

Review

Synthesis, Microstructure and Properties of Magnetron Sputtered Lead Zirconate Titanate (PZT) Thin Film Coatings

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Abstract: Compared to aluminum nitride (AlN) with simple stoichiometry, lead zirconate titanate thin films (PZT) are the other promising candidate in advanced micro-electro-mechanical system (MEMS) devices due to their excellent piezoelectric and dielectric properties. The fabrication of PZT thin films with a large area is challenging but in urgent demand. Therefore, it is necessary to establish the relationships between synthesis parameters and specific properties. Compared to sol-gel and pulsed laser deposition techniques, this review highlights a magnetron sputtering technique owing to its high feasibility and controllability. In this review, we survey the microstructural characteristics of PZT thin films, as well as synthesis parameters (such as substrate, deposition temperature, gas atmosphere, and annealing temperature, etc.) and functional properties (such as dielectric, piezoelectric, and ferroelectric, etc). The dependence of these influential factors is particularly emphasized in this review, which could provide experimental guidance for researchers to acquire PZT thin films with expected properties by a magnetron sputtering technique.

Keywords: PZT thin films; magnetron sputtering; fabrication; microstructure; properties



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1. Introduction

Lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) ceramics has been widely employed in sensors, actuators, and transducers due to higher piezoelectric constant (compared with PbTiO_3 , AlN), higher Curie temperature (compared with BaTiO_3), and excellent temperature stability (compared with $\text{Na}_x\text{K}_{1-x}\text{NbO}_3$) [1–5]. However, high-frequency ultrasound transducer arrays for high resolution require thin piezoelectric ceramics which are difficult to manufacture and assemble with low cost and high efficiency [6,7]. PZT thin films could achieve these requirements and have the advantages of low volume and power consumption [8]. Therefore, PZT has been ranked as the most important piezoelectric thin film coating (another one is aluminum nitride, AlN). Owing to its complex stoichiometry, the properties of PZT thin films (such as dielectricity, piezoelectricity, ferroelectricity) could be tailored by controlling fabrication parameters. The characteristics of adjustable properties enable PZT thin films to be applied in a wider range of advanced micro-electric devices, including surface acoustic wave (SAW) devices, sensors, energy harvests, dynamic random-access memories (DRAMs), nonvolatile random-access memories (NVRAMs), transducers and so on [9–12]. Therefore, the focus of PZT research is directed towards synthesizing thin films with desired properties by the optimization of fabrication parameters.

Among PZT thin films fabrication techniques, sol-gel, magnetron sputtering and pulsed laser deposition (PLD) are commonly used and categorized as a chemical method (the first one) and a physical method (the latter two). The comparison of these three common methods is summarized in Table 1. The sol-gel (also called chemical solution deposition, CSD) method is based on the reactions of precursor solutions and the schematic process is shown in Figure 1a [13]. First, precursor solutions with proper stoichiometry of

metal ions were prepared while Pb was usually added in excess of 10%–20% to compensate the volatilization. Then, the solutions were dispersed on the surface of the substrate by spin-coating method. Finally, the sample was annealed at a high temperature to convert the solutions to solid oxide films. This method is advantageous due to its simplicity, low cost, easy composition changes (Zr/Ti ratio and element doping). However, the chemical reactions are hard to control, resulting in the limited composition uniformity and residual impurity that lead to properties degradation. Moreover, PZT thin films must be deposited layer by layer when the total thickness exceeds 100–200 nm, leading to relatively poor interface bonding. Therefore, physical deposition methods have been introduced to fabricate PZT thin films due to their controllable stoichiometric composition and robust interface bonding.

Table 1. Comparisons of sol-gel, pulsed laser deposition (PLD) and magnetron sputtering technique for the fabrication of PZT thin films.

Type	Basic Process	Advantages	Disadvantages
Sol-gel (Chemical process)	Precursor solutions; Spin-coating; Annealing	Cost: low Substrate: large Thickness: thick Doping: convenient	Crystallinity: low Interface: weak Uniformity: low Impurity: yes
PLD (Physical process)	Laser generation; Heat evaporation; Vapor deposition	Crystallinity: high Interface: strong Uniformity: high Impurity: no	Cost: high Substrate: small Thickness: thin Doping: complex
Magnetron sputtering (Physical process)	Ar Ionization; Bombardment; Vapor deposition	Cost: low (industry) Substrate: large Crystallinity: high Interface: strong Uniformity: high Impurity: no	Doping: complex Cost: high (research) Thickness: medium

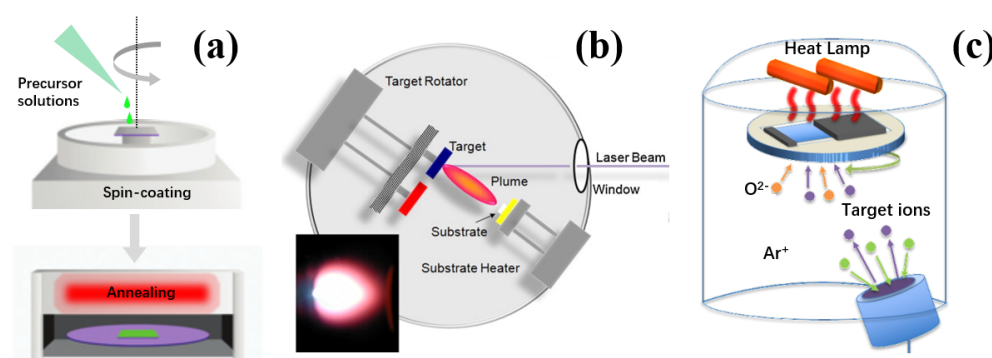


Figure 1. Schematic process of different fabrication methods for PZT thin films; (a) sol-gel including spin-coating and annealing based on chemical reactions. [13]; (b) pulsed laser deposition based on physical interactions by laser heating. Reprinted with permission from [14] Copyright 2010 Elsevier; (c) magnetron sputtering technique based on physical interactions by ion bombardment. Reprinted with permission from [11] Copyright 2018 John Wiley and Sons.

PLD and magnetron sputtering technique are two typical physical vapor deposition methods for PZT thin films. The diagrammatic sketch of PLD is displayed in Figure 1b and the deposition is achieved by vaporization of target materials due to the laser heating [14]. First, the PZT ceramic target is prepared using determined stoichiometry with 10~20% Pb excess. Then, the generated laser is focused on the target surface, which is heated to evaporate. Finally, the atoms move to the surface of the substrate and form PZT thin films. The advantages of PLD are guaranteed complex stoichiometries, excellent crystallinity and

strong interface bonding. However, the deposition rate is extremely low while it is difficult to prepare PZT thin films with a large area (3 inches and above) and greater thickness (more than 500 nm). Therefore, such a method is not suitable for applications targeting large and thick PZT thin films. In comparison, the magnetron sputtering technique could achieve the efficient synthesis of large-scale and thick PZT thin films.

The magnetron sputtering process is exhibited schematically in Figure 1c and the deposition is realized based on the transformation of target molecules or atoms due to ion bombardment [11]. First, the target with desired composition was fabricated by a similar method to PLD including PZT ceramics or Zr–Ti–Pb alloys. Then, Ar in reactor chamber will be ionized and bombard the target surface to eject molecules or atoms. Finally, those ejected materials will migrate to the substrate surface and form films. Compared with PLD, magnetron sputtering technique is widely used for large-scale production owing to high deposition rate and strong plasma glow while it could also realize high film quality (interface bonding and crystallinity). Moreover, the magnetron sputtering technique has high compatibility with an IC (integrated circuit) which is beneficial in terms of lower cost and wider applications in advanced microelectronic devices. Therefore, the magnetron sputtering technique is worthy of deep investigation for the fabrication of PZT thin films.

Based on our previous researches on metal/oxide multilayer systems by the magnetron sputtering technique, the fabrication parameters could strongly influence the microstructure and consequently affect the properties [15–18]. Therefore, it is important for practical applications to understand the intrinsic relationships between these three factors, especially for PZT thin films. However, to the best of our knowledge, there is no reported review article emphasized on magnetron sputtered PZT thin films with explicit intrinsic relationships between fabrication parameters and microstructure or properties. In this paper, we summarize related research on PZT thin films and present a review to comprehend the intrinsic relationships between those three factors. To achieve this goal step-by-step, this review is conceived into three parts. In Section 2, the sputtering process is clarified and compared in detail. In Section 3, the effects of fabrication parameters on microstructural characteristics are explained. Section 4 illustrates the influences of microstructure on properties. This review could provide an overall understanding for researchers interested in PZT thin films by the magnetron sputtering technique. Furthermore, it may lay a theoretical and experimental foundation for the wider application of PZT thin films.

2. Sputtering Classifications

Magnetron sputtering technique is often employed in thin film deposition, especially for complex oxide films. The fabrication of PZT thin films was first introduced in 1976 [19,20]. According to the target raw materials (metals or ceramics), the sputtering method could be classified into two forms as shown in Figure 2. One is DC (direct current) reactive sputtering and the other is RF (radio frequency) sputtering. The comparisons of these two sputtering methods are summarized in Table 2.

Table 2. Comparisons of RF sputtering and DC reactive sputtering.

	DC Reactive Sputtering	RF Sputtering
Target	Metals (Oxidation)	Ceramics (Bombardment)
Oxygen	Necessary	Optional
Advantages	Deposition rate: High Composition range: Large Target area: Large	Impurity: No Target fabrication: Simple Repeatability: Stable
Disadvantages	Target fabrication: Complex Impurity: Yes Repeatability: Unstable	Deposition rate: Limited Composition range: Small Target area: Limited

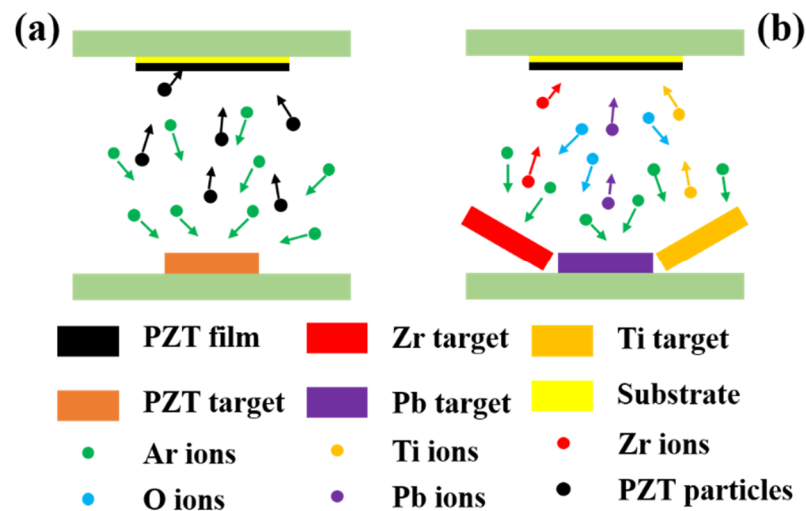


Figure 2. Schematic diagram of (a) RF sputtering and (b) DC reactive sputtering. RF sputtering usually employs ceramic targets while DC reactive sputtering often applies to metal targets.

The introduction of DC reactive sputtering to PZT thin films could be traced back to 1981 [21]. Generally, the metal targets of Zr, Ti, and Pb are employed to deposit PZT films in the presence of oxygen as shown in Figure 2a. During the process, metals are oxidized and then these metal oxides would form solid solutions (namely PZT thin films) on the surface of the substrate after migration. In addition to individual metal targets, an alloy target could also be employed. Due to the difference in sputtering yield for various atoms, many target designs have been proposed to realize high composition uniformity and satisfactory stoichiometric composition of PZT thin films, as shown in Figure 3 [22]. Therefore, it is convenient to tune the Zr/Ti ratio of PZT thin films by changing the area ratio (alloy target) or the power supply (individual metal target). Moreover, high power could be applied due to the excellent thermal conductivity of the metal target, inducing the high deposition rate. However, there are still some challenges to overcome. For example, the alloy target design is complex and the target fabrication is also difficult. Moreover, the oxidation of bombarded metal atoms is random and uncontrollable while some residual metal atoms without oxidation may exist in deposited thin films. It is worth mentioning that a PbO ceramic target could be introduced to replace Pb metal target due to the similar sputtering yield but lower volatility than Pb during the reactions.

For RF sputtering, PZT ceramics (sometimes powders) with stoichiometric composition are often applied as shown in Figure 2b. Generally, excess PbO (10%~20%) was added into the target to compensate for the loss of Pb due to the high vapor volatility [23]. The molecules of PZT are bombarded out and move to the surface of the substrate to form films with a similar composition to the target without obvious chemical reactions. Therefore, it is easy to obtain PZT thin films with controllable and expected composition while the target fabrication is relatively simple. However, the ceramic target has low thermal conductivity and it is easy to form cracks at high power supply. Therefore, relatively lower power must be applied and the deposition rate is also limited. In addition, it is hard to determine a large target (more than 6 inches) with high uniformity due to the difficulty in target sintering to prepare large-scale PZT thin films [22]. However, these problems could be minimized by available methods, such as continuous water cooling of the targets. To the best of our knowledge, RF sputtering is more commonly used for PZT thin films owing to its high feasibility and steady controllability compared to DC reactive sputtering.

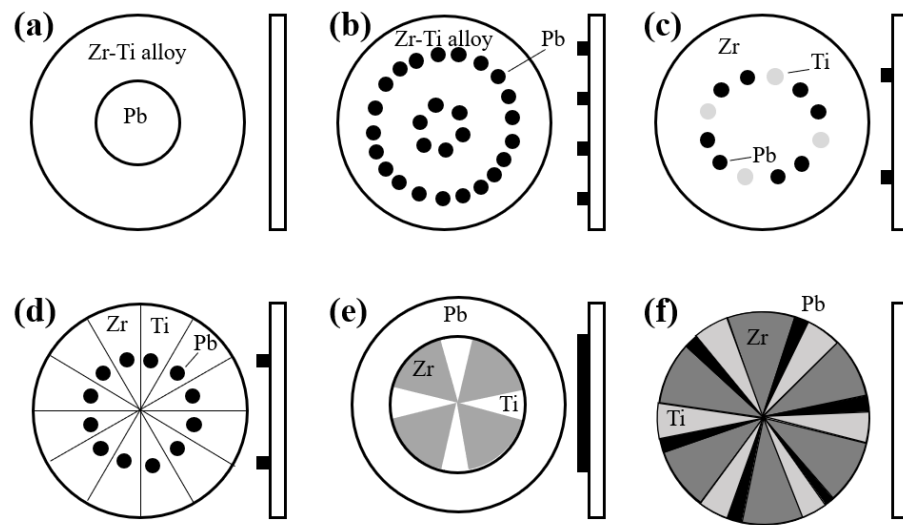


Figure 3. Different target designs for DC reactive sputtering. Reprinted with permission from [22] Copyright 2005 Elsevier. (a) Zr–Ti alloy with Pb in the center; (b) Zr–Ti alloy with Pb cylinders on the surface; (c) Zr target with Pb cylinders and Ti cylinders on the surface; (d) Zr–Ti alloy with flabellate distribution and Pb cylinders on the surface; (e) Pb target with fan-shaped Zr–Ti alloy in the center; (f) Zr–Ti–Pb ternary alloy target with flabellate distribution.

During the sputtering process, there exist many complicated sputtering parameters, such as target composition and condition, substrate, distance between target and substrate, temperature, heating or cooling rate, gas atmosphere, power, and annealing conditions, which have huge effects on the properties of PZT thin films (including dielectricity, piezoelectricity, ferroelectricity). Furthermore, the properties of PZT thin films could be influenced by complex interactions from different fabrication parameters, simultaneously. Therefore, it is difficult to establish clear and universal relationships between sputtering parameters and film properties. Therefore, the microstructure of PZT thin films (such as composition, crystallinity, orientation, and grain size) is greatly important to serve as a linkage between fabrication and property. The next section reviews the effects of fabrication parameters on the microstructure of PZT thin films.

3. Fabrication–Microstructure Correlations

Among all the sputtering parameters, substrate, deposition temperature, gas atmosphere and annealing condition are the most influential. Therefore, the impacts of these fabrication parameters on the microstructure are discussed in detail.

3.1. Substrate

Owing to the epitaxial growth of thin films during magnetron sputtering, the deposition and microstructure of PZT film is strongly dependent on the substrate, for example, the lattice and thermal mismatch [24,25]. Generally, the substrate should possess a similar lattice constant and coefficient of thermal expansion (CTE) compared to PZT. Several materials often used as the substrate and bottom electrode are listed in Table 3 [26].

As shown in Figure 4a, the substrate has significant effects on the orientation of PZT thin films even under same growing conditions (deposition temperature and bottom electrode) due to the lattice mismatch [27]. On Pt(100)/MgO substrate, mainly (001)-oriented even completely (001)-oriented PZT thin films could be obtained despite the presence of (110) and (111) orientation. As a contrast, PZT thin films deposited on Pt(111)/Si or Pt(100)/R-Al₂O₃ showed obvious polycrystalline orientations including (110), (111), and (001). However, the idea of a lattice mismatch cannot explain all the orientation changes, especially on the same substrate, because various orientations could be achieved by the regulation of other factors.

Table 3. Comparison of materials and their properties for substrate and bottom electrode. Reprinted with permission from [26] Taylor & Francis 2007.

Material	Type	Lattice Constant (Å)	Coefficient of Thermal Expansion ($\times 10^{-6}/\text{K}$)
$\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$	Insulator (Tetragonal)	$a = 4.036c = 4.146$	~11
SrTiO_3	Insulator (Cubic)	$a = 3.905$	10.4
MgO	Insulator (Cubic)	$a = 4.216$	10.5
$\alpha\text{-Al}_2\text{O}_3$	Insulator (Hexagonal)	$a = 4.758$ $c = 12.99$	5.6 (a-axis) 5.3 (c-axis)
Si	Semiconductor (Cubic)	$a = 5.430$	3.59
Pt	Conductor (Cubic)	$a = 3.924$	8.8
Ir	Conductor (Cubic)	$a = 3.840$	6.5
SrRuO_3	Conductor (Pseudocubic)	$a = 3.930$	-

When considering the microelectronics applications, platinized silicon substrate (Si/SiO₂/Ti/Pt) is the most used. Pt possesses excellent chemical stability with a similar lattice constant to PZT while it can also act as a bottom electrode for electrical connections. Usually, Ti or TiO_x as the adhesive layer is introduced to improve the interfacial bonding between Pt and Si [28,29]. More importantly, Ti also plays an essential role in controlling the Pb/(Zr + Ti) ratio, as shown in Figure 4b [30]. It is worth mentioning that the Ti/Pt ratio has an optimal range (normally 0.02~0.17) to obtain PZT thin films. Lower ratio would result in the formation of pyrochlore (Py) structure due to the inadequate supply of Pb while higher ratio would induce the occurrence of excessive Pb (in the form of lead oxide phase impurity). The diffusion model is established in Figure 4c and the mechanism is also analyzed [31]. During the heating or pre-sputtering period, Ti in pure Ar atmosphere could diffuse into the grain boundaries and finally to the surface of the Pt layer. As we know, PZT thin films tend to form a perovskite (Pe) structure if Pb is adequate, otherwise Py structure occurs [32]. Attributed to the better incorporation of Pb, Ti on the surface could attract and maintain more Pb than original Pt. Moreover, the good wettability between Ti and Pt guarantees that a large area could be covered by the out-diffused Ti. As a result, large amounts of nucleation sites are provided to promote the formation of Pe structure. In contrast, the diffusion process of Ti in an oxygen atmosphere is also discussed. Ti firstly diffuses into the grain boundaries and then is oxidized on the way to the surface. Therefore, the diffusion would be suppressed. Furthermore, titanium oxide has poor wettability with Pt, resulting in the nucleation sites being provided only by the Pt surface near the grain boundaries. Therefore, it is scarcely effective to obtain Pe structure PZT thin films even though Ti is introduced to the substrate [33].

Seed layer can also be employed to improve the crystallinity of PZT thin films [11]. As shown in Figure 4d, as-deposited PZT thin films show Py peaks and there is still a second phase peak after post-annealing. Complete crystallinity and no Py structure or a second phase peak could be observed in as-deposited PZT thin films (Figure 4e) with the introduction of PZT seed layer. Seed layer could provide more nucleation sites to form the Pe structure even without post-annealing. In addition, various oxide films were employed to facilitate the crystallinity or preferred orientation, such as SrRuO₃, PbTiO₃, La_{0.7}Sr_{0.3}MnO₃, IrO₂, TiO_x and so on [34–38]. It is interesting to note that the average grain size of the PZT films on a crystalline substrate was slightly larger than that on an amorphous substrate. Therefore, the choice of substrate (including the bottom electrode)

could affect the composition, crystallinity, orientation, and grain size of PZT thin films due to the mismatch of lattice constant and CTE.

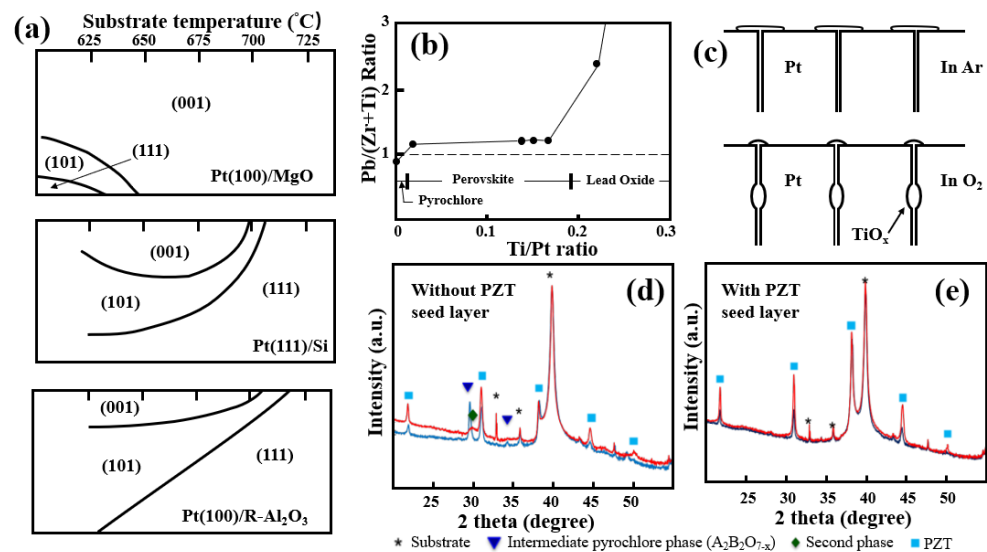


Figure 4. (a) Orientation changes of PZT thin films deposited on different substrate; The longitudinal axis represents the relative ratio of different orientations. Reprinted with permission from [27] Copyright 1991 The Physical Society of Japan and The Japan Society of Applied Physics; (b) Pb/(Zr + Ti) compositional ratio in PZT thin films as a function of Ti/Pt ratio. Reprinted with permission from [30] Copyright 1991 The Physical Society of Japan and The Japan Society of Applied Physics; (c) models for diffusion of Ti through Pt grain boundaries in Ar (upper) and O₂ (lower) atmosphere. Reprinted with permission from [31] Copyright 1998 The Physical Society of Japan and The Japan Society of Applied Physics; XRD patterns of as-deposited and post-annealed PZT thin films (d) without and (e) with PZT seed layer. Reprinted with permission from [11] Copyright 2018 John Wiley and Sons.

3.2. Deposition Temperature

Composition of PZT thin films (especially Pb content) has sensitive dependence on deposition temperature due to the high volatility of Pb. In addition, the phase structure of PZT thin films is influenced by controlling the Pb content in the thin films. Therefore, the appropriate choice of deposition temperature is crucial. As shown in Figure 5a, the Zr/Ti ratio could remain stable with the increase of deposition temperature, which could be attributed to their refractory nature [39]. However, Pb content has a decreasing tendency with the increase of deposition temperature. The mobility and re-evaporation possibility of Pb were greatly enhanced when the deposition temperature increased although the flux of Pb atoms arriving at the substrate could be regarded as constant. Such deviations could be explained by the poor sticking coefficient and high saturation vapor pressure [40].

Figure 5b reveals the relation between phase structure and deposition temperature [41]. The phase structure could transfer from amorphous, pyrochlore (Py) to perovskite (Pe) with the increment of deposition temperature. At elevated temperature, a second phase can be observed due to the slight interface reactions and Pb re-evaporation [42]. Similar results can be observed in other literature [43,44]. A single Pe structure could be obtained at a suitable deposition temperature range which could be controlled by additional PbO target supply. These phase differences could be attributed to the Pb content and epitaxial growth kinetics. It is worth mentioning that PZT tends to form the Pe phase when Pb is excess as described before. However, PZT thin films with high Pb content display amorphous or Py structures at low deposition temperatures due to the insufficient crystallization or the coexistence of PbO. Figure 5c exhibits XRD patterns of PZT thin films deposited at different substrate temperatures [45]. It could be concluded that the crystallization process has a

strong dependence on the deposition temperature. In a given temperature range (such as 285–435 °C), PZT thin films show (111) preferential orientation with almost no other peaks. As a contrast, there exist some other peaks, such as (110) and (100), in films deposited out of above temperature range. Similar conclusions could be drawn in Figure 4a that films deposited at different temperatures may show various orientations. Figure 5d indicates the variation of grain size with deposition temperature [46]. The average grain sizes were estimated by Scherrer's formula from the XRD pattern. For films deposited below 300 °C, the grain size could not be obtained due to the lack of definition in diffraction peaks, possibly due to amorphization. All the PZT thin films showed grains in the nano-scale (40–60 nm) and the size increased with the rise of deposition temperature. Accompanied by the increase of grain sizes, there may occur relative decrease of the density at high deposition temperature. In addition, porous holes or cracks may appear and the film surface becomes rougher when the temperature is too high.

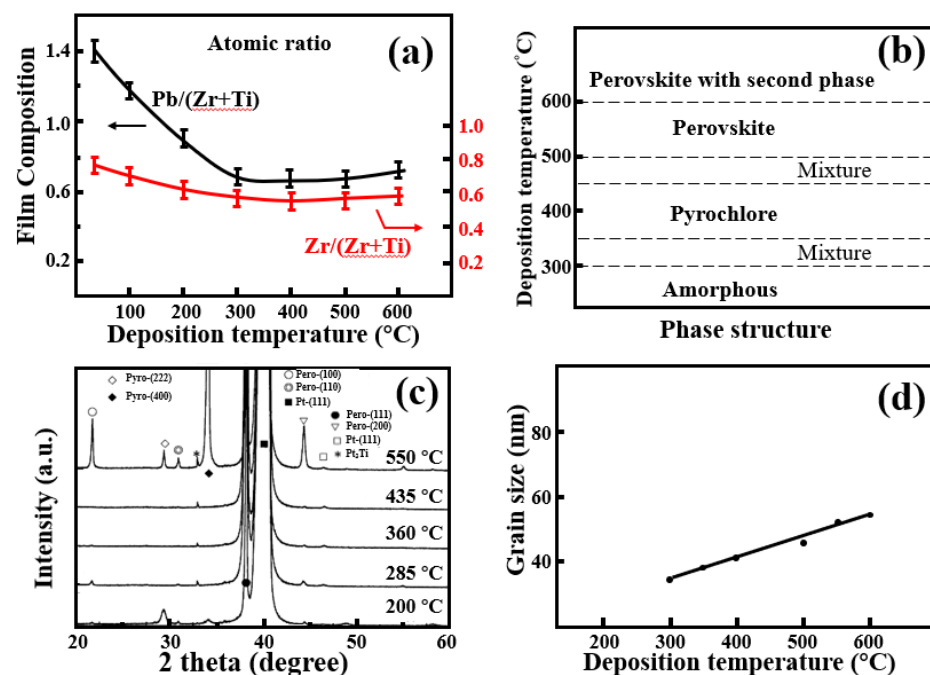


Figure 5. (a) Variation of Pb content and Zr/Ti ratio as a function of deposition temperature. Reprinted with permission from [39] Copyright 1988 AIP Publishing; (b) temperature dependence on the phase structure of PZT thin films. Reprinted with permission from [41] Copyright 1977 AIP Publishing; (c) XRD patterns of PZT thin films deposited at different temperature. Reprinted with permission from [45] Copyright 2000 Elsevier; (d) variation of grain size with deposition temperature. Reprinted with permission from [46] Copyright 1983 AIP Publishing.

In sum, the deposition temperature has strong effects on the surface mobility and re-evaporation of Pb atoms. Therefore, there is an optimal range relevant to other sputtering parameters to realize desired orientation of PZT thin films with Pe structure and fine surface morphology. Moreover, the grain size could also be controlled by the temperature.

3.3. Gas Atmosphere

During the sputtering process, Ar is necessary to generate plasma. Molecules will escape from the target surface owing to the bombardment of Ar^+ . Therefore, the pressure of Ar is essential due to its influences on molecular migrations and subsequent film growth. In addition, O_2 is often employed as a reactive gas to oxidize metal targets or restrain the volatilization of Pb. All the mechanisms are discussed as follows.

Figure 6a indicates the pressure dependence of film composition [47]. It can be observed that Pb content increases first and then tends to be stable with the increment of

pressure. It means that Pb content could realize small fluctuation when compared to that of stoichiometric target. On the other hand, the Zr/Ti ratio could remain steady along with the changes of pressure and it is almost equal to that of target. Figure 6b demonstrates the schematic phase diagram of PZT thin films as a function of pressure and deposition temperature [11]. With the increase of pressure, the amount of pyrochlore (Py) phase decreases while the perovskite (Pe) phase becomes greater. As a result, the PZT phase transformed from a Pb-deficient Py phase to a Pb-sufficient Pe phase and finally to Pb-excess second phase under the same conditions. The remarkable changes of phase structure by the pressure could be attributed to the control of the Pb content and an appropriate value should be employed in order to achieve pure Pe structure. The surface morphology of samples A–C in Figure 6b can be observed in the insets. A large volume of Py phase could be observed in sample A while sample B shows some Py phase at the grain boundaries. Meanwhile, there is no Py phase in sample C, implying the pure Pe phase. It can be concluded that there exist obvious two-phase transition regions where both Pe and Py could be detected. Furthermore, the resultant surface morphology of a two-phase region could be explained by the tilted boundaries decided by uncertain nucleation center [48].

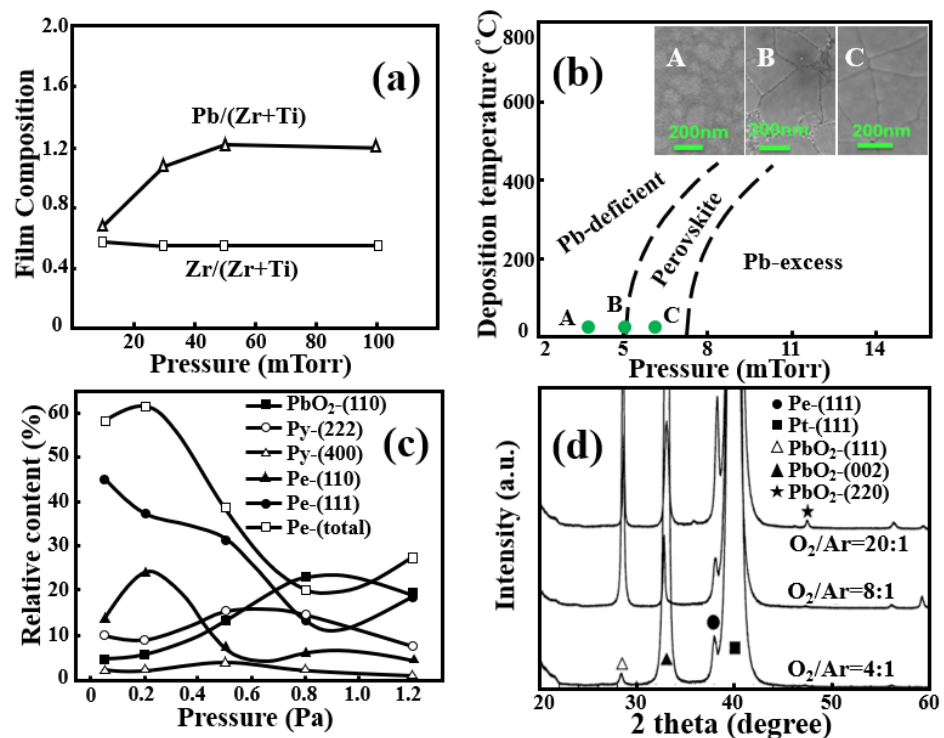


Figure 6. (a) Pressure dependence of film composition. Reprinted with permission from [47] Copyright 1997 Elsevier; (b) schematic phase diagram of PZT thin films as a function of pressure and deposition temperature; the inset is surface morphology of samples A–C. Reprinted with permission from [11] Copyright 2018 John Wiley and Sons; (c) phase structure and orientation evolutions of PZT thin film deposited at different pressure [49]; (d) XRD patterns of PZT thin film deposited at different O₂/Ar ratios. Reprinted with permission from [50] Copyright 2000 Elsevier.

Figure 6c displays the phase structure and orientation evolutions of PZT thin films deposited at different pressure [49]. The relative contents of the Pe phase and lead oxide could be strongly affected by the pressure. The Pe phase would first increase at low pressure and then decrease to a minimum with the increase of pressure. Meanwhile, lead oxide would increase gradually to a maximum peak along with the increment of pressure. Further higher pressure would induce the increase of the Pe structure and decrease of lead oxide. Moreover, preferred orientation ratio of Pe phase could also be influenced while the relative content of the Py phase tends to grow first and then decline with the

increase of pressure. In addition, grain sizes acquired by Scherrer's formula from the XRD pattern remain stable with the changes of pressure. All these results could be explained by the correlation between deposition, re-evaporation and migration during the sputtering process [50]. Therefore, there is an optimal value for pressure, which may be various in different sputtering conditions. Figure 6d demonstrates XRD patterns of PZT thin film deposited at different O₂/Ar ratios [50]. It can be observed that the introduction of more oxygen is advantageous to the formation of Pe phase, especially (111) orientation. As a contrast, the peak intensity of lead oxide was greatly reduced with more oxygen partial pressure, which may be attributed to the fact that more oxygen could stabilize Pb and promote the transformation to Pe structure [51,52]. It should be noted that oxygen is necessary for DC reactive sputtering process because the metal target needs to be oxidized first [53]. Therefore, high oxygen content is required to guarantee complete oxidation without metal impurity in PZT thin films. However, oxygen is optional in the RF sputtering process. The role of oxygen in RF sputtering is to alleviate the evaporation of Pb. Moreover, O₂/Ar ratio could influence the deposition rate due to the surface oxidation of metal target or decreased striking ion density.

Therefore, pressure has obvious effects on the Pb content and the subsequent phase structure. Furthermore, the orientation can be controlled. In addition, the O₂/Ar ratio also plays a critical role in the composition, phase structure and orientation due to the oxidation process and stabilizing effect.

3.4. Annealing Condition

As-deposited PZT thin films usually display amorphous or pyrochlore (Py) phases in low deposition temperatures. Even in high deposition temperature, there still exist a small amount of Py phases while the orientation of perovskite (Pe) phase is random. Generally, an annealing process is often employed to realize the transformation from Py to Pe and/or to obtain a higher preferred orientation [54].

Figure 7a implies XRD patterns of PZT thin films annealed at different temperatures [45]. There exists Pe phase as well as Py phase and lead oxide in as-deposited PZT thin films. After the annealing process, Py phase and lead oxide decreases to form Pe phase while the crystallization process has a dependence on annealing temperature. When annealing temperature increases, better crystallinity can be realized, inferred by higher and sharper diffraction peaks of Pe phases. Further higher annealing temperature would provide enough energy to make grains grow along with other orientations, resulting in polycrystalline structure instead of a single preferred orientation. If too high annealing temperature was applied or it took too long, the intensity of the Pe phase may decline accompanied by serious Pb deficiency while peaks of Py phases would appear and even increase sharply. Moreover, cracks or pores may occur and density may decrease after long-time or high-temperature annealing process. It is worth noting that there may be no significant improvement in crystallization in PZT thin films without any initial crystallinity even after extended annealing temperature and time. Hence, effective annealing should be based on as-deposited PZT thin films with incipient crystallinity. The optimal annealing temperature to develop single-phase Pe PZT thin films is dependent on the Zr/Ti ratio while Ti-rich PZT thin films need higher annealing temperature. Figure 7b exhibits the correlations among deposition temperature, annealing temperature and relative content of Pe phase in total phases of the PZT thin films [45]. When PZT thin films were deposited at low temperatures (such as 285 °C), the annealing temperature had limited effects on the formation of Pe phases, indicated by the steady changes of relative content. For PZT thin films deposited at high temperatures (such as 360 and 435 °C), the annealing temperature had influences on the formation of Pe phases with an optimal value to achieve higher relative content. When PZT thin films were deposited at higher temperatures (such as 550 °C), relative content of Pe phases increased sharply with an increase of annealing temperature and no peak site could be observed. This can be explained by the fact that a sample deposited at higher temperature has lower reactivity and needs more energy to

realize crystallographic transformation, which means the sample has to be annealed at higher temperature. However, too high an annealing temperature would result in the Pb loss due to its high volatility and the formation of Pb-deficient Py phase [50]. Although the Pb loss could be suppressed if annealed in a PbO atmosphere, it may be ineffective to replenish for the as-deposited PZT thin films with deficient Pb. As a result, Py phases could not transform to the Pe phase completely even after the annealing process. Therefore, it is crucial to fabricate Pb-rich as-deposited PZT thin films.

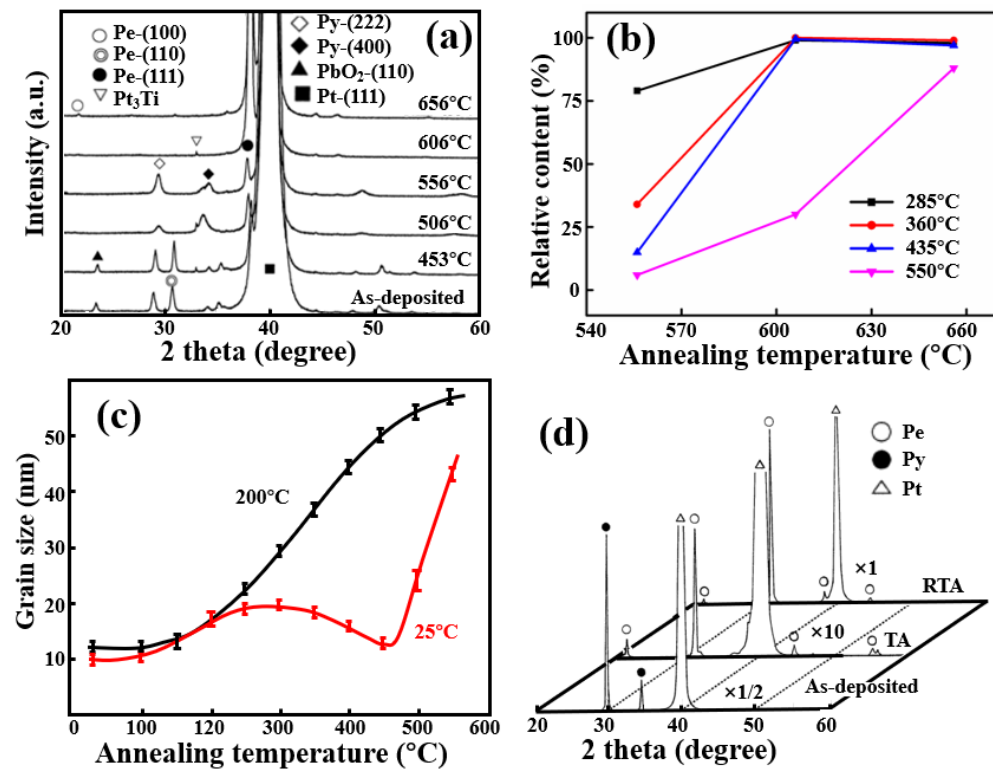


Figure 7. (a) XRD patterns of PZT thin films annealed at different temperatures. Reprinted with permission from [45] Copyright 2000 Elsevier; (b) correlations among deposition temperature, annealing temperature and relative content of perovskite phase in total phases of the PZT thin films. Reprinted with permission from [45] Copyright 2000 Elsevier; (c) grain size as a function of annealing temperature for PZT thin films deposited at different temperature (25 and 200 °C). Reprinted with permission from [55] Copyright 1989 Elsevier; (d) XRD patterns of as-deposited (×1/2), TA treated (×10) and RTA treated (×1) PZT thin films. Reprinted with permission from [56] Copyright 1993 The Physical Society of Japan and The Japan Society of Applied Physics.

Figure 7c shows the variation in grain size with different annealing temperatures for PZT thin films deposited at 25 and 200 °C [55]. The grain size of PZT thin films deposited at 200 °C increased monotonically with the gradual ascent of annealing temperature. However, the changes of grain size in PZT thin films at 25 °C exhibited complex behaviors with the variation of annealing temperature. It first increased slowly and then decreased to a minimum which may be attributed to the structural phase transformation. After the transition point, it increases linearly. Moreover, cracks were more likely to occur in PZT thin films deposited at low temperatures (such as 25 °C) after annealing process. It can be also concluded that grain size is larger in PZT thin films deposited at higher temperatures under the same annealing condition, which is consistent with that mentioned in Figure 5d. Traditional annealing (TA) is usually carried out in muffle furnace with long time and limited heating rate. In order to avoid the degradation of the PZT–substrate interface (interdiffusion of Pb at high temperature), rapid thermal annealing (RTA) was introduced [57]. Figure 7d indicates the XRD patterns of as-deposited, TA treated and RTA

treated PZT thin films [56]. It can be observed that the Py phase has been transformed into the Pe phase after TA or RTA process. However, the intensity of Pe phase in PZT thin films by RTA was about tenfold stronger than that by TA. In addition, samples by RTA could display unchanged surface morphology and Pb content compared to as-deposited samples while there may occur some hillocks, cracks and Pb loss in PZT thin films after the TA process. These results mean that RTA is a better annealing process. It is interesting to note that the most obvious difference between TA and RTA is the grain size. In RTA process, PZT thin films were treated for a short duration and grain growth is limited, resulting in smaller grain size.

Thus, annealing process could enhance the crystallinity and change the preferred orientation of as-deposited PZT thin films by the appropriate choice of annealing temperature and time. Besides, RTA is a better choice to obtain single orientation PZT thin films with pure Pe phase.

3.5. Other Parameters

Besides above parameters, there still exist many other factors, such as sputter power, target, distance between target and substrate, heat transfer mode, heating rate, element doping and so on [11,39,58–60]. For example, sputter power could influence the deposition process in many aspects. First, as the sputter power increases, the target surface would be unstable, leading to formation of metallic nanopillars due to the high thermal density [61]. Second, the increment of power could enhance the removal of PbO rather than TiO_x and ZrO_x due to different surface-binding energies, resulting in the obvious composition variation of Pb content in PZT thin films [52]. Third, lower power may lead to smaller deposition rate. Therefore, sputtered molecules may have more time to migrate on the film surface, resulting in a better preferential orientation [58].

In addition, PZT thin films sputtered by a sintered powder target possess lower Zr/Ti ratio than that by an unsintered powder target due to the different sputtering yield resulting from interactive force between powders. It is of interest to note that there exists obvious composition deviation between the center and the edge of the substrate (maximum to 35% difference) due to the variation of ejection angles or plasma scattering attributed to the different atomic mass. This could be obviated by substrate oscillation and target gun angle deflection to some extent. In addition, other elements could be introduced to target to tailor the properties of deposited PZT films, such as La (for better electrooptic), Mn (for lower dielectric constant) and Nb (for higher piezoelectric constant). It is worth mentioning that all the sputtering parameters can affect the PZT thin films not only on the microstructure but also on the deposition rate [62–65]. With the pressure increased gradually, deposition rate would decrease due to more gas scattering in the plasma. Sometimes, the rate may increase slowly owing to the more striking ions. Similarly, the rate would decrease when deposition temperature increases due to the enhanced surface mobility of incident film material and to a reduced sticking coefficient. Moreover, the deposition rate would increase with shortening the distance between target and substrate while the film uniformity (composition and thickness) may become worse. This may be a compromise between throughput and quality for MEMS applications when considering the productivity and efficiency.

4. Property-Microstructure Correlations

The previous section focuses on the relationships between fabrication parameters and microstructure of PZT thin films based on experimental results. In this section, the influences of microstructure on the properties of PZT thin films will be discussed in detail. In fact, the fabrication, microstructure and property of PZT thin films can be united, which is beneficial to the performance optimization of PZT thin films by the proper changes of fabrication parameters.

4.1. Dielectric Property

The dielectric property of PZT thin films represents the ability to store charges (electrostatic energy) which is different in various applications. For example, PZT thin films should possess high dielectric constants for dynamic random-access memory (DRAM) while the values should be reduced as much as possible for piezoelectric energy harvesters [3,66–68]. The relative dielectric constant (ϵ_r) can be enhanced or reduced by the changes of the microstructure in PZT thin films. The details are analyzed as follows.

Figure 8a shows the relations of relative dielectric constant ϵ_r and Zr/Ti ratio in PZT thin films [55]. It is clear that ϵ_r is strongly dependent on the Zr/Ti ratio. With the increase of Zr content, ϵ_r would increase first and then decrease while there exists a maximum point called MPB (morphotropic phase boundary) where the Zr/Ti ratio is about 52/48. This phenomenon is similar to that in PZT ceramics. In addition, ϵ_r could also be influenced by Pb content and phase structure as shown in Figure 8b [66]. The increment of Pb content can improve the value of ϵ_r while perovskite (Pe) phases possess higher ϵ_r than pyrochlore (Py) phases. Moreover, doping elements could also change the ϵ_r values. For instance, Mn elements are often employed to reduce ϵ_r of PZT thin films.

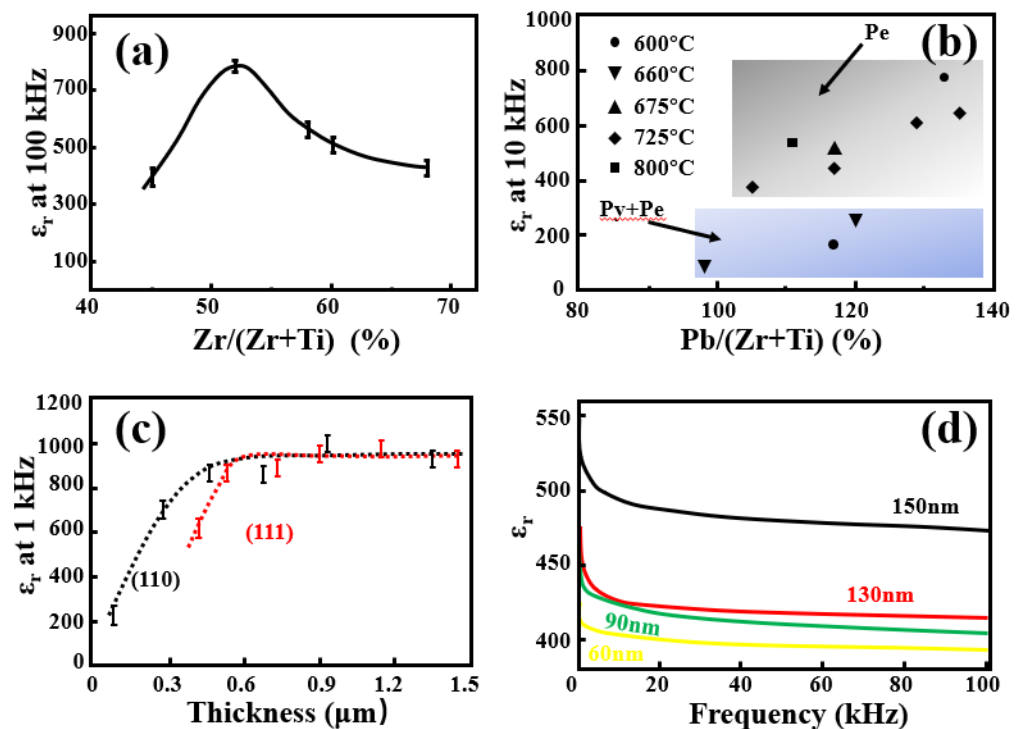


Figure 8. (a) Relations of relative dielectric constant ϵ_r and Zr/Ti ratio in PZT thin films. Reprinted with permission from [55] Copyright 1989 Elsevier; (b) influences of Pb content on ϵ_r . Reprinted with permission from [66] Copyright 1992 The Physical Society of Japan and The Japan Society of Applied Physics; (c) dependence of orientation and film thickness on ϵ_r [69]; (d) effects of ϵ_r on the grain size and frequency. Reprinted with permission from [70] Copyright 2002 Elsevier.

Anisotropy of ϵ_r in PZT thin films could be observed in Figure 8c [69]. When the thickness is small, ϵ_r of PZT thin films with (110) orientation is relatively higher than that with (111) orientation. Similar results were reported that ϵ_r along the c axis was lower than that along a-axis [71]. However, ϵ_r tends to be saturated and then stable with the increase of film thickness. As a result, there is no difference in ϵ_r of PZT thin films with various orientations. Thickness size effects could be explained by the existence of residual stress and a dead layer (non-ferroelectric state with extremely low ϵ_r) at the interface between PZT thin films and substrate. As the thickness increased, the ratio of dead layer became smaller and the influences can be neglected while the stress could be released gradually,

resulting in the increase of ϵ_r . Further studies are necessary to explain the saturation phenomenon. Figure 8d indicates the dependence of ϵ_r on the grain size and frequency (external stimulus) [70]. It is clear that ϵ_r decreases with the increase of frequency, which is consistent with Curie–Von Schweidler relaxation. Moreover, the increase of grain size could promote ϵ_r due to the enhanced mobility of domain walls (boundaries of domains with different polarization orientations). However, further increase of grain size would have no influence even on the opposite effects on ϵ_r because the distance between domain walls is large enough and interactions would become weak. This can be observed elsewhere [72].

In sum, the dielectric performance can be enhanced or reduced by tailoring the composition, phase structure, orientation and grain size. Thus, the dielectric constant ϵ_r can vary in a large range depending on the fabrication parameters and application requirements.

4.2. Piezoelectric Property

For the applications based on piezoelectric effects, the piezoelectric constant (such as d_{33} , d_{31} , e_{31}) is of vital importance, which decides the magnitude of electrical signal (for sensors) and displacement (for actuators).

Figure 9a displays the piezoelectric constant d_{33} of PZT thin films according to the composition (Zr/Ti ratio) [73]. It can be observed that there is an obvious maximum peak when Zr/Ti ratio is about 52/48 (MPB composition), which exhibits a similar tendency to that of bulk PZT ceramics. This can be explained by the metastable coexistence of tetragonal and rhombohedral phases, which is beneficial to the domain switching. Moreover, some researchers thought that the monoclinic phases may occur and induce better poling efficiency and electromechanical activity. It is worth mentioning that d_{33} of films are relatively lower than that of ceramics due to the clamping effects of the substrate [74]. The relationship of d_{33} between PZT thin films and bulk ceramics has been described elsewhere [8].

Figure 9b shows the dependence of orientation on d_{33} under different driving electric fields [75]. PZT thin films with (100) orientation possessed higher performance than that with (111) orientation while films with both (100) and (111) (marked as random) exhibited the intermediate values. This difference has been predicted by theoretical calculation and could be attributed to the effects of ferroelastic domains (90° domains in tetragonal composition) [76]. However, some experiments showed different results whereby d_{33} of (111)-oriented PZT thin films was larger than that of (100)-oriented [77]. More domains in PZT thin films with (111) orientation could be oriented toward the direction of the stress compared to (100)-oriented films. However, (100)-domains along the stress direction should not affect the piezoelectric response. In addition, the piezoelectric response could be strengthened by other factors, such as higher driving electric field due to the enhanced motions of domain walls.

Figure 9c suggests the relationships between grain size and piezoelectric constant d_{31} [78]. On the one hand, finer grain sizes mean more grain boundaries which can make domain reorientation more difficult. Besides, the domain wall motion may be constrained severely, which could reduce the piezoelectric response. On the other hand, large grain size was beneficial to the preferred orientation of PZT thin films, inducing higher piezoelectric properties than that with random or amorphous orientation. Therefore, the piezoelectric response will have an improvement and then tend to be saturated with the growth of grain size.

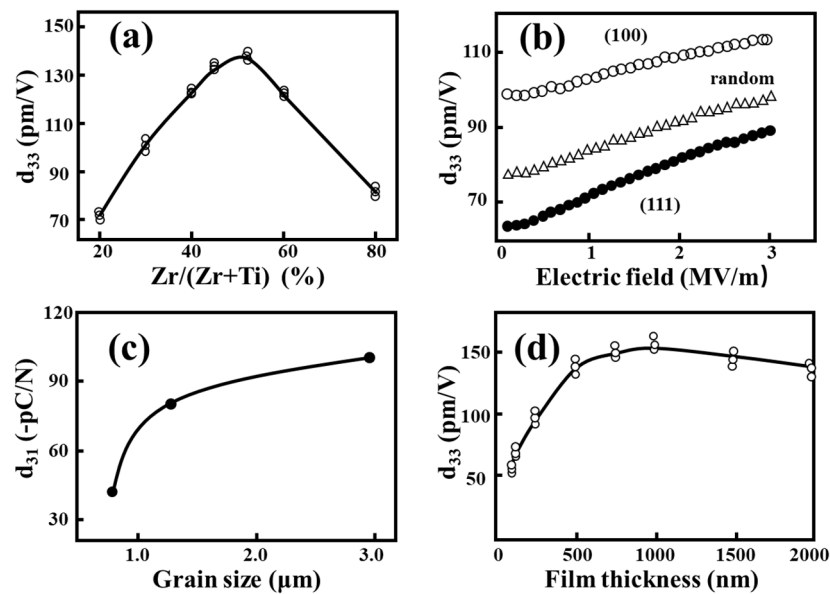


Figure 9. (a) Piezoelectric constant d_{33} of PZT thin films according to the composition. Reprinted with permission from [73] Copyright 2013 Elsevier; (b) dependence of orientation on d_{33} under different electric field. Reprinted with permission from [75] Copyright 2000 AIP Publishing; (c) relationships between grain size and piezoelectric constant d_{31} . Reprinted with permission from [76] Copyright 1999 Taylor & Francis; (d) dependence of d_{33} on PZT thin film thickness. Reprinted with permission from [73] Copyright 2013 Elsevier.

Figure 9d indicates the dependence of d_{33} on thickness of PZT thin films [73]. The values of d_{33} increased first and then remained almost steady with the increment of thickness. There may be two reasons for this. On the one hand, residual stress in PZT thin films due to the lattice mismatch, thermal mismatch and phase transition will decline gradually and then be constant when thickening the PZT thin films. The deterioration of residual stress to piezoelectric properties will become increasingly weak, resulting in the increase and stability of d_{33} . On the other hand, the impacts of the interfacial dead layer with poor performance will become smaller with the increased film thickness, which can also explain the tendency of d_{33} . These two reasons can be attributed to the clamping effects of the substrate. Besides, part of the increase of d_{33} can also be attributed to the growth of grain size because thicker films usually possessed larger grain sizes [79].

Thus, (100)-oriented PZT thin films for sensors and actuators would be very competitive when film composition was MPB. In addition, this can be further enhanced by the optimization of grain size and film thickness.

4.3. Ferroelectric Property

For applications of memory devices, ferroelectric performances are most concerned, such as remnant polarization (P_r) and coercive field (E_c) [80]. Based on a Sawyer–Tower circuit, both P_r and E_c could be observed from polarization–electric field (P–E) hysteresis loops, which is the intrinsic and typical feature of ferroelectric materials.

Figure 10a exhibits the variation of P_r as a function of composition (Zr/Ti ratio) and orientation [81]. For (100) and (110) oriented films, the P_r value decreased first and then increased. There existed a minimum value for these two types of PZT thin films when Zr/Ti ratio was about 52/48 (MPB composition). However, the P_r value of PZT thin films with (111) orientation would reach a maximum at the same composition point. Figure 10b displays the composition and orientation dependences of E_c for PZT thin films [81]. Similar to P_r , the E_c value attained a minimum around MPB composition for PZT thin films with (111) and (110) orientation. However, the E_c value for (100)-oriented films decreased first to a minimum at MPB composition and then remained almost stable with the increase

of Zr/Ti ratio. Besides, the E_c value of (100)-oriented PZT thin films was always higher than that of the others despite the composition changes. It is suggested that polarization reversal in PZT thin films with (100) orientation is more difficult than that with others. These phenomena could be partly explained as follows [80,82].

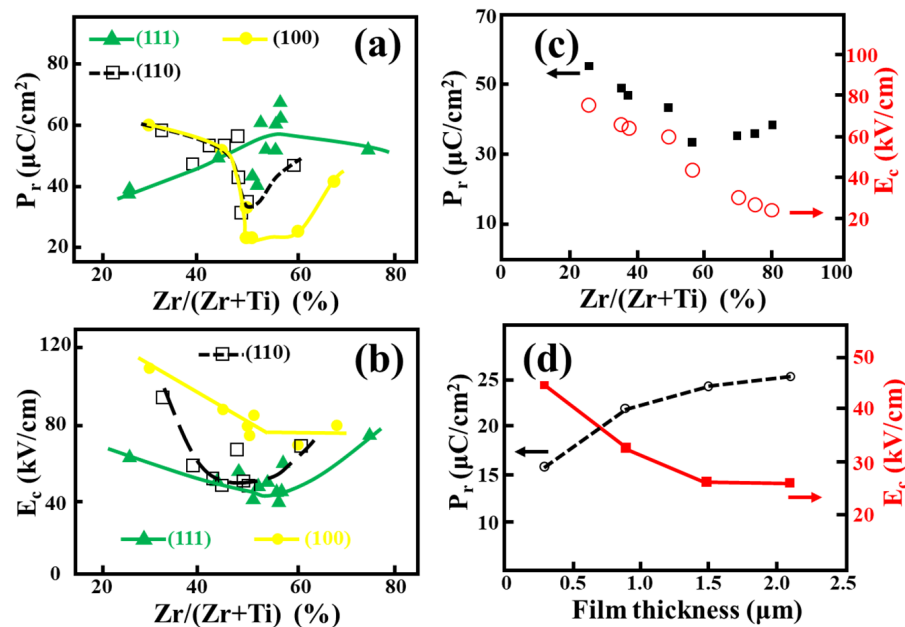


Figure 10. (a) Variation of P_r as a function of composition (Zr/Ti ratio) and orientation. Reprinted with permission from [81] Copyright 2004 AIP Publishing; (b) composition and orientation dependences of E_c for PZT thin films. Reprinted with permission from [81] Copyright 2004 AIP Publishing; (c) composition variations of P_r and E_c values for PZT thin films. Reprinted with permission from [83] Copyright 1997 AIP Publishing; (d) thickness dependence of ferroelectric properties of PZT thin films. Reprinted with permission from [35] Copyright 1999 Elsevier.

The degree of polarization can be decided by orientation and anisotropy. In tetragonal PZT thin films, the lattice parameters a and c will remain increased and unchanged with the increment of Zr content, respectively. As a result, the aspect ratio will attain a minimum near MPB composition. In rhombohedral PZT thin films, anisotropy is decided by the lattice parameter and axial angle. Hence, the anisotropy will be smallest around MPB composition. This small crystal anisotropy can induce the smallest polarization and easiest domain reversal, which results in the occurrences of minimum P_r and E_c . However, the existence of maximum P_r for (111)-oriented PZT thin films cannot be explained. Hence, special domain alignments (such as engineered domain) must be taken into consideration similar to some other materials (PZN-PT and PMN-PT single crystals). However, partially contradictory composition variations of P_r and E_c were also reported as shown in Figure 10c [83]. It can be observed that P_r and E_c decreased monotonously with the increase of Zr content. Moreover, the values and the composition dependence of PZT thin films were different from bulk ceramics, which can be attributed to the clamping effects of the substrate. However, the mechanism was not fully explicated. Therefore, further theoretical and experimental researches should be carried out to establish more clear and convincing explanations.

Figure 10d shows the thickness dependence of ferroelectric properties of PZT thin films [35]. With the increase of film thickness, E_c would decrease while P_r became larger. Both values would attain stability when exceeding a critical film thickness. This could be explained by the changes in grain size. With the increment of thickness, the grain size would become larger, which results in the increase of E_c and decrease of P_r [12,46]. It is worth mentioning that PZT thin films with perovskite (Pe) structure would possess better ferroelectricity while pyrochlore (Py) phases would exhibit paraelectricity or poor ferro-

electricity. Therefore, the phase structure could also influence the ferroelectric properties of PZT thin films.

In sum, the ferroelectric performances could be strongly influenced by the composition, phase structure, orientation and grain size. Different even contradictory results may be obtained under similar conditions and further efforts are demanded to explore the intrinsic mechanism.

4.4. Other Property

Besides those three types of properties, some other properties have also been studied, such as electrooptic properties, pyroelectric performance and so on. Similarly, these properties could also be changed by the control of microstructure in PZT thin films.

Figure 11a indicates the optical absorption spectroscopies of PZT thin films with perovskite (Pe) and pyrochlore (Py) structures [41]. Absorption edge of PZT thin films with Pe phases is 295 nm while the counterpart with Py structure is 330 nm. In addition, the measured refractive indexes (632.8 nm) of PZT thin films with Pe and Py structure are 2.36 and 1.65, respectively. These differences can be explained by the residual lead oxide in PZT thin films with Py structure, which can also be confirmed by the color difference. In general, PZT thin films with pure Pe phases is colorless while films with Py structure show light yellow. Therefore, the existence of lead oxide will affect the refraction of light. Figure 11b illustrates the variation of optical indexes of refraction (632.8 nm) with composition for PZT thin films [82]. The refractive index has a strong dependence on the composition (Zr/Ti ratio) of PZT thin films. With the increment of Zr content, the refractive index declines linearly, which could be employed to determine the composition of PZT thin films by this convenient and reasonably accurate method.

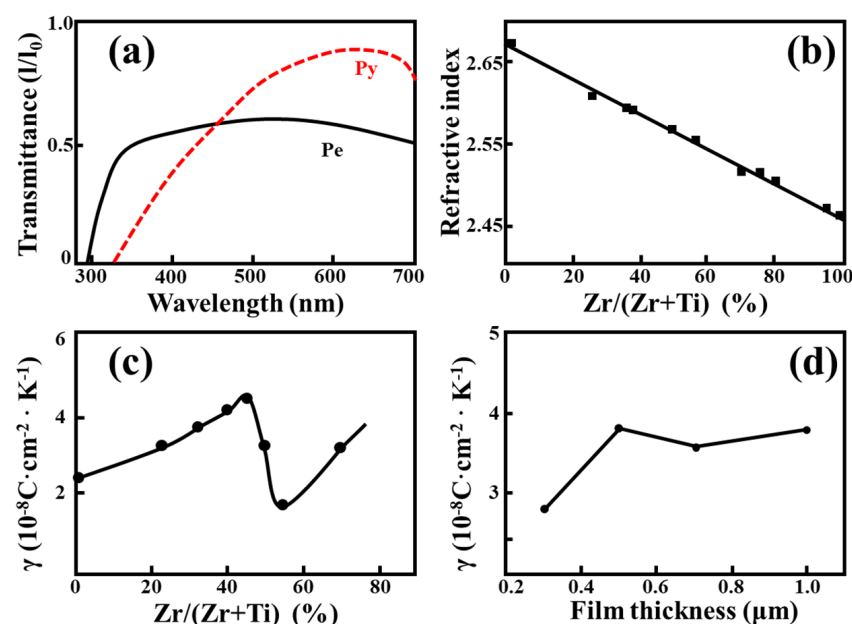


Figure 11. (a) Optical absorption spectroscopies of PZT thin films with perovskite and pyrochlore structure. Reprinted with permission from [41] Copyright 1977 AIP Publishing; (b) variation of optical indexes of refraction (632.8 nm) with composition for PZT thin films. Reprinted with permission from [82] Copyright 1997 AIP Publishing; (c) dependence of film composition on pyroelectric coefficient γ . Reprinted with permission from [84] Copyright 1989 AIP Publishing; (d) Influences of film thickness on γ . Reprinted with permission from [85] Copyright 2003 The Physical Society of Japan and The Japan Society of Applied Physics.

Figure 11c exhibits the dependence of film composition on pyroelectric coefficient γ [84]. With the increase of Zr/Ti ratio, γ increases first to a maximum near the phase

boundary in the tetragonal PZT thin films. The increase of γ can be explained by the decrease of T_c (Curie temperature). As a contrast, γ for rhombohedral PZT thin films diminishes near phase boundary and then increases with further increment of Zr content. It is due to the fact that the polarization axis is parallel to (111) axis, deviating from the direction perpendicular to film plane. Figure 11d implies the influences of film thickness on γ [85]. It can be observed that γ displays a first increase and then relative stability, similar tendency as piezoelectric constant. It may be also attributed to the existence of a dead layer with poor performance near the interface between PZT thin films and the substrate.

5. Summary and Perspective

Lead zirconate titanate (PZT) thin films have attracted more and more attentions as multi-functional materials due to their excellent and controllable properties. In recent years, large-scale PZT thin films with satisfactory properties have become the research focus for the applications of advanced microelectronic devices. Therefore, magnetron sputtering technique is especially emphasized to prepare PZT thin films due to their high efficiency and excellent reliability. Herein, a comprehensive review of PZT thin films is presented including sputtering classifications, fabrication parameters and properties. In particular, the microstructure of PZT thin films is emphasized as a bridge to connect fabrication and property in order to regulate the properties by process parameters, as shown in Figure 12.

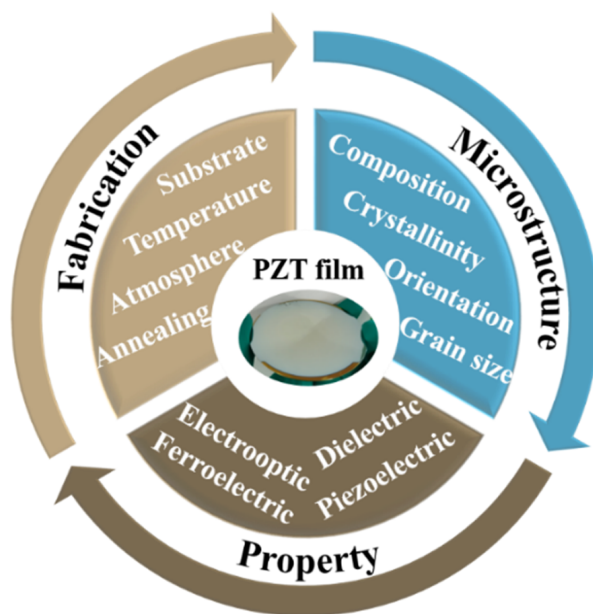


Figure 12. Relationships between fabrication, microstructure and property of PZT film. Picture in the center represents PZT thin film on 3-inch platinized silicon substrate by magnetron sputtering technique in our group.

Magnetron sputtering technique could be categorized as DC (direct-current) reactive sputtering and RF (radio frequency) sputtering. The former employs metal targets and oxygen to form oxide films while the latter applies PZT ceramic target to prepare films by molecules migration. Generally, RF sputtering is more popular due to its simple target fabrication and excellent process controllability. During the sputtering process, there exist many adjustable parameters which can strongly affect the microstructures of PZT thin films. In particular, the substrate, deposition temperature, gas atmosphere and annealing condition are the most concerned factors, which can intensely influence the microstructures, such as composition, crystallinity (perovskite phases or pyrochlore phases), orientation and grain size. For example, Ti element in platinized silicon substrate can act as nucleation sites and attract more Pb to form perovskite (Pe) phase. In addition, rapid thermal annealing (RTA) is more beneficial to form Pe phases rather than traditional

furnace annealing. Furthermore, the properties of PZT thin films have a strong dependence on these microstructural characteristics. Therefore, the properties (such as dielectricity, piezoelectricity and ferroelectricity) can be controlled in a large range to adapt to different applications. For instance, dielectric and piezoelectric properties could reach a maximum peak when the composition is set near MPB (morphotropic phase boundary, Zr/Ti = 52:48). In addition, PZT thin films with (100) orientation will possess the best piezoelectric property while (111)-oriented films can display a more excellent ferroelectric property. It should be noted that film thickness can also affect the properties.

Therefore, the relationships have been established between fabrication and properties of PZT thin films by the linkage of microstructure. These universal effects can be utilized to optimize the process parameters when preparing PZT thin films with specific properties. We think PZT thin films will be employed in advanced microelectronic devices on a larger scale soon. However, there still exist many challenging topics to explore. For example, PZT thin films are polycrystalline and often show multi-orientation. The strong preferential orientation even in single crystal PZT thin film is extremely difficult to fabricate by a steady and efficient technique. Besides, PZT thin films with specific orientation, such as (100) for piezoelectric applications or (111) for ferroelectric applications, are also needed to be further optimized. The precise composition of PZT thin films is also challenging. In terms of properties, PZT thin films usually possess high piezoelectric property e_{31} and dielectric property ϵ_r , which is undesirable in some applications (such as an energy harvester). Therefore, PZT thin films with high e_{31} and low ϵ_r are of high research value.

Although the specific values of fabrication parameters may not help directly due to the complexity of magnetron sputtering, the influential tendency is important. Besides, there still exist many contradictory experimental results while certain mechanisms have not been well explained, especially for ferroelectric or piezoelectric domains. The microstructural characteristics of PZT thin films in this review focus on composition, crystallinity, orientation and grain size, which are still relatively macroscopic parameters, compared to domain volume, interfaces, dislocations, and stacking faults etc [14,80,83]. These nano-scaled structures also greatly influence the properties of PZT thin films. Future research is needed with a special emphasis on ferroelastic and ferroelectric domain characteristics.

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