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Dielectric and Pyroelectric Properties of Compositionally Graded $Pb(Zr_{1-x}Ti_x)O_3$ Thin Films Prepared by Sol-gel Process†

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Compositionally graded ferroelectric lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) thin films were grown on $Pt/Ti/SiO_2/Si$ substrates by using a sol-gel process. The final structure consists of six layers, up-graded graded films starting from $PbZrO_3$ on the Pt electrode to the top PZT(50) layer, it consists of no Ti, 10%Ti, 20%Ti, 30%Ti, 40%Ti, and 50%Ti respectively. Whereas films with opposite gradient are called down-graded graded films. Structure and dielectric properties of the graded films was investigated by X-ray diffraction, Auger electron spectroscopy and by impedance analysis. The up-graded and down-graded PZT films annealed at 600 °C, exhibited the remanent polarization values of 18.0 and 24.2 $\mu C/cm^2$, respectively. The typical small signal dielectric constants and loss tanδ at a frequency of 100 Hz were 523 and 0.018, 544, and 0.020, respectively, for up-graded and down-graded PZT thin films. The temperature dependence of pyroelectric coefficients of the graded PZT films was measured by a dynamic technique. From 20 °C to 82 °C, the pyroelectric coefficients of the up-graded and down-graded PZT films up to 374 and 407 $\mu C/m^2K$, respectively.

Key words: Graded films, $Pb(Zr,Ti)O_3$, Dielectric properties, Pyroelectric properties

I. INTRODUCTION

Recently, compositionally graded ferroelectric thin films have attracted more and more attention due to their pyroelectric, dielectric, and unconventional ferroelectric properties [1-10]. The most important property of graded ferroelectric thin films is that a large dc polarization offset existed in hysteresis loops when they were driven by an alternating electric field. Furthermore, the direction of the polarization offset was related to the direction of the composition gradient with respect to the substrate. However, studies on compositionally graded $Pb(Zr,Ti)O_3$ (PZT) films are less reported. Brazier *et al.* reported the unconventional hystersis behavior and origin of anomalous polarization offsets in compositionally graded PZT thin films prepared by pulsed laser deposition [6], Chen *et al.* made the graded PZT film capacitors by the metalorganic decomposition (MOD) technique [7]. Bao *et al.* measured the ferroelectric properties of graded PZT films on $LaNiO_3$-coated silicon substrates by the MOD technique [8]. Bouregba *et al.* explained that the asymmetrical leakage current as a possible origin of the polarization offset observed in compositionally graded ferroelectric films [9,10]. Most of the graded ferroelectric research work has been concentrated on polarization offsets in hysteresis loops or charge-pumping effects, which involve ferroelectric compositions [5-10]. There are a few papers reported on the pyroelectric properties of graded ferroelectric films. Schubring *et al.* have calculated the pseudo-pyroelectric coefficients of compositionally graded $K(Ta,Nb)O_3$ and $(Ba,Sr)TiO_3$ films from the polarization offsets in hysteresis loops [1,2], present authors have reported the true pyroelectric coefficients of compositionally graded $(Pb,Ca)TiO_3$ films [11].

In this work, we have attempted to study on pyroelectric properties of compositionally graded PZT thin films by a dynamic technique [12,13].

II. EXPERIMENTS

A. Preparation of the films

The sol-gel technique was used to prepare compositionally graded PZT thin films. The method of synthesizing $PbZrO_3$ and PZT precursor solutions is described in detail elsewhere [14,15]. The nominal compositions of the solutions are $Pb_{1.1}(Zr_{1-x}Ti_x)O_3$ (x=0, 10%, 20%, 30%, 40%, and 50%, respectively), the precursor with 10% excess Pb composition was prepared on purpose to compensate for the lead loss in the deposition processing. The precursor solutions were

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spin coated onto Pt(111)/Ti/SiO_2/Si(100) substrates, in sequence: first, PZT(0) solution, then PZT(10) solution, and finally, PZT(50) solution, or vice versa. The 0.2 mol/L coating solution of PZT films was deposited onto Pt/Ti/SiO_2/Si substrates by spin coating at 3600 r/min for 30 s. Each solution was spin coated once. After every one coating, the thin films were annealed in air at 320 °C for 10 min on a hot plate. After coatings six layers, the thin films were annealed in air at 400 °C for 60 min on a hot plate. Finally, the graded PZT films on Pt/Ti/SiO_2/Si substrates were annealed at 600 °C for 10 min by a rapid thermal annealing (RTA) in oxygen atmosphere. For convenience, the films with Zr/Ti ratios varying from $PbZrO_3$ at the substrate to PZT(50) at the top surface are called up-graded films, whereas films with the opposite gradient are called down-graded films. The thickness of the annealed films with six layers, as measured by a field-emission scanning electron microscopy (Philips, Eindhoven, the Netherlands), were 250 nm for the up-graded and down-graded thin films.

B. Characterization of the films

The crystalline structure of the graded PZT films was characterized by X-ray diffraction (XRD) (Philips PW3710, Cu Kα). The thickness distribution and surface morphology of compositions graded PZT films was determined using a combination of XL30 FEG Auger electron spectroscopy (AES) with Ar ion etching and a field-emission scanning electron microscopy (FE-SEM). To investigate the electrical properties of the PZT thin films; top electrodes of 100-nm-thick Au/Cr layer of 0.8 mm diameter were prepared on the top surface of the PZT films through a shadow mask in an vacuum evaporation system. The polarization-electric-field (P-E) hysteresis loop was obtained by a modified Sawyer-Tower circuit [6,7,9]; the reference capacitors were 10, 33, and 100 nF, and the input signal was sinusoidal with a frequency of 1 kHz. The dielectric constant and dielectric loss tanδ were measured by a 4294 A impedance analyzer (Agilent, USA) with a small ac signal of 50 mV. The temperature dependence of pyroelectric coefficient for graded PZT films was measured by a dynamic technique [12,13].

III. RESULTS AND DISCUSSION

A. Structure and surface morphology analysis

Figure 1 shows the XRD patterns of the graded PZT films. The films had a perovskite phase with pseudocubic structure. The positions of the 2θ diffraction angles of the XRD patterns of compositionally graded PZT films were found to be between those of the $PbZrO_3$ and $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films. The XRD patterns also revealed that the up-graded film was polycrystalline with a (100) preferred orientation, whereas the down-graded film was a highly (111) preferred orientation. The degrees of the (100)-type and (111)-type preferred growth, as estimated by the Lotgering factor [16], are 58% and 79% for the (100)-oriented up-graded and (111)-oriented down-graded PZT films, respectively. The difference was believed to be due to the influence of the deposition sequence of the film layers, especially the first layer [14,15].

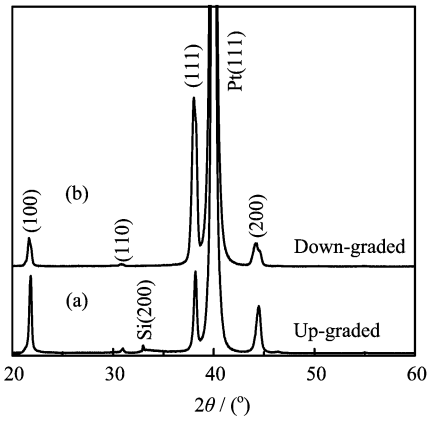

FIG. 1 XRD patterns of (a) an up-graded and (b) a down-graded PZT thin films on Pt/Ti/SiO_2/Si substrates annealed at 600 °C for 10 min in an oxygen atmosphere by RTA.

Figure 2 shows the composition depth profile of a typical down-graded film, determined by using a combination of AES and by Ar ion etching. The resulting plot is the concentration of Pb, O, Ti, and Zr as a function of depth for the PZT graded thin film. The initially formed six single-composition PZT layers have turned into compositionally graded structure. It confirms an increase of relative concentration of Zr and a decrease of relative concentration of Ti in the graded PZT thin film along the depth of etching. A slight off-stoichiometric composition was found in the surface layer of these thin

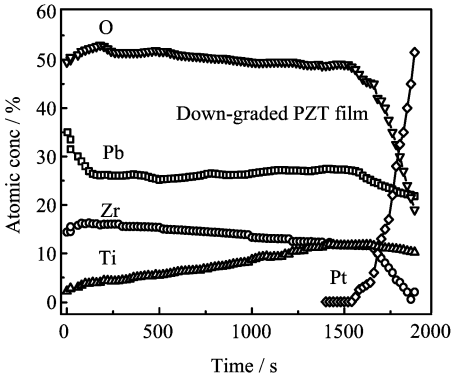

FIG. 2 Thickness distribution of compositions of a typical down-graded PZT thin film.

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films. The film is Pb-rich on the surface. Furthermore, no obvious oxygen deficiency was present in the surface layer. It is partly attributed to the heat treatment under oxygen atmosphere, it may give rise to preventing the oxygen vacancies from formation in PZT graded thin film. Oxygen and lead have no obvious variations across the gradient structure but relative content of Zr and Ti changed continuously across the total thin film. The relative concentrations of Zr and Ti as a function of depth from $Pb(Zr_{0.5}Ti_{0.5})O_3$ to $PbZrO_3$ film indicate that the deposition method produces a smooth, linear composition gradient, for the down-graded PZT film. The continuous variation of Zr or Ti relative concentration in graded thin film was attributed to the diffusion as the heating treatment at 400 °C for 1 h before complete crystallization.

Figure 3 shows the FE-SEM surface and cross-section images of the up-graded and down-graded PZT thin films on $Pt/Ti/SiO_2/Si$ substrate was annealed at 600 °C for 10 min in an oxygen atmosphere by RTA. The measurement conditions are 20 kV, and 10×10^5 and 32×10^3 magnification for up-graded film, and 20 kV and 4×10^4 magnification for down-graded film, respectively. It revealed that a dense, smooth and pinhole-free surface morphology was obtained in the graded PZT films on $Pt/Ti/SiO_2/Si$ substrate. The average grain size is about 30 and 20 nm, respectively for the up-graded and down-graded PZT films. The thickness is about 250 nm for up-graded and down-graded PZT films.

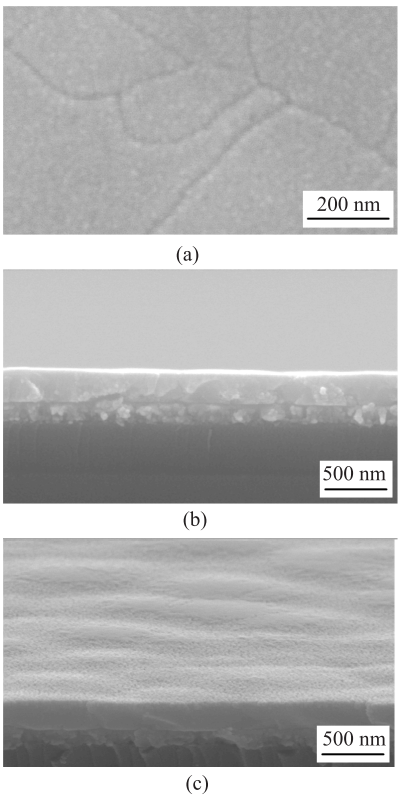

FIG. 3 FE-SEM micrograph of the surface and cross-section of graded PZT film on $Pt/Ti/SiO_2/Si$ substrates were annealed at 600 °C for 10 min in oxygen atmosphere by RTA: (a) and (b) for up-graded, (c) down-graded films.

B. Ferroelectric and dielectric properties

Figure 4 shows the typical polarization-electric field (P-E) hysteresis loops for the up-graded and down-graded PZT thin films on $Pt/Ti/SiO_2/Si$ substrates. The remanent polarization (P_r) and the coercive electric field (E_c) obtained from the P-E hysteresis loops, are 18.0 μC/cm^2 and 83.1 kV/cm, 24.2 μC/cm^2 and 95.6 kV/cm, respectively for the up-graded and down-graded PZT films applied electric field of 600 kV/cm. We did not observe the polarization offset, if discharged the graded film and reference capacitors before measurement. Vilquin *et al.* also reported that no typical offset was observed on hysteresis loops for compositionally graded $Pb(Zr,Ti)O_3$ thin films deposited by a sputtering method [17], suppose that the shifts could arise from asymmetric leakage current through the graded ferroelectric films [17-19]. Time-dependent space-charge-limited conduction as a possible origin of the polarization offsets observed in compositionally graded ferroelectric PZT films [20].

The capacitance and dielectric loss factor were measured by a 4294 A impedance analyzer with a small ac signal of 50 mV. The dielectric constant and dissipation factor measurements were made at room temperature as a function of frequency in the range of 100 Hz-1 MHz for the graded PZT films deposited on $Pt/Ti/SiO_2/Si$ substrates. Figure 5 shows the dielectric constant and dissipation factor as functions of frequency for the graded PZT films deposited on $Pt/Ti/SiO_2/Si$ substrates. The dielectric constant and dissipation factors were 523 and 0.018, 544 and 0.020, respectively, at 100 Hz for the up-graded film and down-graded film annealed at 600 °C

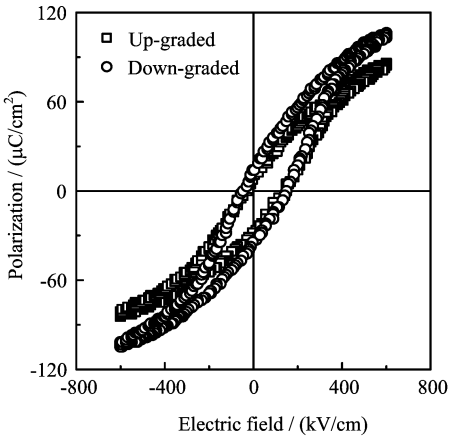

FIG. 4 Typical hysteresis loops of the up-graded and down-graded PZT films: applied electric field of 600 kV/cm.

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for 10 min.

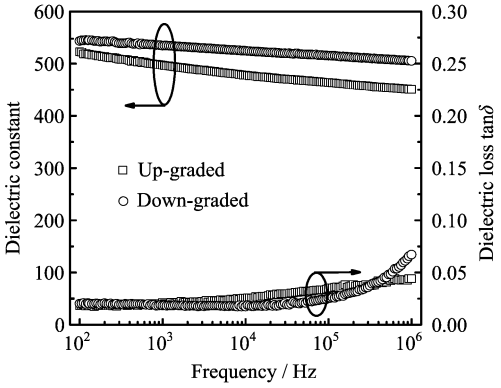

FIG. 5 Dielectric constants and loss tanδ as a function of the frequency for the up-graded and down-graded PZT films.

C. Pyroelectric properties

The temperature dependence of pyroelectric coefficient for graded PZT films was measured by a dynamic technique. At a certain temperature T_0 the sample temperature was sinusoidally modulated ($T(t)=T_0+T_\sim\sin 2\pi ft$) with frequency f=5 mHz and amplitude $T_\sim$=1 K using a Peltier element [12,13]. The pyroelectric current signal was amplified with an electrometer and the 90° out of phase component of the current with respect to the temperature modulation was measured with a lock-in amplifier. After setting to a new temperature T_0 the sample was kept at T_0 for 15 min for the signal to become stable before the pyroelectric measurement was performed [21].

The up-graded and down-graded PZT thin films were first poled at room temperature by applying an ac voltage of amplitude 25 V and frequency of 10 Hz for 0.1 s and then short circuited. Figure 6 shows the pyroelectric coefficients as a function of the temperatures for the up-graded and down-graded PZT thin films. The real part is the true pyroelectric coefficients, the imaginary part is loss, and includes the contributions of the leakage current. For the up-graded PZT film, the pyroelectric coefficients increase from 180 $\mu C/m^2K$ to 374 $\mu C/m^2K$ when the temperature increases from 20 °C to 82 °C. The pyroelectric coefficients decrease from 382 $\mu C/m^2K$ to 196 $\mu C/m^2K$ when the temperature decreases from 82 °C to 20 °C. For down-graded PZT film, the pyroelectric coefficients increase from 229 $\mu C/m^2K$ to 407 $\mu C/m^2K$ when temperature increases from 20 °C to 82 °C, then the pyroelectric coefficients decrease from 394 $\mu C/m^2K$ to 224 $\mu C/m^2K$ when the temperature decreases from 82 °C to 20 °C. At room temperature (25 °C), the pyroelectric coefficients of up-graded and down-graded PZT films are 202 and 250 $\mu C/m^2K$, respectively. Which is higher than that of PZT(52/48) films on RuO_2- and Pt-coated silicon

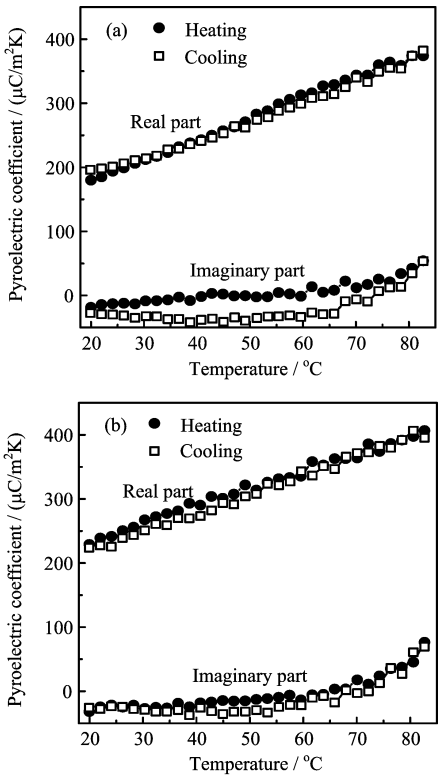

FIG. 6 Pyroelectric coefficients as a function of temperatures for (a) an up-graded and (b) a down-graded PZT thin films.

substrates (p=138, and 145 $\mu C/m^2K$) [22], higher than that of graded PCT films (112 $\mu C/m^2K$) [11], can compare with that of sol-gel derived PZT(30/70) films on Pt-coated silicon substrates (200 $\mu C/m^2K$) [23] and PZT(15/85) films (160-220 $\mu C/m^2K$) [24], and lower that of epitaxial grown PZT(45/55) films on Pt-coated MgO substrates (420 $\mu C/m^2K$) and PZT(90/10) films on Pt-coated sapphire substrates (450 $\mu C/m^2K$) [25]. A useful comparative figure of merit used in comparing pyroelectric materials is defined as $F_D=p/c(\varepsilon\varepsilon_0\tan\delta)^{1/2}$, where c is the heat capacity per unit volume (c=2.5 J/m^3K) [26], ε is the relative permittivity of the graded film, ε_0 is the permittivity of free space, and tanδ is the dissipation factor. The F_D values are 8.85×10^{-6} and 10.2×10^{-6} $Pa^{-0.5}$ at 100 Hz and room temperature, respectively for up-graded and down-graded PZT films. Which is higher than that of PZT(52/48) films ($F_D=7.0\times10^{-6}$ $Pa^{-0.5}$ at 1 kHz) [27], and PZT(30/70) films ($F_D=0.81\times10^{-6}$ $Pa^{-0.5}$ at 1 kHz) [28]; slightly lower that of sol-gel derived PZT(15/85) films ($F_D=13\times10^{-6}$-15×10^{-6} $Pa^{-0.5}$) [24]; and lower than that of epitaxial grown PZT(45/55) ($F_D=20\times10^{-6}$ $Pa^{-0.5}$) and PZT(90/10) ($F_D=17\times10^{-6}$ $Pa^{-0.5}$) films [25]. From the results, the dielectric, ferroelectric and pyroelectric properties of the down-graded PZT film are better than that of the up-graded PZT film. The graded PZT films have

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lower FD value is due to the higher dielectric constant. The F_D value of graded PZT films can being enhanced by using $PbTiO_3$ or $PbZrO_3$ buffered $Pt/Ti/SiO_2/Si$ substrates [29].

IV. CONCLUSION

In conclusion, compositionally graded $Pb(Zr,Ti)O_3$ thin films were grown on Pt-coated Si substrates by using the sol-gel process with rapid thermal annealing. The up-graded and down-graded PZT films annealed at 600 °C, possessed a remanent polarization and coercive electric field of 18.0 $\mu C/cm^2$ and 83.1 kV/cm, 24.2 $\mu C/m^2$ and 95.6 kV/cm, respectively. The typical small signal dielectric constant and dissipation factor at a frequency of 100 Hz were 523 and 0.018, 544, and 0.020, respectively for up-graded and down-graded PZT thin films. At room temperature, the pyroelectric coefficients of the up-graded and down-graded PZT films are 202 and 250 $\mu C/m^2K$, respectively. The F_D values are 8.85×10^{-6} and 10.2×10^{-6} $Pa^{-0.5}$ at room temperature, respectively for up-graded and down-graded PZT films. These results make these materials useful for pyroelectric sensors.

V. ACKNOWLEDGMENTS

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