Effect of sputter deposition parameters on the characteristics of PZT ferroelectric thin films

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Abstract. This study examined the effect of process parameters on ferroelectric properties of Pb(Zr,Ti)O3 (PZT) thin films. Nano-particle PZT ferroelectric thin films were prepared on the Pt/Ti/SiO2/Si substrates by radio-frequency magnetron sputtering. Experiment parameters including sputtering power, sputtering air pressure, ratio of O2/Ar, underlay temperature and annealed temperature are analyzed by uniform design. Five levels are set up in suitable and precise range, quadratic regression equations of experiment factors versus experiment responses were set up by step regression. Analysis of variance revealed that developed models were adequate and there is an optimize potential in PZT ferroelectric thin films preparation process by RF-magnetron sputtering.

1. Introduction
Lead zirconate titanate Pb(Zr,Ti)O3(PZT) is a kind of ferroelectric material with perovskite structure. Because of their excellent properties, PZT thin films have been widely used for preparing ferroelectric and piezoelectric devices [1]. Radio-frequency magnetron sputtering is a complex process to fabricate PZT ferroelectric thin films. Many process parameters, such as sputtering air pressure, sputtering atmosphere, substrate temperature, sputtering power and annealed temperature can change the performance of PZT ferroelectric thin films at the same time. Although the effect of all kinds of sputtering process parameters upon PZT ferroelectric thin films performance are studied, it is only one process parameter that being considered. References about study on the effect of RF-magnetron sputtering process parameter on the performance of the PZT ferroelectric thin films by experiment design are absent by far. In this study, effects of air pressure, substrate temperature, ratio of O2/Ar+O2, sputtering power, annealed temperature on the PZT thin films performance were analyzed by uniform design [2]. Quadratic regression equations of experiment factors versus experiment response were set up by step regression.

2. Experimental
2.1. Experimental process
Pt/Ti bottom electrode was prepared on SiO2/Si substrate with DPS-III high vacuum dual-facing-target magnetron sputtering system. PZT thin films were deposited on Pt/Ti/SiO2/Si substrate by RF sputtering method. The deposition conditions of the PZT thin film are listed in table 2 and the sputtering times are all 3h. Phase and crystalline structure analyses of the PZT films were characterized by X-ray diffraction (XRD), Surface morphology, roughness and particle size of the PZT films were observed with field-emission scanning electron microscopy (SEM PHILIPS XL30).
The thickness of PZT thin film was measured with DEKTAK 6M surface profiler. P-E hysteresis loops were measured using the Sawyer–Tower circuit.

2.2. Uniform experiment design

The effects of atmospheric pressure ($x_1$), substrate temperature ($x_2$), ratio of $O_2/Ar+O_2$ ($x_3$), sputtering power ($x_4$), annealed temperature ($x_5$), on thickness ($y_1$), capacitance ($y_2$), dielectric loss ($y_3$), coercive field ($y_4$), spontaneous polarization ($y_5$) and remnant polarization ($y_6$) of thin films are analyzed by uniform design. The quadratic regression equations of experiment factors $x$ versus experiment response $y$ are set up by step regression. Indistinctive evident variable are excluded and experiment factors which evidently affects experiment response are filtered. The simple term, quadratic term and mutual term of experiment factors which have evident effects on experiment respond are picked out. Respond surface figures that experiment respond versus evident factors could be drawn when other variables keep in zero level (Due to space limitation, skip over them in this paper). The optimal process parameters are founded out when quadratic regression equations are analyzed.

Five levels are set up in suitable and precise range. In order to keep discrepancy, the value $D$ is less than 0.25, the uniform design table $U_{10\times(10^8)}$ is chose to arrange the experiment design. According to the use of table $U_{10\times(10^8)}$, five factors and ten levels experiment matrix is shown in table 1 by pseudo level method.

### Table 1. Uniform experiment design matrix of PZT thin films and experimental results

| No | $x_1$/Pa | $x_2$/°C | $x_3$/Pa | $x_4$/W | $x_5$/°C | $y_1$/nm | $y_2$/PF | $y_3$/tanδ | $y_4$/KV·cm⁻¹ | $y_5$/μC·cm⁻² | $y_6$/μC·cm⁻² |
|----|----------|-----------|-----------|---------|-----------|---------|----------|----------|-------------|--------------|--------------|
| 1  | 1.5      | 150       | 0         | 45      | 800       | 153     | 157      | 0.006    | 79.14       | 37.78        | 19.1         |
| 2  | 1.5      | 250       | 0.1       | 55      | 750       | 229     | 156      | 0.006    | 40.03       | 37.08        | 16.71        |
| 3  | 2        | 450       | 0         | 40      | 700       | 197     | 184      | 0.06     | 50.92       | 32.9         | 17.94        |
| 4  | 2        | 50        | 0.1       | 55      | 650       | 153     | 184      | 0.059    | 47.17       | 46.3         | 11.3         |
| 5  | 2.5      | 150       | 0.2       | 40      | 600       | 117     | 183      | 0.063    | 55.52       | 36.17        | 8.56         |
| 6  | 2.5      | 350       | 0         | 50      | 800       | 264     | 183      | 0.006    | 39.76       | 35.12        | 12.09        |
| 7  | 3        | 450       | 0.1       | 35      | 750       | 51      | 191      | 0.07     | 256.33      | 30           | 14.61        |
| 8  | 3        | 50        | 0.2       | 50      | 700       | 206     | 183      | 0.064    | 52.76       | 34.52        | 12.75        |
| 9  | 3.5      | 250       | 0         | 35      | 650       | 65.9    | 194      | 0.006    | 215         | 23.38        | 14           |
| 10 | 3.5      | 350       | 0.1       | 45      | 600       | 120     | 181      | 0.064    | 103.88      | 30.98        | 14.06        |

3. Results and discussion

3.1. XRD analyze

Considering its high electrical conductivity, low leakage current and good stability in high temperature oxidizing environments, Pt bottom electrode is primarily selected. Ti is introduced to promote adhesion between Pt and silicon substrate. Crystal lattice constant of cube crystal lattice Pt ($a=0.3923\text{nm}$) is close to lattice constant of perovskite PZT ($a=0.4040\text{nm}$). Thickness analyse indicates that the thickness of Pt and Ti layer are about 150nm and 20nm, respectively.

Thin film deposited in room temperature is amorphous. Under conventionality annealed process, pyrochlore structure starts to form at the temperature $300–500^\circ\text{C}$. Only when the annealed temperature continues to increase, the perovskite structure can form on the basis of pyrochlore structure [3]. Furthermore, perovskite structure is the main factor to improve the residual polarization strength of PZT ferroelectric thin film [4].
Fig 1. XRD patterns of PZT thin films of sample 3 and sample 5

The XRD pattern of PZT thin film of sample 5 states that besides Pt in $2\theta = 40^\circ$ epitaxial diffraction peak, perovskite (100) diffraction peak in $2\theta = 31^\circ$ and pyrochlore diffraction peak in $2\theta = 29^\circ$ are very strong. It can be concluded that the perovskite structure and the pyrochlore structure coexist in this condition. Fig 1 also points out that the crystal structure of PZT thin film of sample 3 changes obviously. With the diffract peak of perovskite phase (100) direction stronger and the diffract peak of pyrochlore phase in $2\theta = 31^\circ$ imperfect, PZT thin film exhibits a single perovskite phase.

3.2. SEM analyze

SEM analysis shows that the surface of PZT thin film of sample 1 is homogeneous and dense. Fig 2a gives the surface morphology and fig 2b describes the cross-section morphology. The average grain size is about 30nm as shown in fig 2a. However, it is obviously that there are some maximum grains which size is about 50nm and some little cracks which width is about 40nm in some region. In addition, there are three layers of thin films on the Si underlay are shown in fig 2b. The white layer is the 200nm thickness Pt/Ti bottom substrate. The PZT thin film and SiO$_2$ layers, above and under the Pt/Ti bottom substrate, are about 150nm and 500nm, respectively.

Fig 2. SEM patterns of sample 1 (a) Surface morphology (b) cross-section morphology

3.3. Regression analyze

The experiment results shown in table 1 were analyzed by data operation system "SPSS " professional software in making a quadratic regression analyze [5]. Indistinctive evident variables are excluded and
the experiment factors which evidently affect experiment response are filtered. The regression equation of thickness \( (y_1) \), capacitance \( (y_2) \), dielectric loss \( (y_3) \), coercive field \( (y_4) \), spontaneous polarization \( (y_5) \) and remnant polarization \( (y_6) \) of PZT ferroelectric thin films are shown as follow, \( x_n \) are the experiment factors mentioned in table 1:

\[
\begin{align*}
y_1 &= -82.6027 + 0.005824x_4 + 0.013678x_5 + 3978.59193x_2x_5 - 0.00039x_5x_5 - 0.00707x_1x_4 \\
y_2 &= 214.711 - 12.0965x_1 - 7.44002x_1x_1 - 522.058x_1x_5 - 0.00019x_5x_5 + 0.087587x_1x_5 - 0.0037x_1x_2 \\
&- 0.00324x_1x_2 \\
y_3 &= -0.024 + 0.095x_5x_3 + 9.73 \times 10^{-7}x_2x_2 - 7.5 \times 10^{-7}x_2x_2 - 0.023x_1x_1 + 0.086x_1 + 6.4 \times 10^{-5}x_1x_2 \\
&- 1.1 \times 10^{-6}x_3x_4 + 1.2 \times 10^{-8}x_5x_5 \\
y_4 &= 759.11 - 30.054x_4 + 0.268x_4x_4 + 0.092x_1x_5 + 1.362x_2x_3 - 8333.181x_3x_3 + 1.596x_3x_3 - 0.003x_3x_4 \\
&- 4.049x_1x_1 \\
y_5 &= -97.884 + 5.34x_4 - 4.08x_1x_1 - 0.007x_4x_5 - 0.00020949x_3x_5 + 16.047x_1 + 6.6 \times 10^{-5}x_2x_2 + 3.64 \times 10^{-5}x_2x_2 \\
&- 0.005x_3x_5 \\
y_6 &= -149.573 + 0.394x_5 - 0.037x_1x_4 + 0.207x_2 - 0.00028763x_2x_5 - 0.0002197x_5x_5 
\end{align*}
\]

3.4. Regression equation discussion

With a new factor introduced into regression equations, old factors will be verified one by one and indistinctive factors will be eliminated [6]. Two variables which have the most distinctive effect on experiment responds are extracted in every equation. Three-dimensional surface figure of experiment respond versus two variables which have the most distinctive effect on experiment responds are drawn.

In equation 1, when the annealed temperature is invariable, the relationship between thin films thickness and sputtering power is linear. The more the sputtering power the more the sputtered target particles on the substrate. When the sputtering power keeps invariable, the thin film thickness increases with annealed temperature. It is the reason that when annealed temperature increases, the pyrochlore structure convert to a pure perovskite structure and the epitaxial crystallization vary along with the thin thickness.

The PZT thin films capacitance increase with increasing atmospheric pressure and decreasing ratio of \( \text{O}_2/\text{Ar}+\text{O}_2 \) as shown in equation 2. With increasing atmospheric pressure, the particle’s transportation from target to substrate is blocked, the sputtering efficiency depress, so the film thickness and thin film capacitance increase. In sputtering atmosphere, the more decrease of the ratio of \( \text{O}_2/\text{Ar}+\text{O}_2 \) the more strictness of the oxygen absence, which is a primary absence of PZT thin films.

In the meanwhile, there will be an influence on fatigue characteristic of PZT thin films. The crystal lattice lack oxygen atom after anneal and crystal which lead to a decrease of the dimension of the crystal lattice, a decrease of the thickness of PZT thin films and an increase of the film capacity.

With atmospheric pressure keeping invariable, dielectric loss first increase and then decrease with the substrate temperature in equation 3. That’s because the energy of the grains, at a very low substrate temperature, which were sputtered on the substrate is low too. They are hard to have transference and make the film with uniformity and compactness. On the contrary, the energy of the sputtered grains is so high that they are easy to evaporate when the substrate temperature is high. At an invariable substrate temperature, the curve of dielectric loss as a parabola with a downwards opening ascends and falls down along with the increasing atmospheric pressure. That’s because when the atmospheric pressure is low, the glow discharge is weak and the number of ion sputtered out is low as well. So there are little collisions between ions and they can arrive at the substrate favorably, creating a uniform and compact film. When the atmospheric pressure is high, collisions between the ions are frequent and the ions cluster is made into troubled waters, leading to an equation. With a moderate atmospheric pressure and a substrate temperature either too low or too high, the dielectric loss might be large. On the contrary, the least dielectric loss would be caused at a moderate substrate temperature and a high atmospheric pressure.

The films coercive field decrease linearly with the sputtering power when the ratio of \( \text{O}_2/\text{Ar}+\text{O}_2 \) keeps invariable in equation 4. The films coercive field first increase and then decrease with the ratio...
of O₂/Ar+O₂ with sputtering power keeps invariable. Equation 5 suggests that in the moderate sputtering power line, spontaneous polarization is influenced slightly by annealed temperature. In other words, spontaneous polarization keeps invariability in very wide range. The equation 6 response surface of thin films remnant polarization is a plane. Thin films remnant polarization is sensitive to annealed temperature and insensitive to sputtering power.

4 Conclusions
Pt/Ti bottom electrodes were fabricated on SiO₂/Si substrate by magnetron dual-facing-target sputtering system. The thickness of Pt and Ti bottom substrate are 150nm and 20nm respectively. Nano-particles PZT ferroelectric thin films of which thickness is about 100–200nm are prepared on Pt/Ti/SiO₂/Si underlayer by RF-magnetron sputtering. XRD shows that these thin films have good crystallization behavior and pure perovskite structure. SEM results show that the surface of the PZT ferroelectric thin film is uniform and dense. The crystal grain size of the PZT ferroelectric thin film is less than 100nm. The effect of magnetron sputtering process parameter on the performance of PZT ferroelectric thin film is analyzed by uniform design. In order to get maximal capacitance, remnant polarization, spontaneous polarization, minimal dielectric loss and coercive field, the process parameters are optimized as follows: air pressure (3~3.5Pa), substrate temperature (200°C), ratio of O₂/Ar+O₂ (0.08), sputtering power (45W), annealed temperature (700~800°C).

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