Preparation and Ferroelectric Properties of PZT Multilayer Film

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Abstract. The PZT multilayer films were prepared by sol-gel method. The effects of formamide content, crystallization temperature and number of layers on the microstructure and ferroelectric properties of PZT films were investigated by optical microscopy, XRD, AFM and SEM. When the content of formamide in the PZT precursor solution is 0.34% by weight, the surface morphology is flat, and the film formation and crystallization are highest when the crystallization temperature is 690 °C. The surface of the four-layer film has low undulation, less impurities, and uniform particle size and particle distribution on the surface of the film. The maximum undulation of the film is 10 nm, the average undulation is 6 nm, and the ferroelectric domain is dominated by 20° domain and 200° domain. When the polarization inversion voltage is 8.0V, the loaded pattern is polarized and flipped, and the flip angle is about 180°. The inverted ferroelectric domain is very stable.

1. Introduction
Magnetolectric materials include single-phase magnetolectric materials and multi-phase magnetolectric materials. Single-phase magnetolectric materials are either weak in magnetolectric coupling or have a low ferromagnetic Curie temperature and are far away from commercialization. Magnetolectric composite materials with many advantages such as large magnetolectric conversion coefficient and high Neel and Curie temperature are hot topics in research and application [1-5]. The magnetolectric composite film material is easy to integrate with the chip compared with the bulk magnetolectric composite material, has good process compatibility of microelectronics and MEMS devices, and is more promising for use in the fields of microsensors and polymorphic storage compared with bulk magnetolectric composite materials, and becomes the focus of research and development. The ferroelectric thin film material with controllable ferroelectric domain structure and good performance is the foundation of composite materials, and ferroelectric devices based on ferroelectric thin films [6-9]. The preparation of ferroelectric thin film materials is of great significance for the research and application of material-device integration for magnetolectric materials. The micro structure and ferroelectric properties PZT multilayer films prepared by sol-gel method are studied in this paper.

2. Experiment
PZT film was prepared on a 10 mm×10 mm Pt/Ti/SiO₂/Si substrate by Sol-Gel spin coating method. The raw materials included lead acetate trihydrate, zirconium nitrate and tetrabutyl titanate. The raw materials were dissolved by stirring, mixed, and stirred at 60°C for 2.5 hours, and ultrasonically dispersed for 1 hour. 500r/s for 6s and 4000r/s for 30s. Slowly heat up to 400 °C and keep warm for 15
min, quickly heat up to the highest temperature (about 690 °C) and keep warm for 10 min, so that the pyrochlore phase in the film is completely converted into a perovskite phase.

AFM morphology and ferroelectric properties were observed using a CypherTM S atomic force microscope from Oxford Instruments. In the atomic force microscope PFM mode, the probe is applied with a flip voltage (determined by the coercive force test), so that the probe is scanned on the surface of the sample according to the loaded pattern, and the domain structure of the loaded pattern can be obtained by scanning the surface of the sample according to the loaded pattern and inverting its domain structure. The surface morphology of the sample was observed by the SmartLab (9) intelligent target X-ray diffractometer, and the surface optical morphology was observed by Nikon 80i cheating microscope. The on-line morphology was characterized by Japanese electronic JSM-7800F thermal field emission scanning electron microscope.

3. Experimental Results and Analysis

3.1. Effect of Formamide Content on Morphology and Phase of PZT Film

The optical morphology of the PZT film prepared with different formamide content in the PZT precursor solution is shown in Figure 1. The microscopic surface morphology is the most flat when the formamide content in the PZT precursor solution is 0.34wt%. The surface of the film prepared by the two solutions has certain defects such as bubbles, holes, and bright and dark areas.

![Figure 1. Surface morphology of PZT film with different formamide content](image)

(A—0wt%; B—0.34wt%; C—0.68wt%)

The XRD patterns of different amounts of formamide added to the PZT precursor solution is shown in Figure 2. The peak at a diffraction angle of about 22 and 38 is a diffraction peak of Pb₂(TiZr)O₃, indicating the formation of a PZT phase in the film. It can be seen from the XRD pattern that when the content of formamide in the solution before PZT is 0.34wt%, the peak of the PZT phase is the highest, indicating that the prepared film crystal is relatively sufficient. When the amount of formamide in the solution before PZT is 0% and 0.68wt%, the diffraction peak intensity of Pb₂(TiZr)O₃ is low. It can be seen that the growth and formation of the PZT film is optimal when the amount of formamide is added by 0.34wt% by weight.

![Figure 2. Local XRD pattern of different formamide concentrations](image)
3.2. Effect of Heat Treatment Temperature on Morphology of PZT Thin Films
The microstructure of the PZT thin film prepared by observing different crystallization temperatures by optical microscopy is shown in Figure 3. According to the optical surface morphology, when the heat treatment temperature is 690 °C, the surface morphology of the film is the most flat, and the surface of the film prepared by the other three crystallization temperatures has certain defects such as bubbles, holes, bright and dark areas, etc. From this, it was found that the film formability and the microscopic surface topography were optimal at 690 °C.

\[\text{Figure 3. Surface topography of PZT thin films with different crystallization temperatures}\]

3.3. XRD of PZT Thin Films with Different Heat Treatment Temperatures and Layers
The XRD diffraction of PZT thin films with different heat treatment temperatures and different layers is shown in Figure 4 and Figure 5. Figure 4 is an XRD patterns of the diffraction angle of the PZT film at different heat treatment temperatures of 35° - 45°. As can be seen from Figure 4, when the heat treatment temperature is 690 °C, the peak of the PZT phase is the highest, and it is understood that the growth and formation of the PZT film are optimal when the crystallization temperature is 690 °C. It can be seen from Figure 5 that the more the coating, the higher the peak of the film, indicating that the PZT phase increases with the increase of the number of coating layers. From the technical point of view, the more the number of layers, the more surface defects, so the latter experiment mainly studied the PZT film within four layers.

\[\text{Figure 4. Local XRD pattern of PZT film with different crystallization temperatures}\]

\[\text{Figure 5. Local XRD pattern of PZT film with different layers}\]

3.4. SEM of PZT Multilayer Film
A four-layer PZT film was subjected to SEM analysis as shown in Figure 6. It can be seen from the figure that the surface of the film has low undulation, less impurities, and uniform particle size and particle distribution on the surface of the film.
3.5. AFM Topographic Imaging of PZT Multilayer Film

The topographic characterization, particle size and undulation of the film were analyzed by atomic force microscopy. The AFM topographic imaging of the four-layer PZT film is shown in Figure 7. The single particle size is shown in Figure 8. It can be clearly seen from the figure that the particle size is uniform, the particle surface is uniformly grown, and the crystal particle size is about 150 nm, which is consistent with the particle size measured by SEM, and the particle undulation is 1.4 nm.

The flatness of the film surface at the white line portion of Figure 7(a) measured, and the results are shown in Figure 9. The film has a maximum undulation of 10 nm and an average undulation of 6 nm, indicating that the film surface is very flat.

3.6. Ferroelectric Domain Structure of PZT Multilayer Film

The domain structure in the PZT thin film examined in a PFM mode of AFM is shown in Figure 10. It can be seen from the figure that the PZT film has a multi-angle ferroelectric domain and is evenly distributed. To further analyze the multi-domain structure, the white line position in Figure 9 is analyzed to obtain a graph as shown in Figure 11. It can be visually seen from Figure 11 that the
ferroelectric domains of the PZT have a multi-domain structure, and showing 20° domains, 200° domains, 90° domains, but most of them are 20° domains and 200° domains.

Figure 10. Ferroelectric domain structure of PZT thin film

Figure 11. Multidomain structure graph

3.7. Ferroelectric Domain Inversion of PZT Multilayer Film

The hysteresis loop of the ferroelectric material was measured by the PFM mode of AFM, as shown in Figure 12. The hysteresis loop is the macroscopic property of the ferroelectric domain under the action of an external electric field. The magnitude of the ferroelectric domain inversion voltage is obtained from the measured hysteresis loop. In general, the inversion voltage is greater than the coercive voltage in the hysteresis loop. It can be seen from the figure that the coercive voltage measured by PFM is 5.0V, and the flipping effect is optimal when the polarization inversion voltage is 8.0V.

The hysteresis loop measured by the above PFM actually determines the flip voltage of the PZT film, which is about 8.0V. In the PFM mode of AFM, a voltage of 8.0 V is applied to the probe to scan the surface of the sample according to the loaded pattern, and the domain structure is inverted to obtain the domain structure of the loaded pattern. The flip voltage applied during scanning is ±8.0V, the scanning rate is 1HZ, the phase of the picture “纣纣” is set, and the domain structure is flipped according to the set picture. The result is shown in Figure 13, where “Deg” indicates the domain angle.

It can be visually shown in Figure 13 that the processed region can reach the nanometer level, and the positive and negative domain polarization inversion is approximately 180°. In order to study the domain angle in detail, the position of the white line in Figure 13 was further studied and analyzed. It can be intuitively seen from Figure 14 that the inverted domain is mainly 25° domain and 220° domain, so the flip voltage of ±8.0V is added, and the flip angle is about 180°, indicating opposite direction of polarization.

Figure 12. PZT thin film hysteresis loop diagram

Figure 13. phase after ferroelectric domain flipping

Figure 14. Domain angle diagram

Using the “write domain” function mode in the piezoelectric power microscope (PFM) mode, 8V is applied to the tip of the needle, the mode of contact between the probe and the material is changed to “Contact” mode, the scan rate is set to 1 Hz, and the specific load is loaded. The domain distribution
pattern scans the surface of the material to obtain a patterned ferroelectric domain distribution. The graph loaded in this experiment is “[::-]”, and the surface ferroelectric domain distribution after the probe scanning is completed is shown in Figure 15. The appearance distribution of the loaded “[::-]” shape can be clearly seen in the figure.

The domain-reading domain was performed on the prepared PZT thin film using the PFM mode of the atomic force microscope. After the domain structure was read, the domain was read for 30 min, and the read domains were compared under the same conditions and under the same conditions to test the stability of the PZT thin film. The sample tested is shown in Figure 16.

From the comparison of Figure 16(a) and Figure 16(b), it can be found that there is almost no difference between the two figures in the plan view, indicating that the ferroelectric domain polarization has almost no change with time after the polarization of the ferroelectric domain is reversed, so the PZT film The stability is very good.

4. Conclusion
When the content of formamide in the PZT precursor solution is 0.34wt%, the morphology is the most flat and the crystallization is the best. When the crystallization temperature is 690 °C, the film formation and microscopic surface morphology are optimal and the peak of the PZT phase is the highest.

The surface of the film is relatively flat, the maximum undulation is 10 nm, the average undulation is 6 nm, and the ferroelectric domain is dominated by 20° domain and 200° domain.

When the polarization inversion voltage is 8.0V, the loaded pattern is polarized and flipped, and the flip angle is about 180°. The angle of the ferroelectric domain is very stable and does not change with time.

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