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Characterization of PZT/PT multilayer thin film by sol–gel

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Abstract

By using sol–gel method, ferroelectric $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT) thin film with $PbTiO_3$ (PT) buffer layers are deposited on $Pt/Ti/SiO_2/Si$ substrates to investigate the effect of PT buffer layers on the microstructure and properties of PZT thin films. PT layers are served as interfacial layers between Pt and PZT thin films. After annealing at 600 °C for 1 h, the thickness of PZT/PT multilayer film is about 650 nm. The microstructure of the thin films has been investigated by X-ray diffraction (XRD). Dielectric properties and leakage current are determined by HP4284A LCR meter and Keithley 6517A picoameter. Experiment results show that PT buffer layer is helpful to decrease the annealing temperature of PZT thin film. After annealed at 600 °C, PZT/PT multilayer thin films can get perovskite structure, while PZT thin films without PT buffer layer annealed at 600 °C, a second phase appears. PT buffer layer can also improve the dielectric properties of PZT thin film. The dielectric constant and the dielectric loss of PZT/PT multilayer thin films are lower than those of the pure PZT thin films.

Keywords: C. Dielectric properties; D. PZT; D. Perovskite; PT buffer layer; Leakage current

1. Introduction

To develop high performance pyroelectric infrared detectors, efforts have been made to improve the desired properties of PZT thin films, since they have outstanding physical and electrical properties [1–3]. The sol–gel technique is one of the most important methods in preparing high quality PZT thin films [4]. For high performance pyroelectric detectors, dielectric constant and dielectric loss are of the most importance. But the conflict between the high figure of merit for high performance and a high dielectric constant for high output capacitance seems inevitable. In the PZT family thin films, the dielectric constant of PZT is relatively high for pyroelectric detectors, on the other hand, that of the PT thin film is lower. It is possible to decrease the relative dielectric constant of PZT by using PT thin films as buffer layers.

There are only a few reports on buffer layers [4–7]. By using PT buffer layer, Highly (1 0 0) oriented films can be deposited at 550 °C. Low dielectric loss is found in the stacking PZT/PT structure, and the insertion of a thin PT layer can also improve the crystallization behavior of the PZT thin films [4,5]. $BaTiO_3$ (BT) buffer layers can suppress the interaction between Pt and Pb and also increase the crystallinity of the PZT layer. But the dielectric constant of BT is higher than that of the single PZT films. So it is impossible to reduce the dielectric constant of PZT thin films [6]. Ferroelectric PZT(40/60)/PZT(60/40) heterolayered thin films show dense and homogeneous structure without presence of the rosette structure. The dielectric properties such as dielectric constant, remnant polarization and leakage current density are superior to those of single composition PZT(40/60) and PZT(60/40) films [7]. The results are thought that the lower PZT(40/60) layers provide the nucleation sites for the formation of perovskite phase in the upper layers.

The objectives of the present study are to investigate the effect of different PT buffer layers on the electrical, ferroelectric properties of the PZT thin films, and to develop high quality thin films for high performace IR detectors.

2. Experiment

The substrates used in this experiment are $Pt/Ti/SiO_2/Si$. After cleaning in alcohol, acetone, and rinsing several times in deionezed water, the substrates are dried under clean room conditions. To measure electrical properties, top Au electrodes are deposited by direct current sputtering at room temperature.

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The precursor solutions are prepared using mixed solutions of lead acetate trihydrate, tetrabutyi titanium, tetrabutyl Zirconium, dissolved in ethylene glycol monomethyl ether. For PT precursor, tetrabutyl zirconium is omitted. After removing the volatile products, PZT and PT powders are synthesized successfully.

After dissolving separately in ethylene glycol monomethyl ether, the 20% PZT and PT precursor solutions are filtered by a 0.22 μm membrane filter and aged for about 12 h. Afterwards, the precursors are coated on the substrates by the spin coating method (3000 rpm, 20 s) and dried at 120 and 500 °C separately. Finally, the whole film is annealed at 600 °C for 1 h. To obtain a thick film, the above coating process is repeated 10 times, PT layers are deposited first, and PZT layer are deposited later. Total thickness for PZT/PT multilayer thin films is approximately 650 nm.

The structure phase and the crystallinity of thin films are analyzed by X-ray diffraction (XRD) from a D8 diffractometer using Cu Ka radiation. Dielectric properties are checked by a HP4284A LCR meter. The leakage current density is determined by the current–voltage (*I–V*) measurements using a Keithley 6517A picoameter.

3. Results and discussion

3.1. XRD results

Fig. 1 shows the results of X-ray diffraction patterns of PZT thin films with PT buffer layer, for comparison, the XRD pattern of pure PZT thin films is also shown in the figure. Deposition conditions for all films are the same. It can be seen that PZT/PT multilayer thin films annealed at 600 °C were composed of pure perovskite phase without any detectable pyrochlore impurity, but PZT thin films with no PT buffer layer annealed at 600 °C have the second phase. The crystallizing temperature of pure PZT thin films is 650 °C. So it can be known that the crystallization of PZT is improved when PT thin films are used buffer layers, and PT buffer layer is helpful to decrease the annealing temperature of PZT thin film. The structure shown in the PZT/PT multilayer thin films is the result of superimposition of the diffraction peaks from PZT and PT in the films.

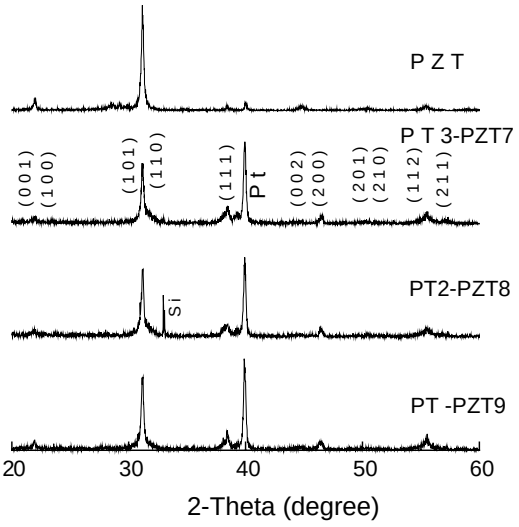

Fig. 1. XRD pattern of PZT/PT multilayer thin films and pure PZT thin films annealing at 600 °C for 1 h.

3.2. Dielectric properties

The dielectric constants and dielectric losses of PZT thin films and PZT/PT multilayer thin films are shown in Table 1 and Fig. 2 reveals the dielectric constant and dielectric loss of pure PZT thin film and PT/PZT multilayer thin films as a function of frequency with an oscillation level at 100 mV. The PZT/PT multilayer thin films exhibit lower dielectric constant than that of the pure PZT thin films due to the low dielectric constant of PT layers. The experimental results in our work show that the dielectric constant of the PT thin films prepared with the sol–gel method is approximately 100–150 and that of the pure PZT thin films is about 400–500. It is obvious that dielectric constant of PZT can be easily decreased by adjusting the relative layers of PT in this multilayer structure. Dielectric loss of PZT can also be improved by inserting different PT layers, the multilayer thin films exhibited lower dielectric loss than that of the pure PZT thin films at 10 and 100 kHz, respectively.

It is obvious that PT buffer layers can improve the dielectric properties of PZT thin films. The dielectric loss of PZT thin films can be controlled below 0.015 at 10 kHz by inserting different PT layers. It is a very important feature to improve the pyroelectric properties of PZT thin films.

3.3. Leakage current characteristics

Fig. 3 displays the dependence of leakage current on applied voltages (*I–V*) of PZT/PT multilayer thin films and PZT thin films. The reported *I–V* data are corresponding to a 20 s delay time after the application of each voltage step and the thin film capacitors are not poled prior to the *I–V* measurement. Up to an applied voltage of 10 V, the leakage current in the PZT and PZT/PT multilayer thin films is no more than 6 nA. However, the leakage current of PZT/PT multilayer thin films is higher than that of the pure PZT thin

Table 1
Dielectric properties of PZT thin films with PT buffer layers

Sample name	Dielectric constant		Dielectric loss	
	10 kHz	100 kHz	10 kHz	100 kHz
PZT	423	404	0.033	0.037
PT1/PZT9	414	398	0.031	0.037
PT2/PZT8	362	351	0.029	0.029
PT3/PZT7	335	325	0.027	0.025

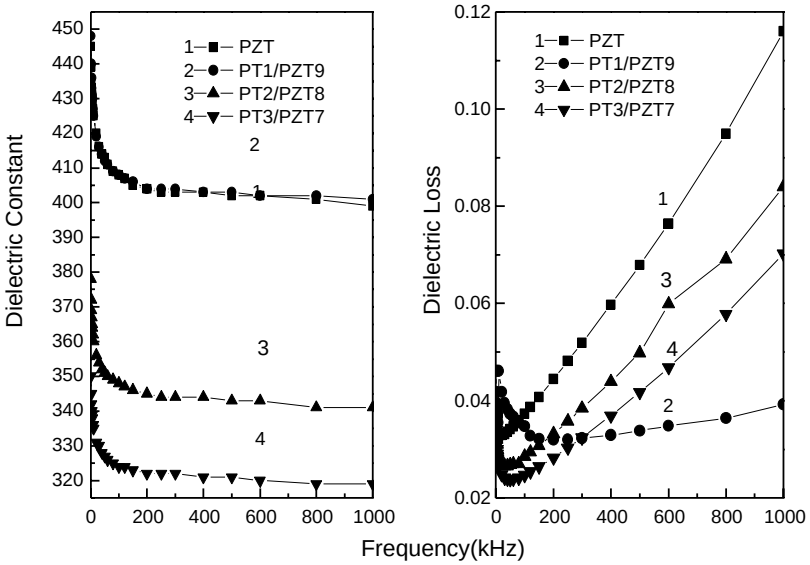

Fig. 2. Dielectric constant and dielectric loss of PZT; PZT/PT multilayer thin films.

films and an abrupt current increases take place at 6 V in PT2/PZT8.

It can be found that the mutilayer structure can not reduce the leakage current of PZT thin films, in contrary, the leakage current of PZT were increased because of PT buffer layers. As we know, the extrinsic additives affect the nature and the distribution of defects present in the PZT thin films [8]. Defect distribution and their subsequent mobility have a direct impact on leakage current. Therefore, it can be speculated that the decrease of ferroelectric properties exhibited in PZT/PT mutilayer thin films has a close relationship with the PT buffer layers. Oxygen defect of PZT thin films may increase when PT thin films were used to be buffer layers.

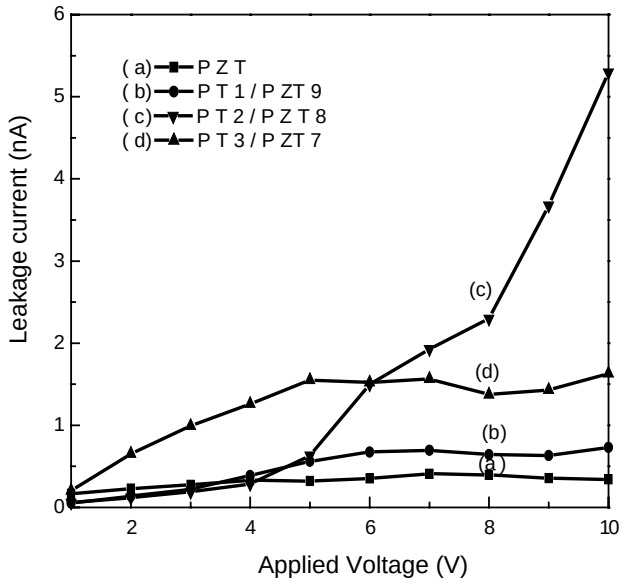

Fig. 3. Leakage current characteristic of PZT/PT multilayer thin films and PZT thin films vs. applied field.

At the same time, PZT thin films have the same structure as PT thin films. So the leakage current of PZT/PT mutilayer thin films and PZT thin films are all below 6 nA. Then if the PZT/PT multilayer thin films were used in pyroelectic detectors, the thickness of PT buffer layers must be optimized carefully.

4. Conclusion

In conclusion, the microstructure and electrical properties of the PZT layer are improved by employing the novel multilayer thin films structure that combines the PZT with the PT layers. Using PT buffer layer, the annealing temperature of pure PZT thin films can be decreased from 650 to 600 °C. Crystallizing property of the PZT thin films can also be improved.

As the layer of PT thin films increasing, the relative dielectric constant and dielectric loss are decreased in succession, however, the leakage current of PZT/PT multilayer thin films is higher than that of the pure PZT thin films. For pyroelectric IR detectors application, these two factors must be considered.

Acknowledgements

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