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Effects of oxygen pressure on characteristics of $0.05Pb(Al_{0.5}Nb_{0.5})O_3-0.95Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films grown on alumina substrates by pulsed laser deposition

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ABSTRACT

Binary system of $0.05Pb(Al_{0.5}Nb_{0.5})O_3-0.95Pb(Zr_{0.52}Ti_{0.48})O_3$ (PAN–PZT) thin films were deposited on alumina substrates by a pulsed laser deposition method and we investigated effects of oxygen pressure on ferroelectric domain structure and the piezoelectric characteristics of the films by piezoelectric force microscope (PFM). The films in optimum oxygen pressure exhibited the remnant polarization of 58.4 and 24.4 μC/cm^2, and 180° and 90° domain switching behavior were observed from PFM analysis. We obtained a large effective piezoelectric constant (d_{33}) value (~110 pm/V) in the films. As a result, we can determine the ferroelectric domain structure and improve the piezoelectric properties of the PAN–PZT films using an oxygen pressure control during the process and it helps to obtain suitable piezoelectric thin films for sensors and actuators applications.

1. Introduction

Piezoelectric films are used in a variety of applications in the micro-electronics industry for example in micro electro mechanical systems (MEMS) [1], sensors [2], actuators [3,4], ultrasonic motors [5], etc. Especially, lead zirconium titanate (PZT)-based thin film materials are attractive for sensors and actuators because of its large piezoelectric coefficient and flexibility. Their piezoelectric performances are influenced by the microstructure, crystallinity, and orientation of the films. Furthermore, as a demand of small size piezoelectric devices is increasing, microscopic techniques allowing for the evaluation of their piezoelectric properties with nanoscale resolution become important. As one of the techniques, piezoelectric force microscopy (PFM) becomes an interesting opportunity for the measurements of local electromechanical properties of the piezoelectric films [6].

In terms of substrate material for PZT-based materials, the alumina is attractive due to its low-cost and the excellent match of the thermal expansion coefficient with PZT-based materials. So, higher processing temperatures cause less strain which affects the piezoelectric properties. Moreover, alumina substrate is widely used for microwave devices, for example, antennas and filters, due to outstanding dielectric properties [7–9]. Integration of these devices with piezoelectric devices can be expected to explore a new application by the realization of the piezoelectric films on alumina substrate.

In our previous works, it was found that $0.05Pb(Al_{0.5}Nb_{0.5})O_3-0.95Pb(Zr_{0.52}Ti_{0.48})O_3$ (PAN–PZT) ceramics exhibited the high curie temperature ($T_c > 350\,°C$), the piezoelectric constant (d_{33}) of 390 pC/N, and the remnant polarization (P_r) of 90.5 μC/cm^2 [10,11]. In this works, we select this composition for high quality piezoelectric devices. Although a pure lead aluminum niobate $Pb(Al_{0.5}Nb_{0.5})O_3$ (PAN) perovskite compound has not been successfully synthesized, we used the PAN as modifier of PZT and demonstrate PAN–PZT thin films on an alumina substrate by a

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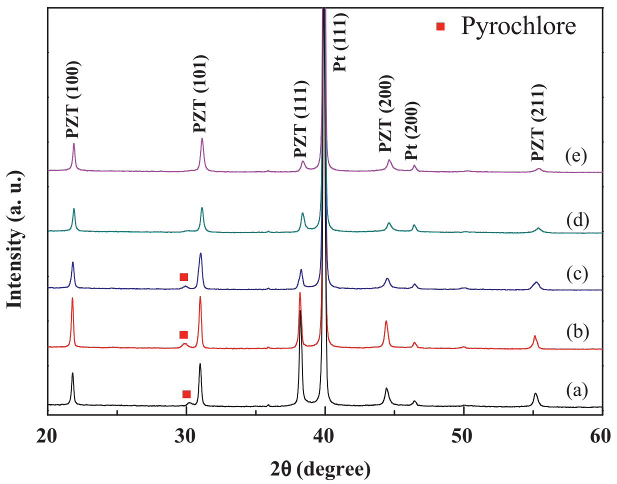

Fig. 1. X-ray diffraction (XRD) patterns for the PAN–PZT thin films with different oxygen pressure of (a) 50 mTorr, (b) 100 mTorr, (c) 200 mTorr, (d) 300 mTorr, and (e) 400 mTorr.

pulsed laser deposition method. In order to evaluate and determine the piezoelectric performance of the films, we investigated the effect of the oxygen pressure on ferroelectric domain structure and the piezoelectric characteristic of the films by PFM.

2. Experimental procedure

1-μm-thick PAN–PZT thin films were prepared by pulsed laser deposition (PLD) using a KrF excimer laser (COMpexPro 102, Coherent) onto Pt coated alumina plates. The deposition working pressure was changed from 50 to 400 mTorr and the laser energy density, repetition rate, and substrate temperature were maintained at 2.5 J/cm^2, 5 Hz, and 650 °C, respectively. X-ray diffraction (HTK 1200N, Anton Paar), scanning electron microscope (XL-30 FEG, Philips), and atomic force microscope (Dimension 3100, Nanoscope IV, Digital Instrument) were employed to evaluate the structural properties of the films. For electrical measurements, 100-nm-thick Pt thin film was deposited as a top electrode through a shadow mask on the PAN–PZT film by dc magnetron sputtering. The polarization–electric field (P–E) curves were measured by ferroelectric tester (RT66A, Radiant). The piezoelectric domain structure and effective piezoelectric constant (d_{33}) were measured by piezoelectric force microscope (PFM). The atomic force microscopy was used for the PFM measurement. A lock-in amplifier (SR830, Stanford Research) was employed for simultaneous piezoresponse phase and amplitude. The measurement were performed with a conductive Pt/Ir coated Si tip cantilever (PPP-NCHPt, Nanosensors) with the nominal spring constant with 43 N/m and resonance frequency 344 kHz. Piezoelectric response phase and amplitude image of domains were acquired in scanning mode, with a typical modulation ac signal frequency with 102 kHz and amplitude with 1.5 V.

3. Results and discussion

3.1. Structural characteristics

Fig. 1 shows the X-ray diffraction (XRD) patterns for the PAN–PZT thin films with a different oxygen pressure. The pattern for PAN–PZT grown at 50 mTorr exhibited the perovskite polycrystalline structure with a small pyrochlore phase and the peaks revealed (1 1 1) preferred orientation as shown in Fig. 1(a). The crystallinity of the PAN–PZT thin film was enhanced with increasing of the oxygen pressure to 100 mTorr but the pyrochlore phase was still remained (Fig. 1(b)). The pyrochlore phase was eliminated with increasing oxygen pressure but the intensity of the perovskite peaks were also reduced as shown in Fig. 1(c)–(e). Generally, the higher oxygen pressure plays an important role to improve crystallinity and reduce a secondary phase when the oxide thin films are deposited by PLD [12]. However, the higher working pressure resulted in a small size and higher density of plume, and the films were grown with different mechanism in this case. We believe that the degradation of the crystallinity of the films relates to this reason in spite of an oxygen rich ambient. Furthermore, the diffraction peaks of the films were shifted to the higher angle with increasing oxygen pressure. It indicates a lattice constant of the PAN–PZT films were changed due to a composition changes or internal stresses. Moreover, a tetragonal structure was observed in the films grown at 50 mTorr, 300 mTorr, and 400 mTorr, and a rhombohedral structure was observed in the films grown at 100 mTorr and 200 mTorr.

Table 1
Remnant polarizations and coercive fields of PAN–PZT thin films.

Oxygen pressure	Remnant polarization (μC/cm^2)	Coercive field (kV/cm)
50 mTorr	3.2	22.4
100 mTorr	58.4	30.8
200 mTorr	24.4	25.4
300 mTorr	2.3	22.5
400 mTorr	14.2	42.1

The surface microstructure and root-mean-square roughness ($R_{\rm rms}$) of the PAN–PZT thin films for the different oxygen partial pressure are shown in Fig. 2. The surface morphology of the film grown at 50 mTorr showed large agglomerates about 500 nm and the grain size without agglomerates were remarkably smaller than the other samples. The micrograph corresponding to the films grown at 100 mTorr (shown in Fig. 2(b)) showed the presence of fine grains, with a grain size of about 150–250 nm and the grain size of the films decreased with increasing oxygen pressure. The higher oxygen pressure forms a lot of agglomerates on the film surface as shown in Fig. 2(d) and (e). We expect that the higher oxygen pressure relate to these agglomerates, for example, the higher plume density due to the higher oxygen pressure with high laser energy make clusters in the plume and the clusters collide with substrate. In this case, the stable clusters nucleated on the substrate occur the island growth and grow in three dimensions to form islands. This phenomenon happens when atoms or molecules are more strongly bound to each other than to the substrate [13]. The grain sizes of the films grown at 300 mTorr and 400 mTorr without agglomerates were about 50–100 nm. These results demonstrated that the higher oxygen pressure helped to reduce the grain growth and crystallinity as reveals in the previous XRD data. The roughness of the films related to the adhesion, contact resistance, electrical conduction behavior, and manufacturability for the MEMS and sensor applications was measured by AFM as shown in Fig. 2(f). The roughness of the films grown at 50, 100, 200, 300, and 400 mTorr exhibited 36.5, 5.9, 10.5, 20.9, and 12.3 nm, respectively. The agglomerates or large grains clearly increased the roughness of the films. The film grown at 100 mTorr showed the best roughness among the films despite of large the grain size.

3.2. Piezoelectric and ferroelectric characteristics

Fig. 3 shows P–E hysteresis curves for the PAN–PZT thin films for different oxygen partial pressure, and remnant polarization ($P_{\rm r}$) and coercive field ($E_{\rm c}$) values of the samples are summarized in Table 1. The films grown at 100 and 200 mTorr showed typical ferroelectric characteristics with $P_{\rm r}$ of 58.4 and 24.4 μC/cm^2 and $E_{\rm c}$ of 30.8 and 25.4 kV/cm, respectively. An attempt was also made to measure the hysteresis loops of the other samples, but no hysteresis loops