mirror surfaces were used as substrates. These substrates were cleaned in organic solvents, etched in HCl solution, and rinsed in deionized water. MgO substrates were annealed at temperatures above 1000 °C in air for the improvement of MgO surface quality.[13] The substrates were spin-dried with ethanol and spin-coated with the precursors at 2000 rpm in a dry nitrogen environment. In differential scanning calorimetry of dried precursors, the exothermic peak due to oxidation and pyrolysis of organic groups of the methoxyethanol-based precursor was observed at temperatures as low as 210 °C. Therefore, the coated substrates were heated in oxygen at 300 °C for 2 min for oxidation and pyrolysis to obtain dense amorphous films. The preannealed films were immediately heated to crystallization at a specified temperature for