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Structure and Electrical Properties of (111) Oriented Pb(Mg_{1/3}Nb_{2/3})O₃–PbZrO₃–PbTiO₃ Thin Film for High Frequency Transducer Applications

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Abstract

Ternary lead magnesium niobate-lead zirconate titanate system 0.4Pb(Mg_{1/3}Nb_{2/3})O₃–0.25PbZrO₃–0.35PbTiO₃ (40PMN-25PZ-35PT) thin film with a thickness of 1.5 μm was grown on Pt(111)/Ti/SiO₂/Si substrate via chemical solution deposition. XRD and TEM (spell out) results suggested the film obtained was highly (111)-oriented. The remanent polarization and coercive electric field of the film were found to be 25.5 μC/cm² and 51 kV/cm, respectively. In addition, at 1 kHz, the dielectric constant was measured to be 1960 and the dielectric loss 0.036. The film was observed to undergo a diffuse ferroelectric-to-paraelectric phase transition at around 209°C. The leakage current appeared to depend on the voltage polarity. If the Au electrode was biased positively, the leakage current was dominated by Schottky emission mechanism. When the Pt electrode was biased positively, the conduction current curve showed an ohmic behavior at a low electric field and space-charge-limited current characteristics at a high electric field.

Keywords

Electrical properties; PMN-PZT; Thin film

1. Introduction

In the past decades, lead-based ferroelectric PbZr_{1-x}Ti_xO₃ (PZT) thin films have been subjected to extensive studies for applications in electronic devices and Micro-ElectroMechanical Systems (MEMS) due to their excellent properties [1,2]. Meanwhile, there has been a growing interest in development of new materials with better properties. Because of their higher dielectric constant and larger piezoelectric response, (1-x)Pb[Mg_{1/3}Nb_{2/3}]O₃-xPbTiO₃ (PMN-PT) thin films have been envisioned as a replacement for PZT thin films. However, the relative low Curie temperature (around 150°C) [3] of PMN-PT thin films, which affects the device's temperature stability, is a fatal weakness in limiting its applications to a great extent.

Recently, a new interesting ternary lead magnesium niobate-lead zirconate titanate system (1-x-y)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbZrO₃-yPbTiO₃ (PMN-PZT) has been reported by Zhang et. al. [4–8]. Near the morphotropic phase boundary, the electromechanical coupling factors at

the room temperature of the composition $0.4\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.25\text{PbZrO}_3-0.35\text{PbTiO}_3$ (40PMN-25PZ-35PT) crystal are $\geq 90\%$ for k_{33} and $\sim 87\%$ for k_{32} , respectively, comparable to PMN-PT crystal [5]. Moreover, the Curie temperature of 40PMN-25PZ-35PT crystal is above 200°C much higher than that of PMN-PT crystals [5–7]. Hence, it is worthwhile to investigate this ternary system thin film for MEMS applications. Although, to date, there have been several papers about PMN-PZT films [9–11], no literature has reported 40PMN-25PZ-35PT thin film.

More recently there has been an increase in interest in non invasive ultrasonic investigation and manipulation of living cells and biological tissues (cite one of Jungwoo Lee's papers here) which require the frequency to be as high as 500 MHz in order to obtain the required precision. As a result, ultrahigh frequency (>500 MHz) transducer is needed. The challenge of ultrahigh frequency (>500 MHz) transducer fabrication is to synthesize high quality piezoelectric thin films with a thickness around $1\text{ }\mu\text{m}$.

In this paper, the process, structure and electrical properties of 40PMN-25PZ-35PT thin films prepared from a sol-gel process, because of its low cost and easy composition control, are reported. An understanding of the electrical properties of the thin film, especially the current-voltage (I–V) characteristics, is of critical importance for the successful implementation of the film into a device.

2. Methods

A spinning process was repeated to fabricate 40PMN-25PZ-35PT films. High-purity lead acetate trihydrate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, Aldrich Chemical Co., Milwaukee, WI), magnesium ethoxide ($\text{Mg}(\text{OC}_2\text{H}_5)_2$, Aldrich Chemical Co.), niobium ethoxide ($\text{Nb}(\text{OC}_2\text{H}_5)_5$, Chemat Technology, Northridge, CA), titanium isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, Aldrich Chemical Co.), and zirconium *n*-propoxide ($\text{Zr}(\text{OC}_3\text{H}_7)_4$, Aldrich Chemical Co.) were used as the starting materials and 2-methoxyethanol (2-MOE, Aldrich Chemical Co.) as the solvent. Stoichiometric amount of $\text{Ti}(\text{OC}_3\text{H}_7)_4$, $\text{Zr}(\text{OC}_3\text{H}_7)_4$, $\text{Mg}(\text{OC}_2\text{H}_5)_2$ (3 mol% excess) and $\text{Nb}(\text{OC}_2\text{H}_5)_5$ according to the targeted composition were dissolved in 2-MOE and refluxed at 125°C in an argon atmosphere. Meanwhile, Stoichiometric amount of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ (15 mol% excess) was dissolved in 2-MOE and dehydrated at 125°C under vacuum. The excess of lead and magnesium added in this experiment could compensate for the evaporation of MgO and PbO during the sintering process. The solution contained Pb was mixed with the Mg-Nb-Ti-Zr complex solution while stirred, and then was refluxed at 125°C in an argon atmosphere for 2h. After the mixture solution was cooled down to the room temperature, acetyl acetone and acetic acid were added to adjust the viscosity of the solution and prevent cracking of film. Finally the 0.4 M 40PMN-25PZ-35PT solution was achieved. Before depositing on the Pt(111)/Ti/SiO₂/Si(100) substrate, the solution was filtered with a filter paper to avoid particulate contamination. Then, the solution was spin-coated at 3000 rpm for 30 s. After 2 min heat treatment on a hot plate at 200°C and 400°C to drive out the solvent and decompose organic compounds, each layer was crystallized at 750°C for 60 s using a rapid thermal annealing (RTA) furnace. This step was repeated to obtain the desired thickness.

Structural orientation of the film was analyzed by X-ray diffraction (XRD, Model XDS2000, Scintag, Cupertino, CA) with nickel filtered (CuK_α) radiation. Cross-sectional morphology of the films was observed using a scanning electron microscope (SEM) (Hitachi, S-3500N, Tokyo, Japan). The surface microstructure of the film was characterized with a transmission electron microscope (TEM, JEOL JEM 2010, Japan). To characterize the electrical properties of the thin film, 1.5 mm diameter circular Au-top electrodes were sputtered onto the film through a shadow mask. Low field leakage current and high field

hysteresis properties were characterized using an RT6000 (Radiant Technology, Albuquerque, NM) ferroelectric test system with a voltage amplifier. The dielectric constant and loss were measured using an impedance analyzer (HP4194A, Hewlett-Packard).

3. Results and Discussion

Figure 1 shows the crystalline structure characteristics of 40PMN-25PZ-35PT thin film determined by XRD. The XRD pattern reveals that 40PMN-25PZ-35PT thin films are polycrystalline and retain a perovskite structure without any detectable pyrochlore phase. The peaks at (100), (111), (200) and (211) can be observed and the relative peak intensity of $I(111)/\sum I(hkl)$ is calculated to be 0.88 for the 40PMN-25PZ-35PT thin film, indicating that 40PMN-25PZ-35PT thin film deposited on Pt(111)/Ti/SiO₂/Si substrate has a preferential $\langle 111 \rangle$ grain orientation. The small lattice-mismatch between the spacing of Pt (110) planes and the spacing of 40PMN-25PZ-35PT (110) planes is the main reason why the nucleus of 40PMN-25PZ-35PT thin film has a preferred $\langle 111 \rangle$ orientation along with the (111)-textured Pt bottom electrode. A scanning electron microscope (SEM) cross-sectional micrograph of the 40PMN-25PZ-35PT film is depicted in the inset. It shows that the 40PMN-25PZ-35PT film with the thickness of about 1.5 μm on the platinum buffered silicon substrate is dense and crack-free.

The plane-view high-resolution TEM (HRTEM) image of the 40PMN-25PZ-35PT film is shown in Figure 2. As can be seen, the 0.288 nm interval of the lattice fringes observed in this image corresponds to the distance between two (110) crystal planes, indicating that the arrow points to the [110] direction. According to the perovskite structure, the direction perpendicular to the atom plane characterized by HRTEM is [111], so it proves that [111] is the growth preferential direction for the 40PMN-25PZ-35PT thin film, which is further supported by the electron diffraction (ED) pattern also obtained from the surface of 40PMN-25PZ-35PT thin film, as shown in the inset of Figure 2.

Figure 3 depicts the 40PMN-25PZ-35PT film's ferroelectric hysteresis loop which exhibits a good symmetry. It shows that the remnant polarization (P_r) and the saturation polarization (P_s) of the 40PMN-25PZ-35PT thin film are 25.5 $\mu\text{C}/\text{cm}^2$ and 50.2 $\mu\text{C}/\text{cm}^2$, respectively, while the coercive field (E_c) is 51 kV/cm. In comparison with the single crystal, the 40PMN-25PZ-35PT thin film has larger coercive field due to the stress between films and substrate. The same phenomenon has been observed in PMN-PT thin films [12, 13]. It is worth noting that the remnant polarization of the film, comparable to those of the single crystals reported in the literature [4–7], is much higher than that of (111)-oriented PMN-PT thin film ($P_r=16.1 \mu\text{C}/\text{cm}^2$) on a Pt(111)/Ti/SiO₂/Si substrate [14].

Figure 4(a) shows the variation of the dielectric constant (ϵ_r) and loss (δ) as a function of frequency for the 40PMN-25PZ-35PT film measured at room temperature. As the frequency increases, the dielectric constant decreases while the loss is almost unchanged. At 1k Hz, the dielectric constant and loss are 1960 and 0.036, respectively. Obviously, the Permittivity of the 40PMN-25PZ-35PT thin film, comparable to that of a PMN-PT thin film (around 2000) [15], is much larger than that of the PZT thin film (around 1000)[16]. Figure 4(b) displays the dielectric constant of 40PMN-25PZ-35PT film as a function of temperature from 50°C to 250°C at 1k Hz. The dielectric constant shows a broad peak, indicating a rather diffuse phase transition. The maximum dielectric constant is found at approximately 209°C, corresponding to the transition from ferroelectric to paraelectric (tetragonal to cubic) phase. The phase transition temperature is much higher than that of the PMN-PT. Additionally, there is a shoulder located at around 150°C, which may be caused by the rhombohedral to tetragonal phase transformation temperature (T_{R-T}). The results are similar to those found

for 40PMN-25PZ-35PT single crystals [7]. The $\epsilon_r - T$ relationship of ferroelectric materials is often empirically fitted into the following equation:

$$1/\epsilon_r - 1/\epsilon_{r\max} = (T - T_{\epsilon_r\max})^\gamma / C \quad (2)$$

where, both C and γ are constants. The parameter γ called Curie–Weiss exponent, gives information on the character of the ferroelectric-paraelectric phase transition. For normal ferroelectric, $\gamma=1$, a normal Curie–Weiss law is obtained; for relaxor, $\gamma=2$, it reduces to the quadratic dependency which describes a complete diffuse phase transition. The plot of $\ln(1/\epsilon_r - 1/\epsilon_{r\max})$ vs $\ln(T - T_{\epsilon_r\max})$ for 40PMN-25PZ-35PT thin film is shown in inset of Figure 4(b). A linear relationship has been observed. The value of γ , determined by the slope of the fitting curve, is calculated to be 1.72 proving that the ferroelectric-to-paraelectric phase transition is of diffuse type [3].

Figure 5(a) shows the leakage current density of the Au/40PMN-25PZ-35PT/Pt thin film capacitor as a function of voltage in the range -20V to 20V . No matter which electrode is positively biased, the leakage current density is always lower than $2.37 \times 10^{-5} \text{ A/cm}^2$. An understanding of the origin of nonlinear conductivity in a thin insulator is pertinent to the development of ferroelectric film devices for microelectronics. Several possible mechanisms, such as Schottky emission [17], Poole–Frenkel emission [18] and space-charge-limited current (SCLC) [19–21], could be proposed for leakage current. All the mechanisms may simultaneously contribute to it but only one plays the major role. The leakage current density (J) for Schottky emission mechanism could be expressed by the equation:

$$J = A^* T^2 \exp[-(\Phi_b - \beta_s E^{1/2})/k_B T] \quad (3)$$

Where $\beta_s = (e^3/4\pi\epsilon_0\epsilon_r)^{1/2}$, A^* is the Richardson coefficient, which incorporates the carrier mobility, Φ_b is the zero-field Schottky barrier height and e is the electron charge. In the Poole–Frenkel emission process, the expression of leakage current density could be given by:

$$J = A_0 E \exp[-(\Phi_a - \beta_{PF} E^{1/2})/KT] \quad (4)$$

where $\beta_{PF} = (e^3/\pi\epsilon_0\epsilon_r)^{1/2}$, A_0 is a constant, Φ_a is the activation energy and e is the electron charge. For SCLC mechanism, the leakage current density could be described by

$$J = 9\epsilon\epsilon_0\mu E^2/8d \quad (5)$$

where μ is the mobility and d is the thickness of the insulator layer. It is noted that in the three equations above, E , ϵ_r and ϵ_0 represent the electric field, the relative dielectric constant and the permittivity of the free space, respectively.

According to the equations (3) and (5), it is concluded that the Schottky emission can be expressed as $\log(J)$ proportional to the square root of the applied electric field (E), and that the SCLC can be expressed as $\log(J)$ proportional to $\log(E)$. To verify the conduction mechanism in the 40PMN-25PZ-35PT film, the leakage current density J is plotted against $E^{1/2}$ and $\log(E)$ in semilog scale in Figure 5(b) and 5(c), respectively. As shown in Fig 5(b), a linear relationship between $\log(J)$ and $E^{1/2}$ is observed when the Au electrode is under the a

positive bias voltage, which suggests that the leakage current shows a Schottky emission. That is to say, if the electric potential of Pt electrode is lower than that of Au electrode, the 40PMN-25PZ-35PT/Pt interface forms a Schottky barrier at the dc bias from 0 to 20V. In the plot of $\log(J)$ versus $\log(E)$, as shown in Fig 5(c), the slope is close to 1.0 in the low electric field (<50 kV/cm) region, indicating that Ohm's law dominates conduction in the low electric field when the Pt electrode is positively biased. The main reason is that the density of thermally generated carriers in a film is predominant over the injected charge carriers. At the field over 50 kV/cm, the slope of $\log(J)$ versus $\log(E)$ is close to 2, which agrees well with the equation (5), so the entire leakage current is dominated by SCLC mechanism in this case. As the applied voltage is increased, a strong injection of the charge carriers in the film takes place. The space-charge effects are observed when the injected free carrier density exceeds the volume generated free carrier density.

4. Conclusion

In summary, 1.5 μm -thick highly (111)-orientated 40PMN-25PZ-35PT film with a Curie temperature of 209°C was fabricated on Pt(111)/Ti/SiO₂/Si substrate by a sol-gel process with rapid thermal annealing. The film had a remanent polarization of 25.5 $\mu\text{C}/\text{cm}^2$ and coercive electric field of 51 kV/cm. At 1k Hz, the dielectric constant and loss of the thin film were 1960 and 0.036, respectively. The leakage current was found to depend on the voltage polarity. When the electric potential of an Au electrode was higher than that of the Pt electrode, the leakage current behaved like a Schottky emission process. If the Pt electrode was biased positively, at low electric fields (<50 kV/cm), it appeared that Ohm's law dominated the conduction, while at high fields (>50 kV/cm), the conduction current showed a SCLC behavior. These results suggest that sol-gel derived highly (111)-oriented 40PMN-25PZ-35PT thin films may be promising for ultrahigh frequency ultrasound transducer applications.

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Figure 1. XRD pattern of 40PMN-25PZ-35PT film on Pt(111)/Ti/SiO₂/Si substrate. (Inset: SEM cross-sectional micrograph of the 40PMN-25PZ-35PT film on Pt(111)/Ti/SiO₂/Si substrate)

Figure 2. Surface high-resolution TEM (HRTEM) image of the 40PMN-25PZ-35PT film. (Inset: the electron diffraction (ED) pattern of surface of 40PMN-25PZ-35PT film)

Figure 3.
Typical polarization-electric field (P-E) hysteresis loop of the 40PMN-25PZ-35PT film

Figure 4.

(a) Dielectric constant and loss as a function of frequency for the 40PMN-25PZ-35PT film at room temperature. (b) Dielectric constant of 40PMN-25PZ-35PT film as a function of temperature from 50°C to 250°C at 1k Hz. (Inset: the plot of $\text{Ln}(1/\epsilon_r - 1/\epsilon_{r\max})$ vs $\text{Ln}(T - T_{\epsilon_{r\max}})$ of the film)

Figure 5.

(a) Leakage current density of the Au/40PMN-25PZ-35PT/Pt thin film capacitor versus dc bias voltage. (b) Plot of $\log(J)$ versus $E^{1/2}$ of the thin capacitor when the Au electrode was under a positive bias. (c) Plot of $\log(J)$ versus $\log(E)$ of the film capacitor when the Pt electrode was under a positive bias.