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Preparation and electrical properties of sol–gel derived $(1-x)Pb(Sc_{1/2}Nb_{1/2})O_3-xPbTiO_3$ ($x=0.6$) thin films

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Abstract

The films of $(1-x)Pb(Sc_{1/2}Nb_{1/2})O_3-xPbTiO_3$ ($x=0.6$, PSNT(40/60)) were successfully deposited on $Pt/Ti/SiO_2/Si$ substrates via spin coating method. Using combination of homogeneous precursor solutions and two-step heat treatment, it was possible to obtain the PSNT(40/60) thin films of perfect perovskite phase with virtually no pyrochlore phase after annealing just above 550°C. The root-mean-square surface roughness of a 240-nm-thick film was 3 nm as measured by atomic force microscope (AFM). The PSNT(40/60) films annealed at 650°C showed a well-saturated hysteresis loop at an applied voltage of 7 V with remnant polarization (P_r) and coercieve voltage (V_c) of 14 μC/cm^2 and 1.5 V. The leakage current density was lower than 10^{-6} A/cm^2 at an applied voltage of 7 V. © 2001 Elsevier Science Ltd.

Keywords: Ferroelectric properties; $(1-x)Pb(Sc_{1/2}Nb_{1/2})O_3-xPbTiO_3$; Sol–gel processes

1. Introduction

Relaxor ferroelectrics and especially their solid solutions with $PbTiO_3$(PT) have attracted much attention recently due to their remarkable dielectric and electromechanical properties.[1] The large piezoelectric responses and unique dielectric behaviors make these materials very fascinating for high frequency ultrasonic transducers, actuators, pressure sensors, various dielectric and microelectromechanical systems-based applications.[2] For these applications benefiting from integrated devices, deposition of relaxor ferroelectrics-PT thin films is required. $Pb(Sc_{1/2}Nb_{1/2})O_3$(PSN) is a well-known relaxor ferroelectric. In the bulk state, their PT-solid solutions and other PSN-based systems such as lantanium (La) doped PSN-PT have been widely studied for electromechanical and dielectric properties.[3] The solid solutions of $(1-x)$ PSN-xPT near morphotropic phase boundary (MPB, $x\approx0.42$) show excellent piezoelectric coefficients and dielectric constants.[4] Tyunina et al. prepared PSNT thin films with compositions near the MPB by pulsed laser deposition (PLD) on $La_{0.5}Sr_{.5}CoO_3/MgO(100)$.[5] However, the preparation and characterization of the sol–gel derived PSNT films on conventional $Pt/Ti/SiO_2/Si$ substrates have not been reported yet. The sol–gel technique has been used extensively for the preparation of ferroelectric films, due to the advantages of high-purity, low processing temperature and cost effectiveness. Thus, in this study, we report the preparation of the PSNT(40/60) thin films on $Pt/Ti/SiO_2/Si$ fabricated by the sol–gel technique and their structural, electrical, and ferroelectric properties.

2. Experimental procedure

The PSNT(40/60) thin films were processed from an alkoxide solution precursor. The solution was prepared under controlled inert gas atmosphere. Lead acetate trihydrate $[Pb(CH_3COO)_2 3H_2O]$, scandium acetate hydrate, niobium ethoxide $[Nb(C_2H_5O)_5]$ and titanium isopropoxide $[Ti((CH_3)_2CHO)_4]$ were used as starting chemicals and 2-methoxyethanol as solvent. To compensate for lead loss during thermal annealing, 10 mol% excess lead was added to the precursor solution. Lead acetate trihydrate and scandium acetate hydrate were dissolved separately and dehydrated in 2-methoxyethanol. Niobium ethoxide

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and titanium isopropoxide were dissolved and mixed together with Sc-alkoxide solution. The mixed Sc–Nb–Ti alkoxide and the Pb-alkoxide solution were finally reacted and refluxed to a concentration of 0.3 M.

The precursor solution was deposited on Pt/Ti/SiO_2/Si substrates by spin-coating technique. The as-deposited layer was dried on a hot plate in air at 150°C for 7 min to evaporate alcohol and organics. The spin-coating and drying process was repeated three times, and then the PSNT(40/60) thin films were finally pyrolyzed and annealed at various temperatures in a pre-heated furnace. The thickness of the annealed films with three layers was measured by cross-sectional SEM and found to be 0.24 μm.

The structural analysis of the films was investigated by a Rigaku X-ray diffractometer using CuK_α radiation ($\lambda = 1.5418$ Å). The surface morphology of the films was characterized by an atomic force microscope (AFM, Digital Instrument's Dimension 3000) using a trapping mode with amplitude modulation. For electrical measurements, the top platinum electrodes of 0.2 mm diameter and 80 nm thickness were deposited by rf sputtering. The top electrodes were annealed at 550°C for 10 min. The P–V hysteresis loops were measured using a standardized RT66A ferroelectric test system operating in the Virtual-Ground mode. The current density–voltage (J–V) characteristics were studied to find the feasibility of utilizing the sol–gel derived PSNT(40/60) thin film for application.

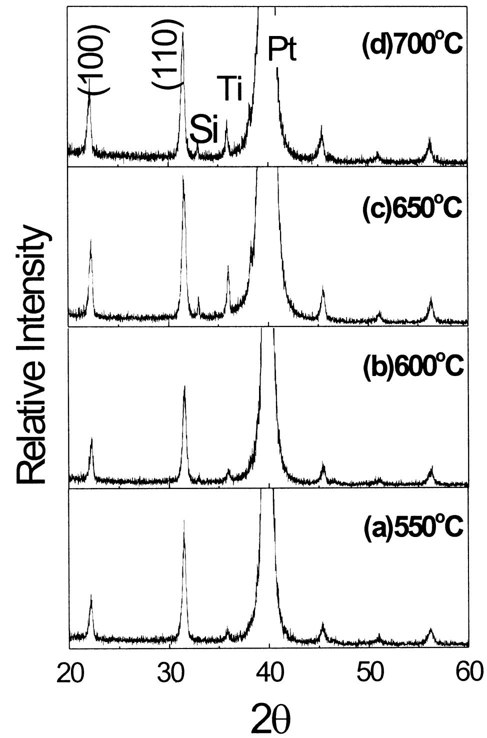

Fig. 1. X-ray diffraction patterns of PSNT(40/60) films on Pt/Ti/SiO_2/Si substrates annealed at (a) 550°C, (b) 600°C, (c) 650°C, (d) 700°C.

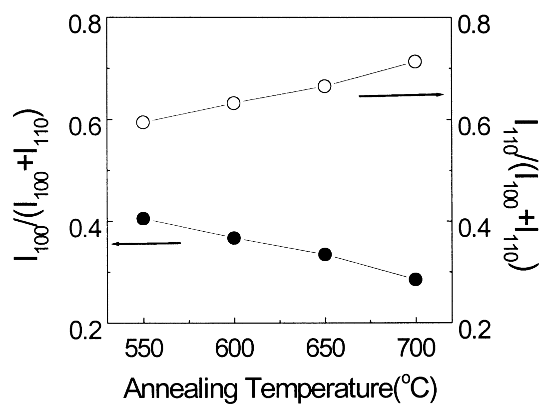

Fig. 2. Peak intensity ratios of the two orientations of PSNT(40/60) films as a function of annealing temperatures on Pt/Ti/SiO_2/Si substrates.

3. Results and discussion

Fig. 1 shows the XRD patterns of PSNT(40/60)/Pt(100nm)/Ti(10nm)/SiO_2/Si thin films annealed at various temperatures. All the PSNT(40/60) thin films were annealed above 550°C temperatures and they are of single perovskite phase without pyrochlore phase. No other phases are observed. The diffraction patterns indicate that our thin films are randomly oriented with slight (110) preferential tendency regardless of annealing temperatures. By increasing the annealing temperature, however, the fractional intensity of the (110) peak, $I_{(110)}/\{I_{(110)} + I_{(100)}\}$, decrease and that of the (100) peak, $I_{(100)}/\{I_{(110)} + I_{(100)}\}$, increases as shown in Fig. 2. In addition, the line splittings of (001)/(100) and (101)/(110) peaks of the PSNT(40/60) films are not found, line broadening of a pseudocubic phase is observed as already reported in other ferroelectric-PT thin films.[6] This broadening may well be attributed related to structural deformations due to the microstrains at grain boundaries and at interfaces between the PSNT(40/60) films and the Pt-electrode, Pb loss and due to the diffusion and oxidation of Ti in the bottom electrode during annealing.[6]

The SEM micrographs of PSNT(40/60) films as a function of annealing temperature are illustrated in Fig. 3. It can be seen that the microstructure of the films is strongly influenced by the annealing temperature. The average grain size rapidly increases from 50 to 275 nm, as the annealing temperature increases from 550 to 700°C. The grain size as a function of annealing temperature is illustrated in Fig. 4. Fig. 3 also exhibits that dense and homogeneous films without thermal cracks are synthesized.

Fig. 5 shows the three-dimensional AFM image of a PSNT(40/60) film annealed at 650°C for 30 min. The root-mean-square surface roughness of the 1 μm×1 μm region is 3nm, with the maximum peak-to-valley height of approximately 26 nm which is generally reported in the sol-gel derived thin films.[1,2]

The P–V hysteresis loops for a $PSNT_{40/60}$ films annealed at 650°C for 30 min are plotted in Fig. 6. The films are almost symmetrical in reference to the voltage axis and display typical remnant polarization (P_r) and coercive voltage (V_c) values of 14 μC/cm^2 and 1.5 V, respectively, at an applied voltage of 7 V, although the dielectric constants are somewhat lower than is reported for bulk ceramics.[3,4] The well-saturated hysteresis loop profiles indicate that the films are in the ferroelectric perovskite phase.

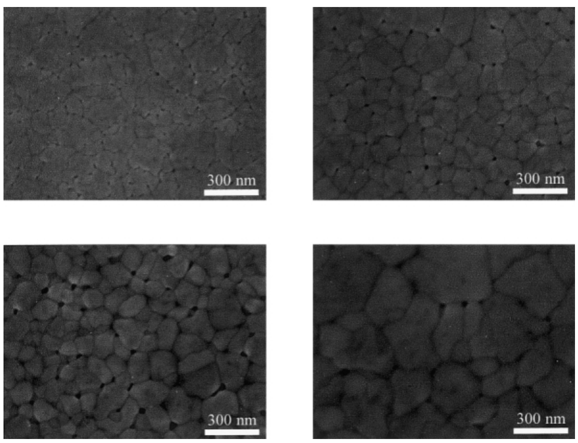

Fig. 3. Plan view SEM micrographs of PSNT(40/60) films annealed at (a) 550°C, (b) 600°C, (c) 650°C, (d) 700°C for 30 min.

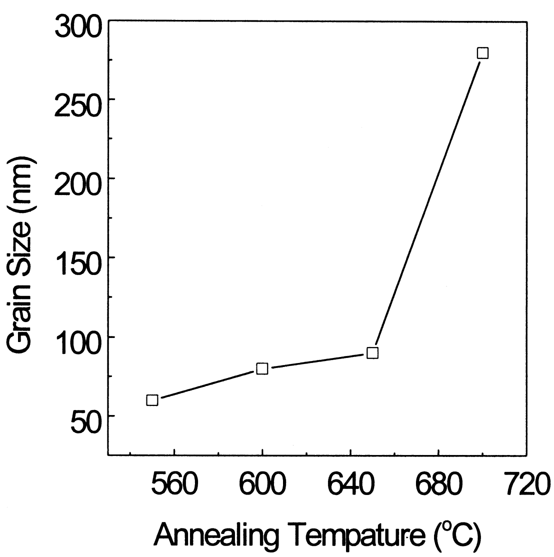

Fig. 4. Grain size of PSNT(40/60) films as a function of annealing temperatures on $Pt/Ti/SiO_2/Si$ substrates.

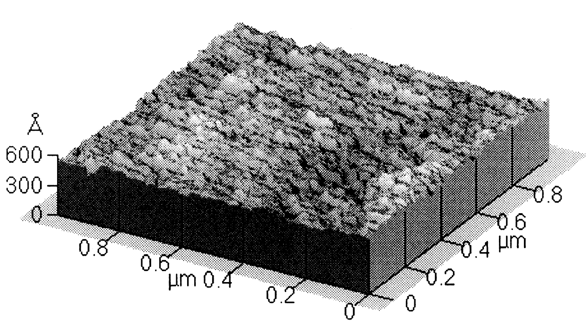

Fig. 5. The AFM picture of PSNT(40/60) films on $Pt/Ti/SiO_2/Si$ substrates annealed at 650°C for 30 min.

Fig. 7 exhibits the leakage current density vs voltage curve of a PSNT(40/60) film after annealing at 650°C for 30 min. For applied voltage smaller than 2.5 V, the leakage current density is below 10^{-6} A/cm^2. As the voltage increases above 2.5 V, the leakage current density increase around 10^{-5} A/cm^2 which is usually observed for the lead-based ferroelectric capacitors with some defects. According to the previous reports, the leakage current density is affected by the microstructure and surface morphology of the films, the very poor chemical affinity between the PSNT film and the top/bottom Pt-electrodes and the Schottky barrier height formed at the interface between the film and the electrodes.[6,7] Thus we consider that the leakage current density in the $Pt/PSNT_{40/60}/Pt/Ti/SiO_2/$ Si capacitors is related to the microstructure as well as to

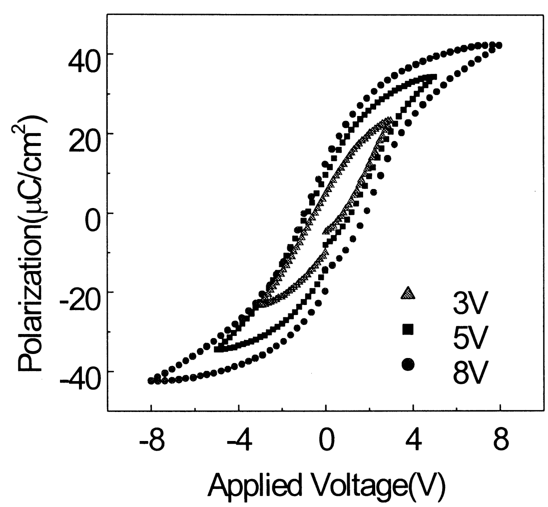

Fig. 6. Hysteresis loops of PSNT(40/60) films annealed at 650°C for 30 min with thickness of 240 nm at various applied voltages.

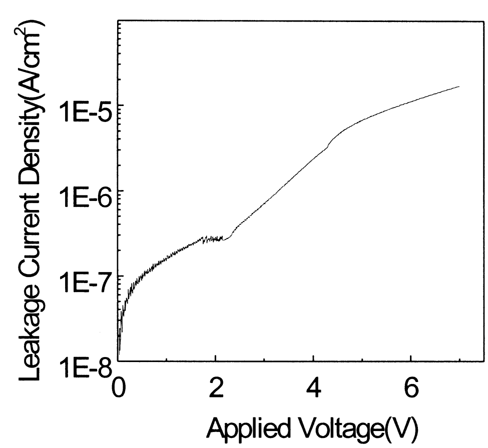

Fig. 7. Leakage current density–voltage curve of PSNT(40/60) films on $Pt/Ti/SiO_2/Si$ substrates annealed at 650°C for 30 min.

the shown in Figs. 3(c) and 5 and the unsatisfactory interface between the PSNT(40/60) film and the Pt-electrodes which can be overcome by control of the experimental factors such as incorporating a seeding layer, modifying the electrodes and optimizing heat-treatment.

4. Summary

Based on our study of crystallization, microstructure, surface morphology and electrical behaviors in PSNT (40/60) thin films on the Pt(100 nm)/Ti(10 nm)/SiO_2/Si substrate, the following conclusions can be drawn:

(1) PSNT(40/60) thin films on the Pt(100 nm)/Ti(10 nm)/SiO_2/Si substrate have been successfully fabricated by the sol–gel technique.

(2) The films showed very high structural quality without pyrochore phase, well-saturated hysteresis loops up to the maxium 7 V with P_r and V_c of 14 μC/cm^2 and 1.5 V, although the relative dielectric constants are somewhat lower than what was obtained in bulk materials.

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