Article
Research on Raman-scattering and Fabrication of Multilayer Thin Film with Different Structures and Components Based on Pt/Ti/Si₃N₄/SiO₂/Si Substrate

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Using the same conditions and various starting materials, such as lead acetate trihydrate, tetrabutylin titanate, zirconium n-butoxide, and acetylacetone, two kinds of solid precursors, lead zirconate titanate (PZT, Zr/Ti=15/85) and lead titanate (PT), were fabricated. With three different combinations, namely, PZT, PT/PZT-PZT/PT, and PT/PZT/-/PZT/PT, three multilayer thin films were deposited on three Pt-Ti-Si₃N₄-SiO₂-Si substrates by a modified sol-gel process. The fabrication process of the thin films is discussed in detail. We found that there is a large built-in stress in the thin film, which can be diminished by annealing at 600 °C, when the gel is turned into solid material through drying and sintering. The Raman scattering spectra of the films with different compositions and structures were investigated. With the help of X-ray diffraction (XRD) analyzer and Raman scattering spectra analyzer, it was found that the thin films with the PT/PZT-PZT/PT structure have reasonable crystallinity and less residual stress. XRD testing shows that the diffraction pattern of the multilayer film results from the superimposition of the PZT and PT patterns. This leads to the conclusion that the PT/PZT-PZT/PT multilayer thin film has a promising future in pyroelectric infrared detectors with high performance.

Key words: Multilayer thin film, Pyroelectric, Sol-gel, Raman, XRD analysis

I. INTRODUCTION

Recently, there has been considerable interest in pyroelectric thin films, especially in the lead-zirconate-titanate (PbZr₁₋ₓTiₓO₃, PZT) system for their potential applications in microelectronic technology [1-3]. The pyroelectric detector has the advantages of operation at room temperature, a wide range of infrared absorption wavelength, and low processing cost [4,5]. Compared with bulk ceramic pyroelectric infrared detectors of similar materials, the thin film pyroelectric infrared detector has more merits. One of the merits is that the sensitivity of the thermal detectors can be improved by the reduced heat capacity of the detecting elements in thin film devices. Another merit is the potential to integrate the thin film detectors into a standard process of silicon chip fabrication [6-10].

A considerable amount of research has been focused on the growth and device fabrication process of ferroelectric thin films for applications in piezoelectric transducers, pyroelectric infrared detectors and non-volatile random access memory devices [11-13]. Lead titanate (PbTiO₃) (PT) is a perovskite-type-ferroelectric-compound desirable for pyroelectric infrared detectors because of its relatively large pyroelectric coefficient and spontaneous polarization. However, much attention has been paid to the modification of PT; that is to say, doping is used for the improvement of mechanical and electrical properties.

The incorporation of off-valent (La³⁺, Sm³⁺, Nd³⁺, Gd³⁺) and isovalent ions (Ca²⁺, Ba²⁺, Sr²⁺) into PT ceramics is reported to improve the dielectric, piezoelectric, ferroelectric, and pyroelectric properties [14]. By modifying PT ceramics with these ions, the lattice anisotropy is reduced [15-17] resulting in hard and dense samples with high mechanical strength.

In the present work, we perform experiments aiming at substitution of Zr²⁺ ion in PbZr²⁺ sites. PZT is one of the ferroelectric materials that have a promising application future for its extremely wide field of applications as piezoelectric material. PZT has better coupling coefficient between electrical and mechanical properties. In this work, the PZT and PT thin films were combined “in series” for pyroelectric infrared detector application (see Fig.1). Three kinds of structures were finished: pure PZT (11PZT, dPZT/(dPT+dPZT)=0, dPT is total thickness of PT layers in film and dPZT is total thick-
the temperature is raised to 124

ondly, the acetic acid is added into this mixture, and

with magnetic beater for 2 h at room temperature. Sec-

For the purpose of uniformity, the mixture is stirred

and acetylacetone are mixed together at 1:1 molar rate.

ether as the solvent. Firstly, the tetrabulyl tittanate

acetylacetone as the chelating agent, and glycol methyl

crystal water in the acetic acid lead. 10% excess lead

a reaction which is sustained for 10 min, to remove the

The output of this laser is 8 mW. At room tempera-

the light of the 514.5 nm line as an excitation source.

of xerogels are saved easily. By dissolving the xerogel

into glycol methyl ether, taking its proportion as 20%,

the collosol is made. After stewing for a period of time,

the collosol is coated on the Pt/Ti/SiN4/SiO2/Si sub-

strate; the rotation speed for coating is controlled at

3600 r/min. The pure PZT, PT/PZT-PZT/PT, and

PT/PZT-/PZT/PT thin films were prepared by using a

modified sol-gel process. Three kinds of thin films

were prepared by repeating the spin-coating steps 11
times. The post-annealing thickness of each layer of

PZT or PT thin film in one spin-coating step is approxi-
mately 50 nm, thus, total thickness, for every struc-
ture (the pure PZT, PT/PZT-PZT/PT, and PT/PZT/-/

/PZT/PT) is approximately the same: 550 nm.

SEM micrographs of the thin films with different

structures and components are shown in Fig.2. Fig-

er 2 (a) and (b) are SEM micrographs of pure PZT

structures and components are shown in Fig.2. Fig-

semiconductor (SEM), Raman scattering and X-

ray diffraction (XRD). The characterizations show that

the PT/PZT-PZT/PT multilayer thin films have per-

fect surface densification, good crystallization, and less

residual stress. Hence, it has great prospects in develop-

ing high performance infrared detectors.

II. EXPERIMENTS

PZT ferroelectric film has a typical perovskite struc-
ture, which has good piezoelectric and pyroelectric
performance, larger pyroelectric coefficient and higher
Curie temperature [10,18,19]. Because the ion radius
(0.061 nm) of Ti\(^{4+}\) is close to that of Zr\(^{4+}\) (0.072 nm),
and their chemical performances are similar, PbTiO\(_3\)
and PbZrO\(_3\) can form a solid solution with any propor-
tion. Accordingly, the performances of dielectric, piezo-
electric, ferroelectric, and pyroelectric can be changed
by using different ratios of Zr/Ti and different doping
methods [20,21].

Lead acetate trihydrate (Pb(CH\(_3\)COO)\(_2\)\(_3\)H\(_2\)O),
tetrabulyl tittanate (Ti(OC\(_4\)H\(_9\))\(_4\)) and zirconium n-
butoxide (Zr(OC\(_4\)H\(_9\))\(_4\)) are selected as raw materials,
acetylactone as the chelating agent, and glycol methyl
ether as the solvent. Firstly, the tetrabulyl tittanate
and acetylactone are mixed together at 1:1 molar rate.
For the purpose of uniformity, the mixture is stirred
with magnetic beater for 2 h at room temperature.
Secondly, the acetic acid is added into this mixture, and
the temperature is raised to 124 °C. This will result in
a reaction which is sustained for 10 min, to remove the
crystal water in the acetic acid lead. 10% excess lead
acetate trihydrate is added into the mixture to compen-
sate for possible lead loss during the heat treatment of
the thin films. Thirdly, this mixture is separated into
two parts. One is used to fabricate the PT solid pre-
cursor, and the other for the PZT solid precursor with an
addition of zirconium n-Zr(OC\(_4\)H\(_9\))\(_4\) at 80 °C. The

By the above steps, two kinds of xerogels, PT and
PZT are obtained. In PZT, the rate of zirconium and
titanium is 0.15:0.85. What is more, these two kinds of
xerogels are saved easily. By dissolving the xerogel
into glycol methyl ether, taking its proportion as 20%,
the collosol is made. After stewing for a period of time,
the collosol is coated on the Pt/Ti/SiN\(_4\)/SiO\(_2\)/Si sub-
strate; the rotation speed for coating is controlled at
3600 r/min. The pure PZT, PT/PZT-PZT/PT, and
PT/PZT-/PZT/PT thin films were prepared by using a
modified sol-gel process. Three kinds of thin films
were prepared by repeating the spin-coating steps 11
times. The post-annealing thickness of each layer of

SEM micrographs of the thin films with different
structures and components are shown in Fig.2. Figure
2 (a) and (b) are SEM micrographs of pure PZT
thin film in pre-annealing and post-annealing, respec-
tively. Compared with the pre-annealing film, the post-
annealing film has the merit of surface structure den-
sification. Figure 2 (c) and (d) denote SEM micro-
graphs of PT/PZT-PZT/PT and PT/PZT-/PZT/PT.
According to these experimental results, we can find
that PT/PZT-PZT/PT multilayer thin film structure
has a favorable crystallinity.

III. RESULTS AND DISCUSSION

To search the structure-property relationship be-
tween Pb(Zr,Ti)O\(_3\) (PZT) and PbTiO\(_3\) (PT) ferroe-
clectric materials, micro-Raman scattering technique
has been used to probe the soft lattice modes and phase
transitions [22,23]. It has been well established that
the soft mode spectroscopy allowed researchers to in-
vestigate the phase transition phenomena in bulk ce-
ramics and thin films prepared by various techniques
[24-26]. Micro-Raman measurements were carried out
at room temperature by using an argon ion laser with
the light of the 514.5 nm line as an excitation source.
The output of this laser is 8 mW. At room tempera-
ture, from the PZT phase diagram observation, near
the morphotropic phase boundary (MPB) of PZT, the
tetragonal and trigonal phases are associated with a

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FIG. 2 SEM micrographs of different structures and components (a) pre-annealing pure PZT, (b) post-annealing pure PZT, (c) PT/PZT-PZT/PT, and (d) PT/PZT/-/PZT/PT thin films. The substrate is Pt (150 nm)/Ti (80 nm)/Si₃N₄ (150 nm)/SiO₂ (500 nm)/Si (500 µm).

Figure 3 shows the Raman scattering spectra of the thin films with different structures, namely, pre-annealing pure PZT, post-annealing pure PZT, PT/PZT-PZT/PT, and PT/PZT/-/PZT/PT multilayer thin films. In this experiment, the gel can be changed from a state with porous and loose structure to the other state with compact structure by drying and sintering. There is a big residual stress inside the thin films when the thin films are sintered at 400 °C. When the thin films are sintered and annealed at 600 °C, the residual stress can be remarkably reduced.

Before annealing, the PZT thin film has amorphous structure. Annealing the thin films at higher temperatures results in the PZT perovskite phase developing tetragonal structure. The Raman peak that arises is homologous with the standard Raman peak of the perovskite. As a result, the Raman excitation of active modes becomes stronger and stronger, which is a good indication of the development of crystallinity for the PZT (Zn/Ti=15/85) perovskite phase. The frequency shift of the Raman peaks after 600 °C annealing is smaller than before, which shows that the residual stress is diminished after annealing. The peaks at the wavenumber around 206, 283, 331, 417, 499, 569, 603, 700, 747, and 786 cm⁻¹ are identified as E(2TO), B₁+E, A₁(2TO), E(2LO), E(3TO), R₁,

FIG. 3 Raman spectra of (a) pre-annealing, (b) post-annealing pure PZT, (c) PT/PZT-PZT/PT, and (d) PT/PZT/-/PZT/PT thin films at room temperature.

A₁(3TO), E(3LO), Rh, and A₁(3LO), respectively. The peaks at the wavenumber around 283, 331, and 713 cm⁻¹ are the tetragonal and trigonal phases associated with a phase coexistence region. Compared with the PT/PZT/-/PZT/PT structure, the Raman peaks of PT/PZT-PZT/PT have a smaller frequency shift, so the crystalline state is better than the PT/PZT/-/PZT/PT structure, and its residual stress is smaller. All the Raman modes are assigned according to the results of Burns and Scott [30]. In addition, the Raman spectra of the thin films are similar to the results of

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FIG. 4 Raman shifts of (a) E(2TO), (b) B1+E, (c) A1(2TO), and (d) E(2LO) modes in region of 200-440 cm$^{-1}$. Structure 1, 2, 3, and 4 refer to pre-annealing pure PZT, post-annealing pure PZT, PT/PZT-PZT/PT, and PT/PZT-/PZT/PT, respectively.

Meng et al. [31].

Figures 4 and 5 depict the frequency shift trends of different modes for four kinds of thin films with different structures in mid- and high-frequency regions. The abscissas of Figs. 4 and 5 denote four kinds of thin films: pre-annealing pure PZT, post-annealing pure PZT, PT/PZT-PZT/PT, and PT/PZT-/PZT/PT.

In terms of Figs. 3 and 4, it can be seen that the intensity of Raman diffraction peaks of pre-annealing thin film is small in mid-frequency region and the pre-annealing PZT thin films therefore have poor crystallization performance. It can be observed that in Fig.4, E(2TO), B1+E, A1(2TO), E(2LO) modes have the noticeable upward shift, therefore a large residual stress can be found inside the thin films. However, the intensity of Raman diffraction peaks of post-annealing thin film goes big in the mid-frequency region and its half width peaks and frequency shifts have an obvious lessening. Compared with pre-annealing PZT thin film, post-annealing PZT thin film has better crystallization and less residual stress existing inside the thin film. Among the three post-annealing thin films, it can be noticed that pure PZT thin film has a rather big frequency shift. E(2TO) and B1+E modes of PT/PZT-/PZT/PT multilayer thin film have big frequency shifts, whereas A1(2TO) and E(2LO) modes have small frequency shifts. But the modes of PT/PZT-PZT/PT multilayer thin film are close to the normal Raman modes, therefore, the residual stress inside PT/PZT-PZT/PT multilayer thin film is released well.

In Fig.5, the Raman modes of pure PZT and PT/PZT-PZT/PT thin films have a noticeable upward shift, and so do the PT/PZT-/PZT/PT multilayer thin films, except for the Rh and A1(3LO) modes. The experiment results show that the residual stress inside the thin film is released well after annealing, but some of the residual stress still remains there, which results in the phenomena of red shift and blue shift. Among six modes in the high-frequency region, only the Raman frequency shift of R1 mode of the pure PZT thin film is smaller than that of the PT/PZT-PZT/PT multilayer thin film, and the other Raman modes show a big frequency shift. Compared with the PT/PZT-/PZT/PT thin film, the Raman frequency shifts of the pure PZT thin film are big except for R1 and E(3LO) modes. The Raman frequency shifts of E(3TO), A1(3TO), E(3LO), and A1(3LO) modes in the PT/PZT-PZT/PT thin film are smaller than that of the PT/PZT-/PZT/PT thin film, excluding R1 and Rh modes. Compared with the pure PZT and PT/PZT-/PZT/PT, the PT/PZT-PZT/PT thin film has residual stress. Through Raman spectrum analysis, we see that the PT/PZT-PZT/PT thin film structure has the best performance among these three structures.

The XRD patterns of the pure PZT, PT/PZT-PZT/PT, and PT/PZT-/PZT/PT thin films are shown in Fig.6. The crystalline nature of the thin films with the different structures was investigated by XRD. The XRD patterns reveal that the films are polycrystalline with no evidence of preferred orientation or secondary phases, i.e., pyrochlore phase. The crystalline phase has a tetragonal structure, and presents an obvious diffraction peak at the (100) orientation of the thin film growth. The reason is the thin film grows on the Pt/Ti/SiO$_2$/Si$_3$N$_4$/Si (100) substrate, following the preferred orientation of (100), which has the smallest nucleation energy.

Figure 6 shows the diffraction peaks after annealing are obviously stronger than before, the crystalline state after annealing is better, and the diffraction peaks of the PT/PZT-PZT/PT and PT/PZT-/PZT/PT struc-
ture in the (100) and (111) orientations are stronger than that of PT/PZT/-/PZT/PT structure. The reason is that the annealing is a crystallization process of the thin film. With the increase of annealing temperature, the crystal grain gradually grows, and so does the compactness of the thin film, therefore, the degree of crystallization increases. The crystallization temperature of the PT is comparatively low, so a layer of PT is coated on the substrate before the PZT, which is propitious to the rime of the PZT. According to the experimental data, we can come to the conclusion that the rime degree of the PT/PZT-PZT/PT structure is better.

In terms of the formation of the Pb(Zr_{0.15}Ti_{0.85})O_3 phase, we can know that it is during the sintering process that the reaction of gel and dissolvent occurs. It is clean in Fig. 6 that the most single perovskite phase can be obtained in the sample at the annealing temperature of 600 °C. There is also a relatively lower PbO peak in this sample due to the excessive amount of it from the starting composition. It is difficult to determine if the synthesized Pb(Zr_{0.15}Ti_{0.85})O_3 films belong to tetragonal or rhombohedral structure, because their diffused diffraction peaks in the XRD patterns are caused by their small size grain.

IV. CONCLUSION

Multilayer films of pure PZT, PT/PZT/-/PZT/PT, and PT/PZT-PZT/PT can be fabricated on the surface of three different Pt-Ti-Si_Na_SiO_2-Si substrates by the sol-gel method. The Raman and XRD analysis of these thin films with different structures were investigated before and after annealing. All test results show that post-annealing thin film has good, fully grown perovskite structure due to the 600 °C annealing temperature. In terms of the XRD tests we can know that the (100) and (111) preferred orientation thin films can be developed on the silicon substrate. Through Raman testing, we can find that the crystal status and residual stress of PT/PZT-PZT/PT structure are better than that of the pure PZT and PT/PZT/-/PZT/PT structures. Moreover, the residual stress at the 600 °C annealing is smaller than that at 400 °C sintering. As far as the results are concerned, XRD test and Raman spectrum analysis are consistent. The experimental results show that the PT/PZT-PZT/PT multilayer thin film is a promising choice for developing high performance pyroelectric infrared detectors.

V. ACKNOWLEDGMENTS

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