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The effect of pyrolyzing temperature to the microstructure of PZT/PT multilayer thin films

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Abstract

By sol–gel method, ferroelectric $Pb(Zr_{0.5},Ti_{0.5})O_3/PbTiO_3$(PZT/PT) multilayer thin films are deposited on $Pt/Ti/SiO_2/Si$ substrates. The effects of different pyrolysis on the crystalline structure are investigated using X-ray diffraction (XRD). Dielectric properties and leakage current characteristic are determined by HP4284A LCR meter and Keithley 6517A. After annealing at 600 °C, the thickness of one layer is about 60–70 nm. It shows that the pyrolysis temperature can affect the dielectric properties of PZT/PT multilayer thin films dramatically. At 100 kHz, the dielectric constant of 255, dielectric loss of 0.0165 is obtained for the PZT/PT multilayer thin films pyrolyzed at 500 °C. By contract, dielectric constant of 126 and 118, dielectric loss of 0.0210 and 0.0235 are obtained for the films pyrolyzed at 400 and 300 °C. The films polyrized at 500 °C exhibit the lowest leakage current. Experimental results showed the PZT/PT multilayer thin film pyrolyzed at 500 °C is a good candidate material for infrared (IR) detectors.

Keywords: C. Dielectric properties; PZT/PT; Pyrolysis temperature; Leakage current

1. Introduction

The solid solution of $Pb(Zr_{0.5},Ti_{0.5})O_3$(PZT) is ferroelectric films and has a large remnant polarization, high piezo- and pyroelectric coefficients. Deposition is usually carried out onto $Pt/Ti/SiO_2/Si$ wafer followed by sputtering of a top electrode onto the surface of the film.

A variety of techniques have been proposed to fabricate ferroelectric PZT thin films such as laser ablation [1,2], electron beam evaporation [3], metalorganic chemical vapor deposition (MOCVD) [4,5], RF magnetron sputtering [6], sol–gel process [7,8]. Sol–gel method is cheap, since it does not involve a vacuum chamber, and can be used to deposit PZT onto a 6 in. SiO_2/Si wafer.

Many factors can affect the properties of PZT, such as the thickness of ferroelectric films [8], annealing temperature [9,10], chemistry of the precursor solution [11]. It has been reported that the transformation kinetics from amorphous to perovskite along with the orientation of the film are strongly depending on the temperature of pyrolysis [12]. But the importance has not been attached to the effect of pyrolyzing temperature on the dielectric and pyroelectric properties of PZT/PT mutilayer thin films.

In this paper, PZT/PT multilayer thin films were fabricated on $Pt/Ti/SiO_2/Si$ substrates using a sol–gel method, and the effects of pyrolysis temperature on the dielectric and pyroelectric properties of PZT/PT multilayer thin films were investigated.

2. Experiment

PZT/PT multilayer thin films are prepared by a modified sol–gel method. The precursor solutions are prepared by reacting lead acetate trihydrate, tetrabutyl titanium, tetrabutly zirconium as molecular precursors, ethylene glycol monomethyl ether as solvent, and acetylacetone as a stabilizing agent. No excess lead acetate trihydrate is added in precursor solution.

Lead acetate trihydrate is dissolved into ethylene glycol monomethyl ether and refluenced at 124 °C with continuous stirring for 30 min. At the same time, tetrabutyl titanium is chelated with acetylacetone in a molar ratio of 1:2 at room

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temperature for 120 min, and then tetrabutly zirconium is added into this mixture solution (for PT precursor, this step is omitted). Afterwards, the lead acetate solution and solution of titanium and zirconium are mixed and stirred at 80 °C for 30 min. At last, the volatile products are removed under reduced pressure below 60 °C for more than 6 h. Light yellow porous PZT precursor powder and PT precursor powder are finally obtained.

The PZT and Pt powders are dissolved in ethylene glycol monomethyl ether in weight percentage of 20% at room temperature by stirring for 1 h. The composition of the final solution is Zr : Ti = 50 : 50. This solution is then filtered using a membrane filter (0.22 μm) to minimize particulate contamination. The filtered solution is aged for about 12 h before the fabrication of coating.

Substrates used in the experiment are Pt/Ti/SiO_2/Si. The thin films are fabricated by spin coating at 3000 rpm. for 20 s under clean room conditions. After the deposition process, each coated film is dried in air at 120 °C for 10 min in the oven, and then pyrolyzed directly at 300, 400, and 500 °C separately for 20 min to remove organics. Spin coating is repeated 10 times. After the 10th deposition cycle, the coated films are annealed at 600 °C for 1 h in air using routine thermal annealing. Total thickness for PZT5/PT5 multilayer thin films is approximately 650 nm.

A F20 filmetrics is used to measure the thickness of thin films. The microstructure of multilayer thin films is checked with a D8 Advanced X-ray diffractometer with Cu Kα radiation. Au top electrode (1 mm diameter) is deposited by direct current sputtering to measure electrical properties. Dielectric properties are measured by a HP4284A LCR meter. A Keithley 6517A picometer is used to check the leakage current.

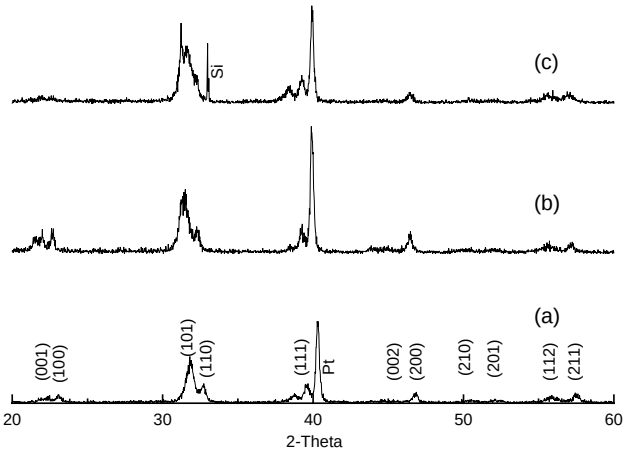

Fig. 1. XRD patterns of the PZT/PT multilayer thin films pyrolyzed at (a) 500 °C, (b) 400 °C, (c) 300 °C, and then finally heated at the same temperature of 600 °C for 1 h.

3. Results and discussion

3.1. XRD results

Fig. 1 shows XRD patterns of the PZT/PT multilayer thin films pyrolyzed at different temperatures and then finally annealed at the same temperature of 600 °C for 1 h. It can be seen that these films are all composed of pure perovskite structure with no pyrochlore phase. It has reported that the pyrolysis temperature affects the orientation of the PZT thin films that is prepared by the rapid thermal annealing (RTA) [12]. But in our results, the pyrolysis temperature has little effect on the microstructure of PZT/PT multilayer thin films. A possible reason is that different heat-treatment method is

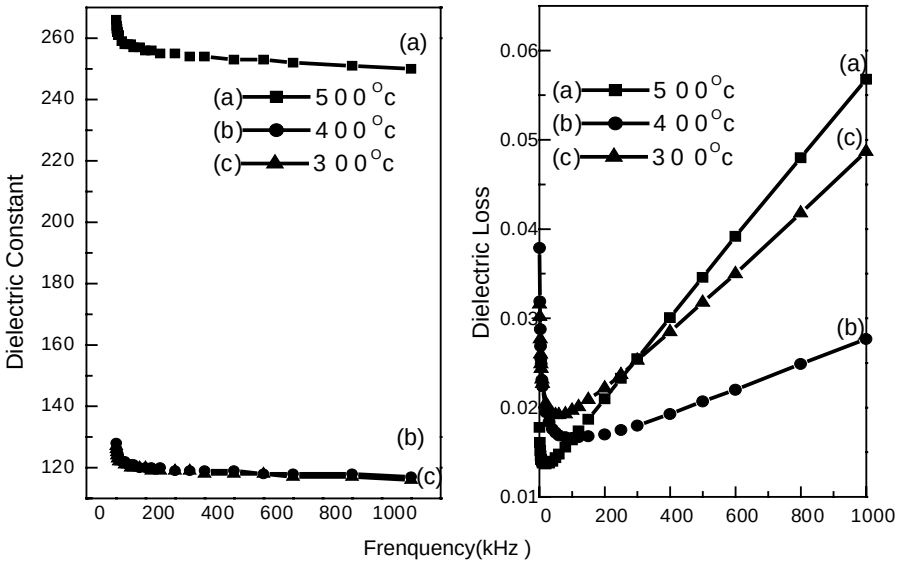

Fig. 2. Dielectric constant and dielectric loss of PZT/PT multilayer thin films pyrolyzed at (a) 500 °C, (b) 400 °C, (c) 300 °C, and then finally heated at 600 °C for 1 h.

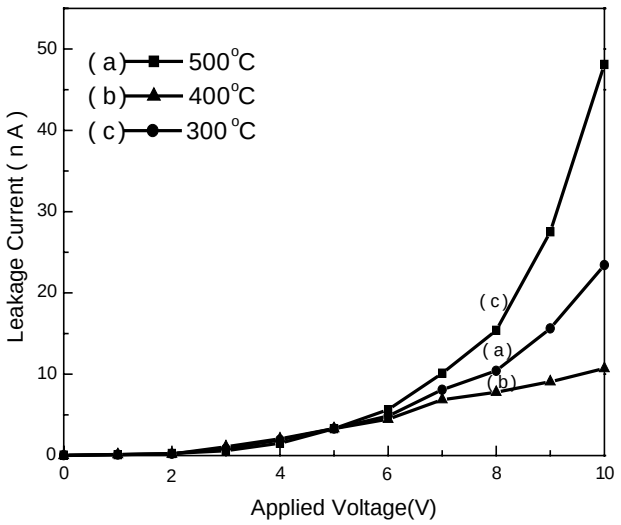

Fig. 3. Leakage current characteristic of PZT/PT multilayer thin films with applied voltage pyrolyzed at (a) 500 °C, (b) 400 °C, (c) 300 °C, and then finally heated at 600 °C for 1 h versus applied field.

used in this experiment, where the deposited films are heated directly at pyrolysis temperature in a muffle furnace.

3.2. Dielectric properties

Fig. 2 reveals the dielectric constant and dielectric loss of PZT/PT multilayer thin films pyrolyzed at (a) 500 °C, (b) 400 °C, (c) 300 °C, and then finally heated at 600 °C for 1 h as a function of frequency with an oscillation level at 100 mV. It can be seen that the dielectric properties of these films pyrolyzed at different temperature are very different. At 100 kHz, the dielectric constant of 255, dielectric loss of 0.0165 is obtained for the PZT/PT multilayer thin films pyrolyzed at 500 °C, which is in between the dielectric properties of pure PZT and pure PT thin films. By contract, the dielectric constant of 126 and 118, dielectric loss of 0.0210 and 0.0235 are obtained for the films pyrolyzed at 400 and 300 °C.

3.3. Leakage current characteristics

Fig. 3 shows the *I–V* characteristic of PZT/PT multilayer thin films pyrolyzed at 500, 400, and 300 °C separately and then finally heated at 600 °C for 1 h. It can be seen that the effect of pyrolysis temperature also strongly affect on the leakage current. As pyrolysis temperature increasing, leakage current decreases accordingly, especially at higher applied voltage (>5 V). The films porolyzed at 500 °C exhibit the lowest leakage current.

Fig. 4 shows the DSC/TG curve of the PZT gel powder dried from solution. It is obvious that most of the organics and other volatiles are removed at temperature <510 °C. A remarkable weight loss is found at about 300 °C. This may be due to the decomposition and vaporization of the organics in the powder. Another strong DSC peak occurs around

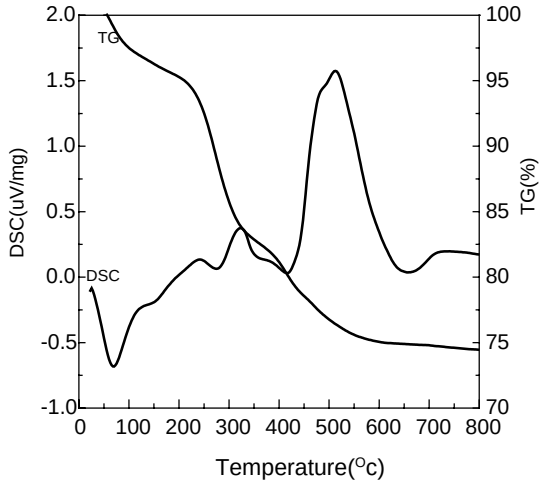

Fig. 4. TG and DSC of PZT gel powders heated in air at 10 °C/min.

510 °C, which seems due to the oxidation and burning of carbon residues from organics. From these results, the organic residue still exists at 300 and 400 °C. The amount of organic residue may affect the nature and the distribution of defects [13]. The difference among the leakage current of these films may owe to it.

4. Conclusion

Ferroelectric PZT5/PT5 multilayer thin films are pyrolyzed at different temperature, i.e. 300, 400, and 500 °C. All films which are heat-treated at 600 °C show single perovskite phase. However, the multilayer thin films pyrolyzed at 500 °C exhibit different dielectric properties from the films pyrolyzed at 300 and 400 °C. As pyrolyzing temperature increasing, leakage current decreases accordingly, and the films polyrized at 500 °C exhibit the lowest leakage current.

Acknowledgements

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