Growth and electrical properties of Pb(Zr,Ti)O₃ thin films by a chemical solution deposition method using zirconyl heptanoate as zirconium source

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Abstract

Pb(Zr,Ti)O₃ (PZT) thin films were prepared on (111) Pt-coated Si substrates by a chemical solution deposition method using zirconyl heptanoate as zirconium source instead of commonly used zirconium alkoxides. The effects of processing conditions on the microstructure and electrical properties of the PZT thin films were investigated. The texture of the PZT thin films could be changed by selecting different heat-treatment methods. Orientation-dependent electrical properties, including dielectric constant, polarization, and coercive field, were examined. The randomly oriented PZT thin films annealed at 600°C for 0.5 h showed a well-defined ferroelectric hysteresis loop with a remanent polarization of 18 μC/cm² and a coercive field of 74 kV/cm.

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1. Introduction

For more than a decade, ferroelectric thin films have been widely studied for the applications in nonvolatile memories, pyroelectric detectors, and microelectromechanical systems [1,2]. Pb(Zr,Ti)O₃ (PZT) thin film is one of the most attractive candidates for these kinds of applications [3,4]. A variety of preparation methods have been used to obtain PZT thin films [5–7]. Chemical solution deposition method has been proved to be a promising one for this aim with the advantages of low annealing temperature, good composition control [8–10]. Usually, in chemical solution deposition process for PZT thin films, zirconium alkoxides such as zirconium isopropanoxide, zirconium n-butoxide, which are chosen as zirconium sources, lead acetate, and titanium alkoxide, are...
used to synthesize PZT precursor solutions [11,12]. However, the precursor solutions obtained are sensitive to moisture in air, and therefore, are unstable. Recently, it has been reported that zirconium oxynitrate and zirconium nitrate have been chosen as zirconium sources instead of zirconium alkoxides to synthesize the PZT precursor solutions, and some investigations on structure and electrical properties of resultant PZT thin films have been done [13–15]. However, the remanent polarization of the PZT thin films obtained was lower than that of the PZT thin films prepared from the solution with zirconium alkoxides as zirconium sources, additionally, the needed annealing temperature is higher. In this work, we selected zirconyl heptanoate to synthesize the PZT precursor solution, and the structure and ferroelectric properties of PZT thin films obtained were studied. It was found that a comparable ferroelectric polarization of PZT thin films was obtained at a relatively low annealing temperature.

2. Experimental procedure

A chemical solution deposition method was used to prepare Pb(Zr0.5Ti0.5)O3 thin films. Lead acetate trihydrate[ Pb(CH3COO)2·3H2O], zirconyl heptanoate[ZrO(C6H13COO)2], and tetra-n-butyl titanate[Ti(OC4H9)4] were used as source materials, and 2-ethoxyethanol was used as solvent to synthesize PZT precursors [16,17]. Firstly, lead acetate trihydrate and zirconyl heptanoate were mixed in 2-ethoxyethanol with stirring and heating to 130°C and holding for 15 min. After cooling to room temperature, PZ solution was prepared. Secondly, lead acetate trihydrate was dissolved in 2-ethoxyethanol with stirring and heating to 124°C for 10 min, then, tetra-n-butyl titanate was added to above lead acetate solution with heating to 130°C for 15 min. The PT solution was synthesized. Thirdly, PZ solution was slowly dropped into the PT solution with vigorous stirring for some time. Thus, the PZT precursor solution with 5% Pb excess was well synthesized for preparing PZT thin films. The thin films were deposited by a multiple spinning technique. The precursor solution was spun onto the Pt-coated Si substrates. The spinning rate and time were 3000 rpm and 25 s, respectively. The wet films obtained were put into an electric furnace for heat-treatment, first pyrolysis, and then annealing. The pyrolysis temperature was varied from 400°C to 480°C, and the final annealing temperature was changed from 500°C to 650°C. In addition, rapid thermal annealing (RTA) method was also used in our experiment in order to obtain (1 1 1) oriented thin films. The thickness of films can be increased by multiple spinning-pyrolysis process. The typical film thickness was about 0.6 μm.

The evolution of the precursor solution with temperature was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The structure of the thin films was analyzed after heat treatment using a Rigaku D/max-2400 X-ray diffractometer (XRD) in the mode of 2θ–θ scan with CuKα radiation. The surface and cross-section morphology of the thin films was examined using a Hitachi S-2700 scanning electron microscopy (SEM). The dielectric properties and capacitance-voltage curves were measured on the films in a metal-ferroelectric-metal (MFM) configuration using a HP4192A LF impedance analyzer, and the hysteresis loop measurements were carried out using a modified Sawyer-Tower circuit under the frequency of 1 kHz. To measure electrical properties, Pt dot electrodes of 1 mm diameter were deposited on the surfaces of the fired films as top electrodes through a shadow mask. The platinum bottom electrode was obtained by etching away a corner of film by using a diluted HF + HCl mixing solution.

3. Results and discussion

Fig. 1 shows DTA and TGA curves of PZT precursor solution. The absorption peak at 135°C was related to the evaporation of solvent. The exothermic peak around 327°C corresponded to the decomposition and combustion of organic substances. After 400°C, no weight loss can be observed, suggesting the completeness of decomposition. The broad peak around 504°C in DTA curve might be attributed to crystallization of
PZT. The heat-treatment schedule for the PZT thin films will be based on the DTA-TGA analysis.

The effect of annealing temperature on crystalline structure of PZT thin films was investigated by X-ray diffraction. Fig. 2 shows XRD patterns of PZT thin films on Pt/Ti/SiO₂/Si substrates annealed at different annealing temperatures, (a) 500°C, (b) 550°C, (c) 600°C, and (d) 650°C for 5 min. The pyrolysis temperature was set at 400°C. As can be seen, at the annealing temperature of 500°C, only pyrochlore phase can be observed in the XRD pattern; at the annealing temperature of 550°C, minor pyrochlore phase and major perovskite phase coexisted in thin films. When the annealing temperature was increased to 600°C, the pyrochlore phase was completely transformed to perovskite phase. At 650°C, no other phases other than perovskite phase can be observed. Shao et al. [13] reported that the PZT thin films prepared from the precursor solutions using zirconium nitrate as zirconium source, still contained pyrochlore phase even the films were annealed at 650°C. A higher annealing temperature of 700°C was needed for a well-crystallized perovskite structure for the PZT thin films prepared from the solution using zirconium oxyxnitrate as zirconium source [15]. These indicated that the formation temperature of PZT perovskite phase in our study is lower, suggesting that zirconyl heptanoate is a promising alternative source for preparing PZT thin films. In addition, it can be seen that the thin films are randomly oriented. A previous study performed by Kwok and Desu [18] showed that, when the pyrochlore intermediate phase was formed, the pyrochlore to perovskite transformation was an interface controlled process which resulted in the formation of randomly oriented thin films.

Fig. 3 shows XRD patterns of PZT thin films on Pt-coated Si substrates with different pyrolysis temperatures, (a) 400°C, (b) 440°C, (c) 460°C, and (d) 480°C. The final annealing conditions (600°C for 0.5 h) are identical for all samples. Obviously, the orientation of the thin films changed with pyrolysis temperature. When the pyrolysis temperature was 400°C, the thin film is randomly...
oriented; with increasing pyrolysis temperature, the (100) preferential orientation was enhanced. The (100) orientation ratio, which is defined as \(I(100) / [I(100) + I(110)]\), is 47% for the film with pyrolysis temperature of 480°C. Note that the randomly oriented film had the value of 22% for (100) orientation ratio. PZT has a close lattice constant with Pt, (111) oriented PZT has the smallest plane-spacing misfit with (111) oriented Pt, and the activation energy for PZT nucleation is the lowest for heterogeneous nucleation on the lattice matched substrate. However, (111) preferential orientation of PZT thin films was not observed under this experimental condition. It should be noted that (100) oriented PZT has the lowest surface energy, thus, the growth plane of PZT with the lowest activation energy is the (100) plane. Therefore, (100) nuclei of PZT will grow more rapidly compared with other oriented nuclei, and the film will have either a (100) preferential orientation or random orientation [19].

It has been confirmed that electrical properties of PZT thin films are strongly dependent on orientation of thin films, much effort has been made to control the orientation [12,20,21]. In our study, by using different substrates and selecting different processing parameters, the PZT thin films with different preferential orientations were obtained. Fig. 4 shows XRD patterns of PZT thin films with (a) (100) preferential orientation, (b) random orientation, and (c) (111) preferential orientation. Note that (a) and (b) have same annealing temperature 600°C for 0.5h, but different pyrolysis temperature 480°C and 400°C, respectively; for (c) the film was heat-treated by RTA method (at 650°C for 5min).
oriented; In Fig. 4(c) the film shows a strong (111) peak and weak (100) and (110) peaks, indicating a (111) preferred orientation. Both (100) and (111) preferential orientations can be obtained under proper heat-treatment control. Table 1 lists the variation of dielectric constants and dissipation factors of thin films with different preferential orientations. The thin films with (100) orientation have higher dielectric constant than the thin films with random orientation and the thin films with (111) preferential orientation. This is in good agreement with the result reported previously [12].

PZT thin films also showed different ferroelectric properties depending on crystalline orientations. Fig. 5 shows hysteresis loops of the thin films with different orientations, (a) (111), (b) random, (c) (100). As can be observed, the shapes of the hysteresis loops and polarization and coercive field values for the various preferentially oriented thin films are somewhat different. $P_s, P_r,$ and $E_c$ of the thin film with (100) orientation were $23 \mu C/cm^2$, $12 \mu C/cm^2$, and $102 kV/cm$, respectively; $P_s, P_r,$ and $E_c$ of the thin film with (111) orientation were $30 \mu C/cm^2$, $19 \mu C/cm^2$, and $72 kV/cm$, respectively; $P_s, P_r,$ and $E_c$ of the thin film with random orientation were $37 \mu C/cm^2$, $18 \mu C/cm^2$, and $74 kV/cm$, respectively. These values indicated that the films have good ferroelectric properties which are comparable to the other results obtained for the PZT thin films prepared from the precursor solutions using zirconium alkoxide as zirconium source [3,12]. The (111) preferentially oriented PZT thin film exhibited better squarness of the hysteresis loop with larger remanent polarization; on the contrary, the (100) preferentially oriented film had an inferior hysteresis loop with a lower $P_r$ value. It was known that the polarization dipoles for the tetragonal structure are aligned with the [001] direction, but not [111] or [100] directions [22].

Table 1

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Dielectric constant</th>
<th>Dissipation factor</th>
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<tbody>
<tr>
<td>(100)</td>
<td>603</td>
<td>0.025</td>
</tr>
<tr>
<td>(111)</td>
<td>427</td>
<td>0.021</td>
</tr>
<tr>
<td>Random</td>
<td>546</td>
<td>0.03</td>
</tr>
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</table>

Fig. 5. Hysteresis loops of the thin films with different orientations: (a) (111), (b) random and (c) (100). Considering that PZT thin films consisted of the grains with a multi-domain structure, this implied the co-existence of two types of domains, 90° domains and 180° domains. The 180° domains, normal to the film surface, mainly contribute to the polarization, whereas 90° domains, parallel to the film surface, which are difficult to reorient, contribute to the polarization only under a larger applied field [22–24]. Domain switching is strongly
dependent on the applied field and film orientation. In the case of (100) preferentially oriented films, the switching of 90° domains from [001] to [100] is not favored by an applied electric field along the film thickness, because strong ferroelastic effect limits the motion of 90° domains. This means that 90° domains cannot contribute to polarization in (100) preferentially oriented PZT films. For a (111) oriented film, the 180° domains are rather mobile, and, thus, they are easily swept out of the grains by applying a proper electric field [19]. Therefore, the (111) preferentially oriented films had better hysteresis loops than (100) preferentially oriented PZT films. Lee et al. [11] also reported that (111) preferential oriented films exhibited better squarness of the hysteresis loop with larger remanent polarization than the (100) preferentially oriented PZT thin films. Additionally, it should be noted that the Ec (102 kV/cm) of (100) oriented film was higher than that (72 kV/cm) of the (111) oriented film, which was not consistent with the result reported previously [12]. This might be related to the different preparation processes. Note that the heat-treatment methods of the thin films in our study, used to control the orientation of the films were different, this would change microstructure and electrical properties of the thin films.

4. Conclusion

Pb(Zr,Ti)O₃ thin films were prepared on (111) Pt-coated Si substrates by a chemical solution deposition method using zirconyl heptanoate as zirconium source instead of commonly used zirconium alkoxides. The effects of processing conditions on the microstructure and electrical properties of the PZT films were investigated. The texture of the PZT films could be changed by selecting different heat-treatment methods. Orientation-dependent electrical properties, including dielectric constant, remanent polarization, and coercive field, were examined. The PZT thin films annealed at 600°C for 0.5 h showed a well-defined ferroelectric hysteresis loop with a remanent polarization of 18 μC/cm² and a coercive field of 74 kV/cm.

References