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Electric field-induced Strains in Antiferroelectric $PbZrO_3$ Thin Films

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Electrical and electromechanical properties of $PbZrO_3$ (PZ) thin films deposited on $Pt/Ti/SiO_2/Si$, Pt/MgO(200), and $Pt/SrTiO_3(100)$ substrates by chemical solution deposition were investigated. Precursor solutions with the Pb/Zr atomic ratio of 1.1 were used. The PZ thin films on $Pt/Ti/SiO_2/Si$ annealed at 650°C and 700°C for 1 h and those on Pt/MgO(200) and $Pt/SrTiO_3(100)$ substrates annealed at 600°C for 1 h exhibited a double hysteresis loop, indicating that electric-field-induced antiferroelectric-to-ferroelectric phase transformation occurred at room temperature. The switching field diminished with increases in measurement temperature, and at 220°C, the polarization hysteresis loop became that of a ferroelectrics. A rectangular displacement hysteresis loop and maximum strains of 6.4-6.6 x 10^{-3} were observed.
Key words: field-induced strain, $PbZrO_3$, MEMS, antiferroelectrics

1. INTRODUCTION

Recently, electric field induced-strains in thin films have been extensively studied due to their potential applications in microelectromechanical systems (MEMS). The origin of the field induced strain is roughly divided into three mechanisms. The first is the inverse piezoelectric effect, the second is the electrostrictive effect, and the third is phase-change-related strains. Since the strain jump at the phase transition is much larger than that in either the antiferroelectric or the ferroelectric state, a rectangular field-strain hysteresis loop appears. This feature can be applied to a digital displacement transducer because of the two on/off strain state.[1] So far, in the field of thin film actuators, the research efforts have concentrated to the materials using the inverse piezoelectric effects, such as ZnO and PZT. On the other hand, the phase-change-related strains in antiferroelectric thin films have not been investigated in detail.

Lead zirconate ($PbZrO_3$, PZ) is a typical antiferroelectric material. For bulk PZ ceramics, field-induced antiferroelectric (AFE)-to-ferroelectric (FE) phase transformation is observed only near the Curie Point (~230°C).[2] A modified composition system, such as $Pb_{0.97}La_{0.02}(Zr_{0.66}Sn_{0.25}Ti_{0.09})O_3$, is used usually for bulk ceramics, and the induced strain reaches up to 0.85%.[3] In the case of thin films, some recent papers have reported that field-induced AFE-FE switching occurred in non-doped PZ films [4,5] and in doped PZ films [6,7] at room temperature.

We recently confirmed that the polycrystalline PZ thin films prepared by chemical solution deposition exhibited the signs of the double hysteresis loop in polarization-field measurement.[8,9] In the present paper, we report the electrical and electromechanical properties of the optimized PZ thin films on various substrates in detail. The non-doped PZ thin films deposited on $Pt/Ti/SiO_2/Si$, Pt/MgO(200), and $Pt/SrTiO_3(100)$ substrates exhibited double hysteresis loops in field-polarization measurement.

2. EXPERIMENTAL

PZ films were fabricated from two sol-gel type solutions. The starting Pb/Zr ratio of the solutions was 1.1/1. The solutions were spin-coated onto a $Pt/Ti/SiO_2/Si$ Pt/MgO(200), and $Pt/SrTiO_3(100)$ substrates. The films were then dried in air at 400°C for 10 min. This process was repeated 3 times, and the films were crystallized in air at various temperatures (600 – 700°C) for 1h.[8,9] The obtained film was (111) oriented on $Pt/Ti/SiO_2/Si$, the thickness was 500nm. Thin film Pt top electrodes were deposited by magnetron sputtering. Depth profile of the films were measured by secondary ion mass spectroscopy (CAMECA, IMS-6F). The polarization hysteresis loops and the dielectric constants were measured by means of a Radiant Technology Ferroelectric tester, RT66A, aixxact ferroelectric tester, TF2000 and Agilent Technology impedance analyzer, 4192A, respectively. The dielectric constants were computed from the capacitance measured in a small signal oscillation voltage of 100mV and frequency of

100kHz. Measurements of the electric-field-induced displacements in PZ films were performed using a combination of scanning probe microscopy (SPM, SEIKO SPI3800N) and a ferroelectric tester (aixACCT TF2000).[10] The period of one measurement cycle was 100ms.

RESULTS AND DISCUSSION

Figure 1 shows the suaface morphologies of PZ films on $Pt/Ti/SiO_2/Si$ annealed at (a) 600°C, (b) 650°C and (c) 700°C, respectively. Figure 2 shows the depth profiles of PZ films on $Pt/Ti/SiO_2/Si$ annealed at (a) 600°C and (b) 700°C, respectively. Judging from the profile of Zr, Pt electrodes appear after about 500s etching. Compared to Zr, Pb is distributed not only in the PZ film but also in the electrode region. It is considered that Pb has the tendency to diffuse into Pt and SiO_2 regions, probably due to the restrained reactivity between Pb and Zr. In this experiment, 10mol % excess Pb was added in the initial solution. It is estimated that the excess Pb compensates for the loss both by the evaporation from the film surface and by the diffusion into electrode and substrate to form $PbZrO_3$ film. Comparing the two figures, Pb diffusion into the electrode and surface regions, and Pt, Ti, and Si diffusion into PZ films, are accelerated by higher temperature annealing.

The polarization hysteresis loops of the PZ films on $Pt/Ti/SiO_2/Si$ are shown in Figure 3. In the films annealed at 600°C, the field-induced phase transformation was not recognized at the field applications up to 400kV/cm. The films annealed at 650°C and 700°C exhibited double hysteresis loops, indicating AFE to FE phase transformation. The field in which phase switching occurs decreases slightly with increases in annealing temperature. This is probably due to the increase of the PZ grain size. The loops of the films on Pt/MgO(200), and $Pt/SrTiO_3(100)$ substrates are shown in Figs. 4 and 5. By using precursor solutions with the Pb/Zr atomic ratio of 1.1, Those films also exhibited double hysteresis loop.

Although pure PZ bulk does not show a double hysteresis loop at room temperature, the PZ film studied here did exhibit a double hysteresis loop. Two possible reasons for this can be proposed. One reason is that the higher breakdown field of the thin films enables a field application which exceeds the switching field. The other reason is that the film has the defect structure similar to the one in the Sn-doped ceramics. At any rate, in terms of control of the manufacturing process, PZ film has an advantage in that it contains only two metal components.

Temperature-dependent polarization hysteresis loops in the PZ films have not reported so far, we measured those for the films annealed at 650°C. The switching field decreased with increases in measuring temperature; for example, 300KV/cm is required to exhibit AFE to FE phase transformation in the forward direction at 23°C, while the phase transformation occurs under 210-220kV/cm at 100°C. The sign of the neck in the loop is barely recognized at 200°C, the loop shape at 220°C were judged to be that of a ferroelectrics. Through the temperature range from 23°C to 220°C, the saturated polarization values were almost identical.

Dielectric anomaly was observed at 224°C on heating. This value is close to the reported value of 230°C in the bulk [2] and corresponds well to the result of the temperature dependent polarization loops.

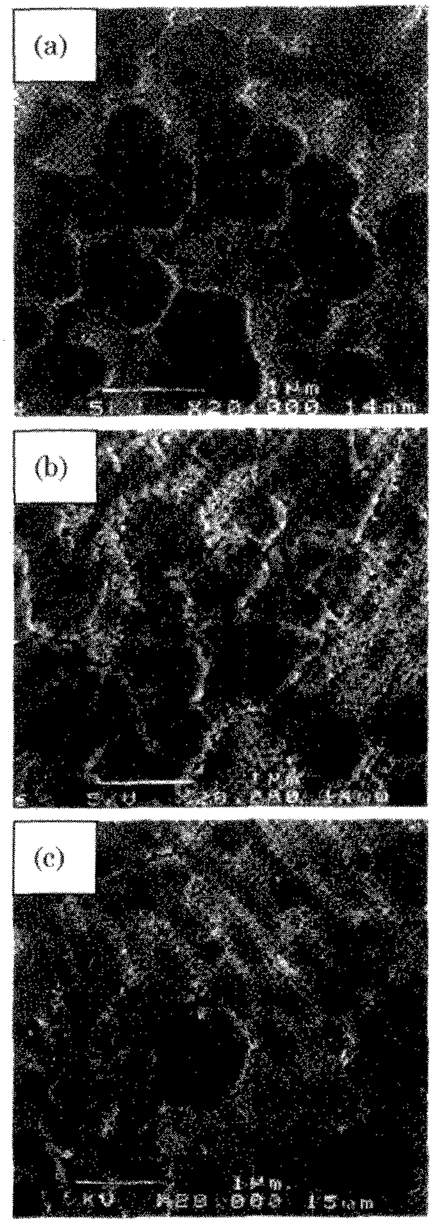

Fig.1 Surface morphologies of the PZ films on $Pt/Ti/SiO_2/Si$ annealed at (a) 600°C, (b) 650°C. and (c) 700°C.

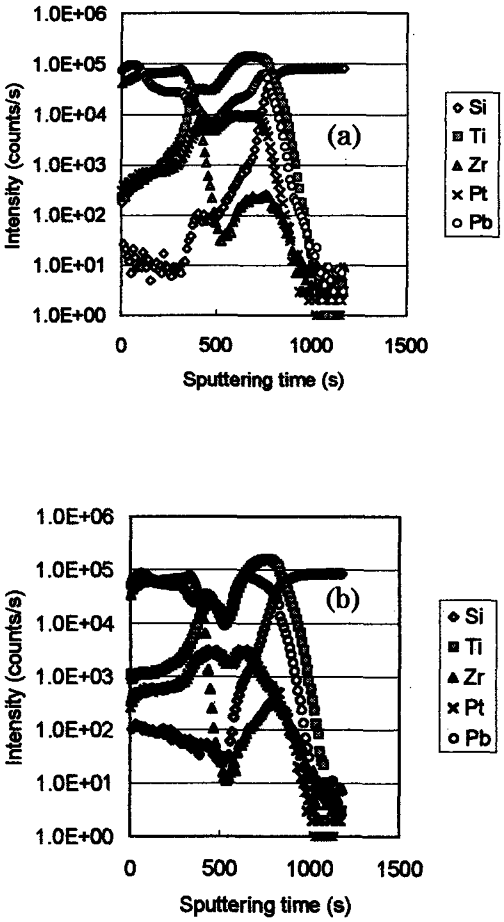

Fig.2 Depth profile of the PZ films on Pt/Ti/SiO_2/Si annealed at (a) 600°C and (b) 700°C.

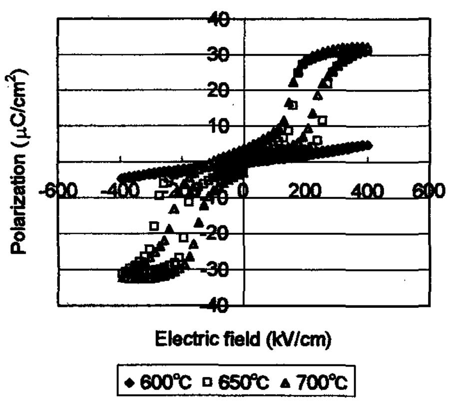

Fig.3 Polarization hysteresis loops of the PZ films on Pt/Ti/SiO_2/Si annealed at 600°C, 650°C, and 700°C.

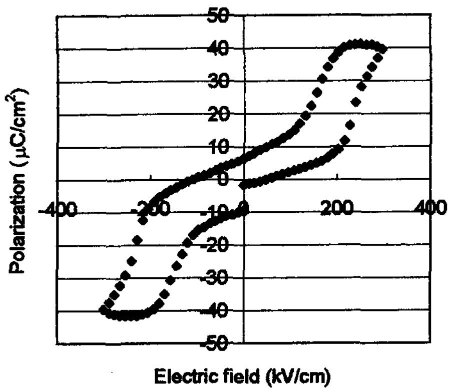

Fig.4. Polarization hysteresis loops of the PZ films on Pt/MgO annealed at 600°C .

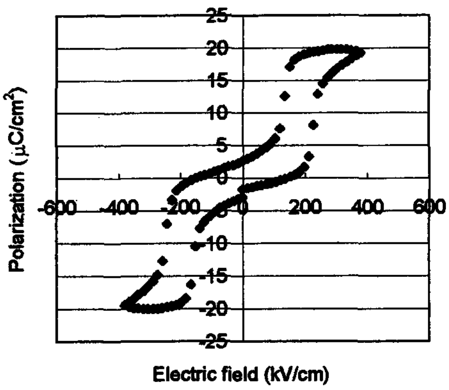

Fig.5. Polarization hysteresis loops of the PZ films on Pt/$SrTiO_3$ annealed at 600°C .

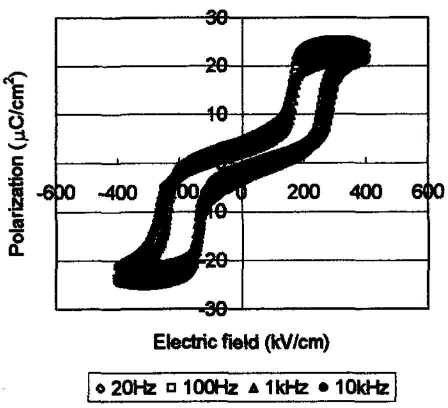

Fig.6. Polarization hysteresis loops of the PZ films on Pt/Ti/SiO_2/Si annealed at 650°C measures at various frequencies.

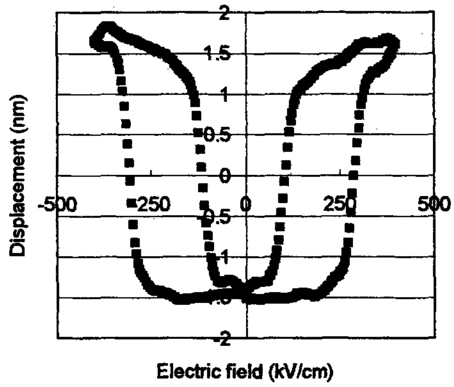

Fig.7. Field-induced displacement loops of the PZ films on $Pt/Ti/SiO_2/Si$ annealed at 650°C measured at various frequencies.

The frequency dependent ppolarization hysteresis loops are given in Figure 6. It is note that almost independent with the measuring frequencies up to 100kHz.

The field-induced displacement for the PZ films annealed at 650°C were measured by scanning probe microscopy with 100ms period of one measurement cycle is given in Figure 7. A typical rectangular field-strain hysteresis loop appears. Tani *et al.* reported the field-strain loop of the sol-gel deposited PZ films measured by interferometer and the loop were asymmetric with the applied field direction. The observed strain loop in this study is almost symmetric and well corresponds to the polarization hyseresis loop. The obtained displacement values of 3.2-3.4 nm are equivalent to strains of 6.4-6.6 x 10^{-3}. These are comparable to the Sn-doped PZ ceramics strain of 8.5 x 10^{-3}.

CONCLUSION

Properties of PZ films on $Pt/Ti/SiO_2/Si$, Pt/MgO(200), and $Pt/SrTiO_3(100)$ prepared by chemical solution deposition were investigated. Without doping, the electric-field-induced antiferroelectric to ferroelectric phase transformation was observed at room temperature. The switching fields were 300kV/cm in the forward direction and 190kV/cm in the backward direction at room temperature. The switching field decreased with increases in measuring temperature, and at 220°C polarization hysteresis loop took the shape of that of a ferroelectrics. While, the saturation polarization were almost identical up to 220°C. In small signal measurement, dielectric anomaly was observed at 224°C. The strain accompanied by the phase transformation was observed by means of scanning probe microscopy. Symmetric rectangular field-strain hysteresis loops, peculiar to the antiferroelectrics, exhibited. The observed maximum strain values were 6.4-6.6 x 10^{-3} and comparable to those of Sn-doped PZ ceramics.

In summary, we demonstrated that the PZ thin films possess both electrical and electromechanical on/off states in the unipolar field direction. The results obtained in this study indicate that PZ thin films have great potential applications in digital displacement actuator, transducer and electrical and mechanical memory devices in miniaturized and integrated systems.

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