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Sol-Gel Derived $Pb(Sc_{0.5}Nb_{0.5})O_3$ Thin Films: Processing and Dielctric Properties

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Relaxor $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) thin films without pyrochlore phase were processed from the modified alkoxide solution precursors. The preparation of single phase PSN thin films has a narrow processing window due to the appearance of an undesirable pyrochlore phase and volatility of PbO. Thin film processing has been improved through selection of precursor solutions, heat treatment and optimized deposition-condition are optimized. Especially, the effects of Pt substrates seeded with additional layers upper of TiO_2 and $La_{0.5}Sr_{0.5}CoO_3$ are investigated through the scanning electron microscopy (SEM) scanning of film/electrode interfaces. Dielectric behaviors of sol-gel derived PSN thin films on two different substrates are observed. They show the evidence of relaxor-like behaviors, i.e. the temperature dependence of the dielectric constant at different applied frequencies. Films on the $TiO_2/Pt/TiO_2/SiO_2/Si$ substrates exhibit better dielectric properties, such as frequency saturation over transition temperature and much lower dielectric loss than those on the $La_{0.5}Sr_{0.5}CoO_3/Pt/TiO_2/SiO_2/Si$ substrates. The differences of transition behaviors between PSN thin films and bulk ceramics are also discussed in relation to the processing temperature, interface phenomena between film and electrode, relatively small thickness and strain effect of films. [DOI: 10.1143/JJAP.41.6765]

KEYWORDS: PSN thin film, relaxor, seed layer, dielectric property

1. Introduction

Due to their advantageous properties and nontrivial characters, relaxors have been a subject of intense research during many years.[1)] The large piezoelectric responses combined with unique dielectric behaviors make them very attractive for application in actuators, high frequency ultrasonic medical imaging transducers, sensors, various dielectric and microelectromechanical systems.[2,3)] For these device fabrication, thin film depositions of relaxor ferroelectrics are much desired.[4)]

Since the spontaneously relaxor-to-normal ferroelectric phase transition was reported in PSN earlier,[5,6)] PSN has attracted very interesting materials for the study of the relaxor behaviors because ordering or disordering of B-site cations and stoichiometry of lead cations that can be controlled by thermal history induce drastic changes in the transition behaviors.[5,6)] Characterized by excellent dielectric and electromechnical properties in bulk materials, PSN thin films are potentially promising candidates for various applications. For fundamental studies, the investigation of the difference between PSN thin films and bulk materials can also give important information on relaxor mechanisms.

In this work, we report the preparation of PSN thin films by modified sol-gel processing and the effect of the two seeded substrates on crystallization and the microstructure. The dielectric properties have been conducted to study the influence of the different substrates and the difference between thin films and ceramics dielectric properties.

2. Experimental Procedure

PSN thin films were processed from a modified alkoxide solution precursor. The solution was prepared under a controlled inert gas atmosphere. Lead acetate trihydrate $[Pb(CH_3COO)_23H_2O]$, scandium acetate hydrate$[Sc(CH_3COO)_{3x}H_2O]$ and niobium ethoxide $[Nb(C_2H_5O)_5]$ were used as precursor materials and 2-methoxyethanol as solvent. To compensate for lead loss during thermal annealing, 15 mol% excess lead was added to the precursor solution. The thin films were deposited via spin coating. After 2-step pyrolysis heat treatment at 220°C for 2 min and 380°C for 2 min, the films were subjected to rapid thermal annealing in 2 step: densification at 680°C for 10 min after annealing at 750°C for 1 min. The orientation and microstructural analysis of the films were conducted by X-ray diffraction (XRD) and scanning electron microscopy (SEM). For electrical measurements, gold top electrodes were deposited by the sputtering method at room temperature. The J–V (leakage current density-voltage) curves were measured using a precision 2000 system. To measure the dielectric constants, an HP 4280A impedance analyzer and a Delta-9023 chamber with controlled cooling rate's function were used.

3. Results and Discussion

Figure 1 shows the XRD patterns of PSN thin films on substrates with different seed layers. Seed layers of 5-nm-thick TiO_2 (Fig. 1(a)) and 30-nm-thick LSCO (Fig. 1(b)) were introduced for easy nucleation and homogeneous grain growth. Both films were crystallized by 2-step rapid thermally annealing. In Fig. 1(a), the PSN film on $Pt/TiO_2/SiO_2/Si$ substrate with the 5-nm-thick TiO_2 seed layer exhibit random orientation with attendance toward (111) orientation while the PSN film of Fig. 1(b), deposited on $LSCO/Pt/TiO_2/SiO_2/Si$ substrate shows the highly (100) preferred orientation. All the XRD patterns exhibit perfect perovskites free of pyrochlore phase and other second phases.

The SEM micrographs of PSN thin films are illustrated in Fig. 2. In Fig. 2(a), an abnormal grain growth of PSN films on $TiO_2/Pt/TiO_2/SiO_2/Si$ substrates is observed. Their grain size is in the range of 50–500 nm. Dense microstructures having the uniform size of grains (100 nm) are showed in PSN films on $LSCO/Pt/TiO_2/SiO_2/Si$ substrate (Fig. 2(b)). These

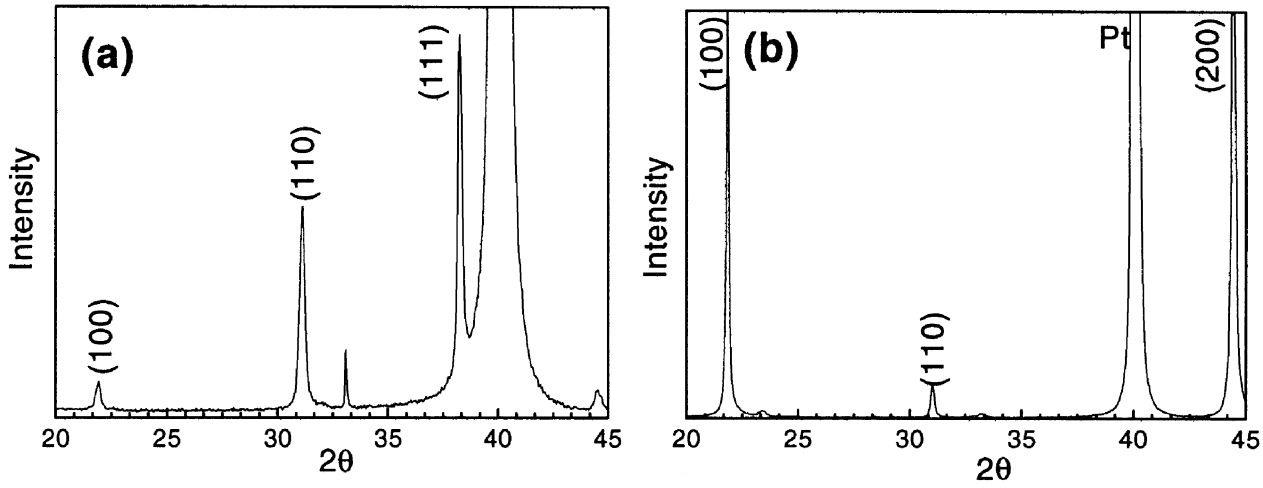

Fig. 1. X-ray diffraction patterns of PSN thin films on (a) $TiO_2/Pt/TiO_2/SiO_2/Si$ and (b) $(La_{0.5}Sr_{0.5})CoO_3/Pt/TiO_2/SiO_2/Si$ substrates rapid thermally annealed at 750°C for 1 min.

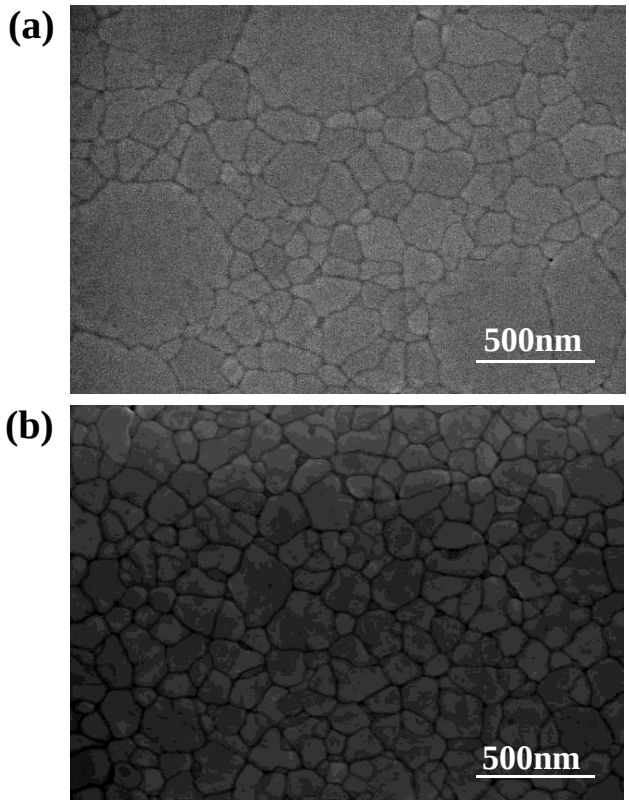

Fig. 2. Plan view scanning electron micrographs of PSN thin films on (a) $TiO_2/Pt/TiO_2/SiO_2/Si$ and (b) $(La_{0.5}Sr_{0.5})CoO_3/Pt/TiO_2/SiO_2/Si$ substrates rapid thermally annealed at 750°C for 1 min.

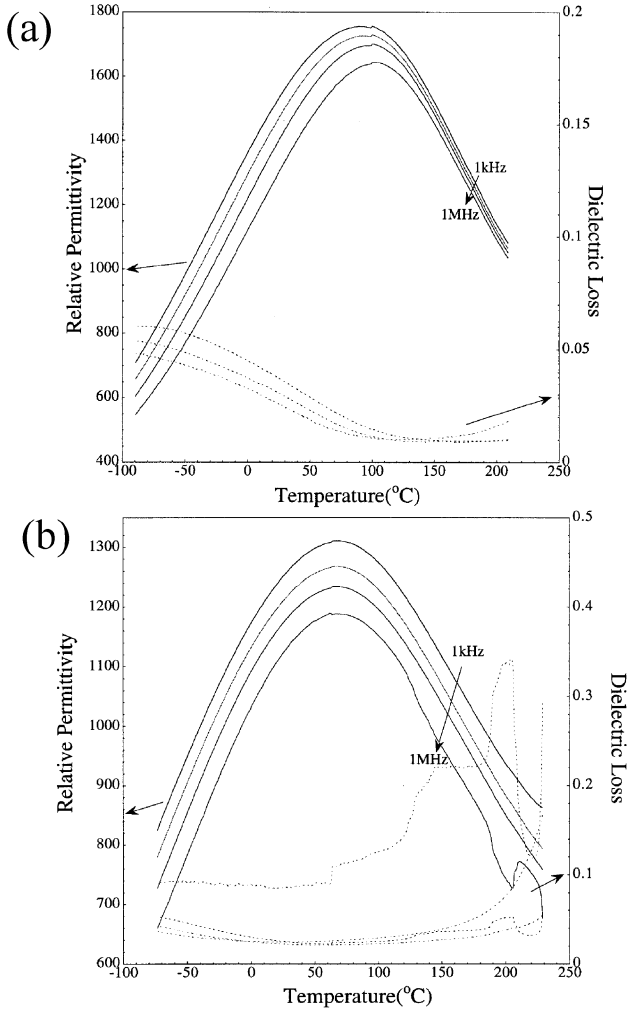

Fig. 3. Temperature dependence of the relative permittivity and dielectric loss of (a) 250-nm-thick and (b) 275-nm-thick PSN thin films annealed at 750°C for 1 min, respectively, on $TiO_2/Pt/TiO_2/SiO_2/Si$ and $(La_{0.5}Sr_{0.5})CoO_3/Pt/TiO_2/SiO_2/Si$ substrates. Measurements were made at 1 kV/cm.

dissimilarities of microstructures may depend on the difference in the nucleation rate and growth mechanism of PSN films on the respective seeded layer.[4)]

Figure 3 is the relative permittivity curve as a function of temperature at different applied frequencies. As can be seen, both films show diffuse phase transition behaviors typical of relaxors, they have, however the lower maximum permittivities (ϵ_m) than those of their bulk materials. PSN film on a $LSCO/Pt/TiO_2/SiO_2/Si$ substrate displays additionally the frequency dispersion even in the paraelectric range and the large shift (δ) of apparent transition temperature (T_m) from that of bulk specimens (Fig. 3(b)). In contrast, the transition temperatures in the paraelectric temperature converges to one line, which in often observed in bulk relaxors, in $Au/PSN/TiO_2/Pt/TiO_2/SiO_2/Si$ capacitors (Fig. 3(b)).

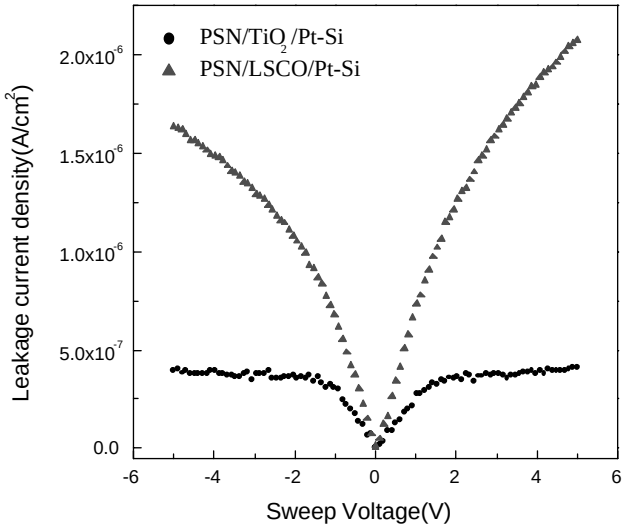

Fig. 4. Current density and sweep voltage curves of Au/PSN(250 nm)/TiO_2/Pt/TiO_2/SiO_2/Si and Au/PSN(275 nm)/$(La_{0.5}Sr_{0.5})CoO_3$/Pt/TiO_2/SiO_2/Si capacitors.

Their T_m are respectively about 95°C (Fig. 3(a)) and 60°C (Fig. 3(b)) and δ is approximately 5°C (Fig. 3(a)) and 30°C (Fig. 3(b)) at 1 kHz. The larger temperature dispersion of the dielectric constant around T_m and the shift of T_m (δ) of the PSN films on LSCO/Pt/TiO_2/SiO_2/Si substrates may be due to the defected interface between the PSN film and the LSCO seed layer that can be worked as dead layer in the Au/PSN/LSCO/Pt capacitor.[7,8] It can be inferred from larger dielectric losses ($\tan\delta < 0.4$) and higher leakage current density ($J_{max} = 4.5 \times 10^{-7}$ A/cm^2) of PSN films on LSCO than those on TiO_2 seed layer ($\tan\delta < 0.05$, $J_{max} = 2 \times 10^{-6}$ A/cm^2). And also, these lower ϵ_m and shift of T_m compared to bulk ceramics may result from thin thickness of the PSN films, low annealing temperature, Au-top-electrode and clamping of them by the substrate (strain effect).[4]

4. Summary

Very homogeneous perovskite PSN thin films have been prepared on substrates seeded with two differet buffer layers (TiO_2 and LSCO) by a modified sol-gel method for the first time.

Both films showed dense and crack free microstructures without second phase precipitation. Their dielectric constants show diffuse transition behavior typical of many relaxors. The films' large dielectric constant dispersion of the dielectric maximum temperature T_m and the shift of the films T_m from that of the bulk specimens' were explained in terms of the interface structure difference between PSN thin films and LSCO seed layers. It is only in the Au/PSN/TiO_2/Pt/SiO_2/Si thin films that showed the convergence of the dielectric constant vs. temperature curve into one line in the paraelectric temperature range regardless of the applied frequencies.

Acknowledgements

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