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Effect of pyrolysis temperature on preferential orientation and electrical properties of sol-gel derived lead zirconate titanate films

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Abstract

Lead zirconate titanate (PZT) films with composition near the morphotropic phase boundary were fabricated on Pt(111)/Ti/SiO_2/Si(100) using sol-gel method, and the pyrolysis temperature effects on the preferential orientation and ferroelectric properties of PZT films were investigated. It has been found that the PZT films pyrolyzed at 450 °C and then annealed at 650 °C shown a dominated (100) orientation, whereas the pyrolysis treatment at lower or higher temperatures favored the (111) orientation. Different pyrolysis temperatures also lead to differences in electrical properties, including dielectric constant, polarization values, leakage current and fatigue behavior.

Keywords: Dielectric properties; Fatigue; Ferroelectric properties; Films; PZT

1. Introduction

Lead zirconate titanate (PZT) films have been extensively investigated for many applications,[1–3] such as memories,[4] micro actuators[5] and sensors.[6] For these applications, it is required that the PZT films are integrated on silicon substrates. A variety of techniques including MOCVD,[7] sputtering[8] and sol-gel process[9–13] have been developed to fabricate PZT films. Among them, the sol-gel process has obtained particular interest because of its chemical homogeneity and facility of stoichiometry control. A further advantage of sol-gel routes is the simplicity. The similarities between sol-gel method and processing of photo-resist layers also make implementation in a microfabrication facility possible.[14]

As have been reviewed elsewhere,[15–18] the characteristics and microstructures of sol-gel derived PZT films are sensitive to the processing conditions, including solution composition, seeding layer, pyrolysis and annealing procedure, and consequently the properties of ferroelectric films depend on the microstructure and texture of the films. It is well known the properties of ferroelectric films depend on the microstructure and texture of the films, which in turn are strongly determined by the processing characteristics as described above. Pyrolysis is an indispensable step for the sol-gel process, whose major function is to remove organics in the precursor solution; however, pyrolysis conditions also affect the crystal orientation of sol-gel derived PZT films, as has been suggested by some studies.[19]

In the present study, the effects of pyrolysis temperature on the microstructure and electrical properties of sol-gel derived PZT films were systematically investigated. For this purpose, PZT films on Pt/Ti/SiO_2/Si(100) substrates were fabricated by sol-gel method, in which the pyrolysis temperatures were varied from 200 to 500 °C to evaluate the pyrolysis temperature dependence of the texture of the PZT films. The composition of films was set at $Pb(Zr_{0.52}Ti_{0.48})O_3$ near the morphotropic phase boundary (MPB) in the PZT system. The ferroelectric properties including relative dielectric permittivity, polarization, capacitance–voltage, fatigue and leakage current properties of the resultant PZT films with different pyrolysis temperatures were investigated with a special attention paid on the influence of the film crystal orientation.

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2. Experimental

Ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$ films with a thickness of 0.5 μm were deposited on conventional Pt(111)/Ti/SiO_2/Si(100) substrates by a modified sol-gel method, whose details were described below. PZT films were prepared by spin coating a 2-methoxyethanol based precursor solution. In sol-gel processing schemes, 5% excess lead was added to the solutions to compensate for the lead loss by the evaporation and suppress the pyrochlore phase formation. Additionally, an appropriate amount of formamide and acetylacetone was added to the solution to prevent the present of cracks in films. Layers were deposited from a 0.5 M precursor solution by spin coating at 4000 rpm for 30 s. Each layer was dried at 200 °C and pyrolyzed at various temperatures varied from 200 to 500 °C for 2 min to remove organics. Subsequent layers were deposited to obtain films with a thickness of 0.5 μm. Additional rapid thermal processing (RTP) was used to crystallize the ceramic PZT films in oxygen atmosphere at 650 °C for 5 min to produce a perovskite structure.

The texture of the perovskite PZT films was examined by X-ray diffraction using Cu-K_α radiation with a Ni filter. The XRD patterns were recorded at a scan rate of 6° per min for phase and texture analysis. The surface morphology and cross-sectional microstructure of the films were observed using field-emission scanning electron microscope (FE-SEM). Top electrodes of platinum, approximately 0.1 μm thick and 0.7 mm in diameter, were sputtered onto the top of the PZT film surface through a shadow mask. All the electrical measurements were carried out using such ferroelectric capacitors across the PZT film. A ferroelectric test module TF Analyzer 2000 FE was employed to evaluate the electrical properties at room temperature. All tests were conducted at a frequency of 1 kHz and electric field of 500 kV/cm. The dielectric constant and loss factor were measured as a function of applied ac voltage. The polarization hysteresis loops of the PZT films were recorded using the ferroelectric tester. The spontaneous polarization and saturation polarization were determined from the hysteresis loops. The fatigue and leakage current properties were also evaluated through the ferroelectric measurement tester.

3. Results and discussion

After the pyrolysis step, performed at temperatures ranging from 200 to 500 °C, the films showed amorphous phase. All X-ray diffraction patterns of PZT films annealed at 650 °C for 5 min show single-phase perovskite peaks. No pyrochlore phase was detected in the PZT films under such processing conditions. Fig. 1 compares the XRD patterns of the $Pb(Zr_{0.52}Ti_{0.48})O_3$ films pyrolyzed between 200 and 500 °C for 2 min and annealed at 650 °C for 5 min. It can be seen that, for PZT films, peak intensity of (100) plane vary a lot as a function of pyrolysis temperature. For the PZT film pyrolyzed at 450 °C, (100) and (200) peaks became significant higher as compared with those pyrolyzed at other temperatures. Analysis of such preferential orientations was performed by calculating the degree of the orientation of the (100) from the formula

$$\alpha_{100} = \mathrm{I}(100)/\{\mathrm{I}(100) + \mathrm{I}(110) + \mathrm{I}(111)\}$$

by using the integrated intensity (I) of the corresponding diffraction peaks.[20] As shown in Fig. 2, as the pyrolysis temperature increases from 200 to 450 °C, the (100) intensity ratio increases from 0.337 to 0.747. As the

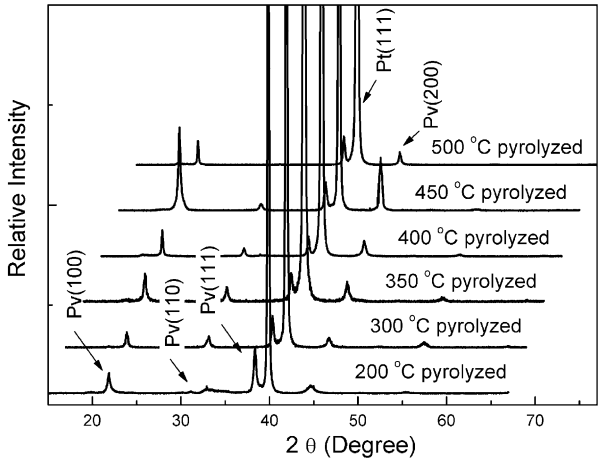

Fig. 1. XRD patterns of $Pb(Zr_{0.52}Ti_{0.48})O_3$ films pyrolyzed between 200 and 500 °C and annealed at 650 °C for 5 min. Pv and Pt denote the perovskite structure and platinum electrode, respectively.

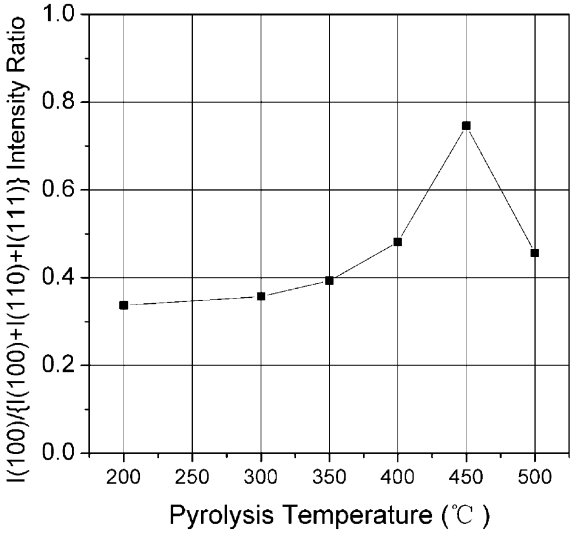

Fig. 2. (100) Intensity ratio dependence of the pyrolysis temperature for PZT films.

temperature increases from 450 to 500 °C, the (100) intensity ratio decreases from 0.747 to 0.456. In contrast, the (111) intensity ratio decreases as the pyrolysis temperature increases from 200 to 450 °C and increase as the pyrolysis temperature increases from 450 to 500 °C. The present results suggested that there existed a growth competition between (100) and (111) textured crystalline grains in the PZT films, and it seemed that pyrolysis at temperatures near 450 °C favored the (100) orientated growth.

Usually, it is believed that PZT films tend to take (111) orientation because the (111) oriented Pt substrates favor the (111) PZT nucleation due to the lattice matching effect and present of the transient intermetallic phase Pt_3Pb in the early stage of the crystallization processing.[21,22] Formation of PZT (111) oriented grains has been attributed to the low interfacial energy between PZT (111) and Pt (111). Pyrolysis at temperatures near 450 °C resulted in other preferential orientation is thought to be due to the following considerations. When pyrolyzed at high oxygen partial pressures and appropriate temperature (about 450 °C), it was reported that PbO seeds precipitate from the amorphous phase.[23] The PbO seeds have good lattice matching with PZT (100) orientation.[24] Our further investigation verified that the PbO seeds took (001) preferential orientation. Pyrolysis at 450 °C can help to crystallize PbO seeds at the interface between the PZT film and the bottom electrode, which can subsequently enhance (100) texture of PZT films. The (111) orientation was formed during annealing treatment at higher temperature, where perovskite crystals directly nucleate from the (111) orientated Pt substrate without the presence of PbO seeds and grow in the amorphous film pyrolyzed at temperatures lower than 450 °C. The pyrolysis at above 450 °C probably suppressed the precipitation of PbO, as a result, the (100) orientation in the annealed PZT film was weakened.

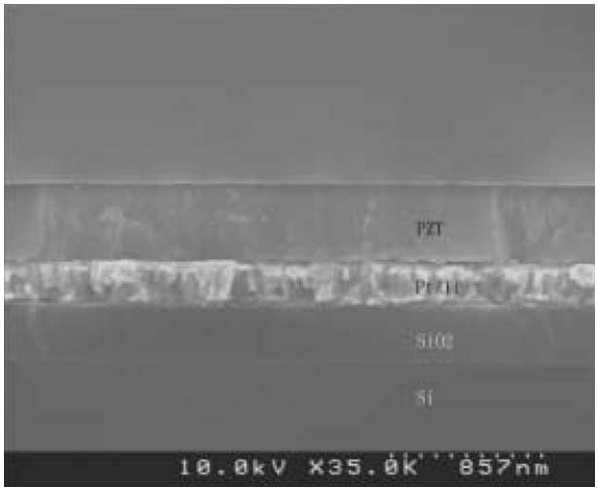

Fig. 3. SEM cross-sectional microstructure of the PZT film annealed at 650 °C through RTP. The substrate is $Pt(111)/Ti/SiO_2/Si(100)$.

Fig. 3 shows a representative SEM picture of a cross-section of the PZT film pyrolyzed at 450 °C and annealed at 650 °C through rapid thermal process. The film has dense and uniform microstructure without any cracks. The film was coated six times, each for about 80 nm, and has a total thickness of 0.51 μm.

The typical plot of the C–V property and loss feature were characterized in Fig. 4 respectively. The specimen was pyrolyzed at 450 °C and annealed at 650 °C for 5 min. The calculated relative dielectric constant of the PZT film ranges from 403 to 1056 as a function of

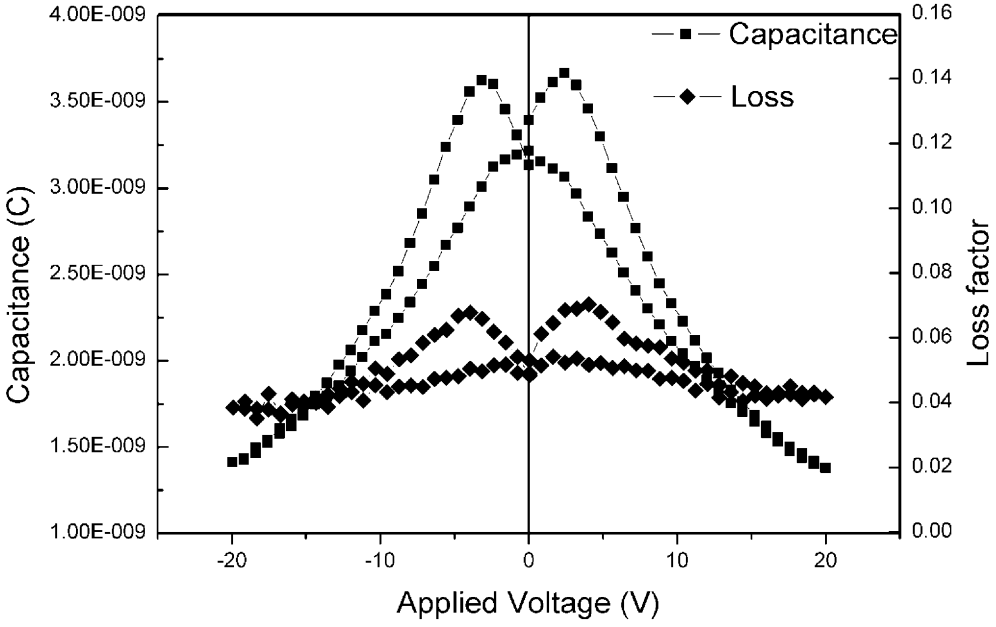

Fig. 4. C–V and loss characteristics of the PZT film pyrolyzed at 450 °C and annealed at 650 °C for 5 min.

applied voltage. The loss values of the PZT films are in the range from 0.07 to 0.04. The dielectric constant and loss factor were derived from data recorded with 5 V amplitude at 1 kHz. The changes in dielectric constant and loss factor are summarized in Fig. 5 as a function of pyrolysis temperature. As the film was pyrolyzed at relatively low temperature, the dielectric constant increased and the dissipation decreased with increasing pyrolysis temperature. However, the dielectric constant dropped when the pyrolysis temperature was increased from 400 to 450 °C, and then returned to the same level corresponding to the pyrolysis temperature of 400 °C when the pyrolysis was conducted at 500 °C. Some corresponding change was observed for the pyrolysis temperature effect on the loss factor of PZT films. It is clear that dielectric property of the PZT film is affected by its crystal orientation resulting from different pyrolysis treatments. This result suggested that the (100)/(111) mixed textured film possessed larger dielectric constant compared to both (100) and (111) strongly oriented PZT

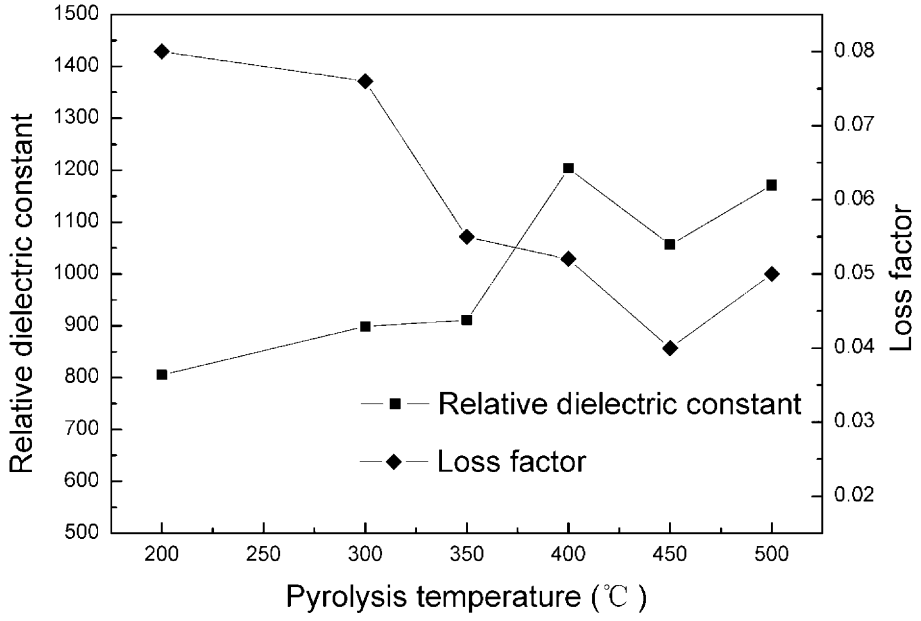

Fig. 5. Relative dielectric constant and loss factor of PZT films as a function of pyrolysis temperature.

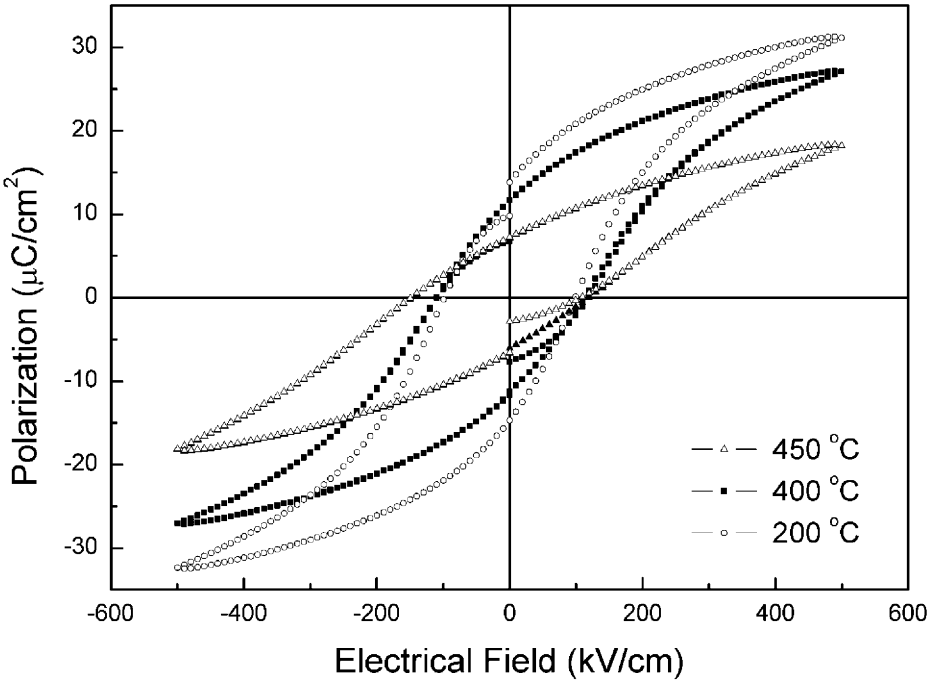

Fig. 6. P–E hysteresis loops of PZT films with different pyrolysis temperatures.

film. In case of pyrolysis at 200 °C, the strong (111) orientation induced lowest dielectric constant. In case of pyrolysis at 450 °C, the strong (100) preferential orientation also reduced dielectric constant.

Fig. 6 illustrates the P–E curves of the PZT film shown in Fig. 3. The test signal was a triangular wave with frequency of 1 kHz. The PZT film pyrolyzed at 200 °C was relatively (111) preferentially oriented, resulting in larger spontaneous polarization 28 μC/cm^2 and saturation polarization 33 μC/cm^2. The film pyrolyzed at 450 °C processed spontaneous polarization of 12 μC/cm^2 and saturation polarization of 18 μC/cm^2 owing to the preferential orientation of (100). The PZT film pyrolyzed at 400 °C, which had intermediate orientation contribution ratio between the two specimens described above, possessed medial spontaneous polarization and saturation polarization values. More detail about the pyrolysis temperature dependency of the polarization characters were illustrated in Fig. 7. It is known that the PZT films with MPB composition consist of the tetragonal phase and the rhombohedral phase, whose spontaneous polarization directions are [001] and [111], respectively. When the PZT film tended to (100) preferential orientation, the polarization became difficult because the preferential orientation is perpendicular to spontaneous polarization [001] of rhombohedral phase. That may be the reason why the spontaneous polarization and saturation polarization are reduced when the films were pyrolyzed at 450 °C.

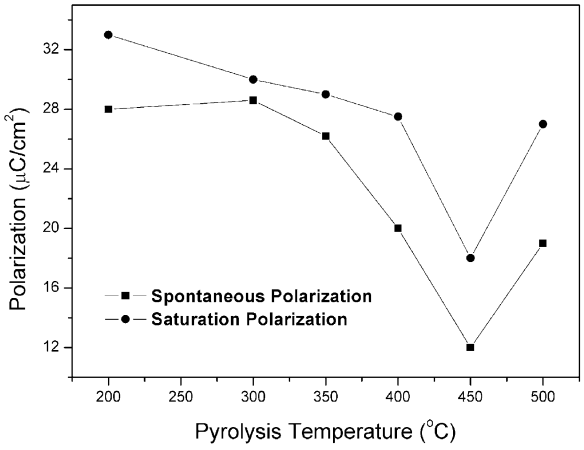

Fig. 7. Spontaneous polarization and saturation polarization as a function of pyrolysis temperature for PZT films.

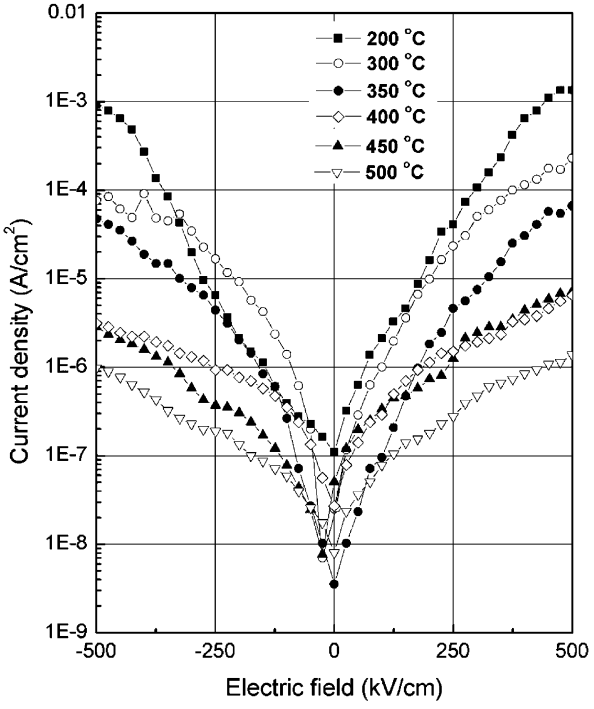

Fig. 8. Current density for the PZT films pyrolyzed at different temperatures as a function of applied electric field.

Fig. 8 shows I–V characteristics of the PZT films with various pyrolysis temperatures. The leakage current density of the films increased gradually with an increase in the applied electric field. For an applied electric field of 500 kV/cm, the leakage current density decreased monotonically with increasing pyrolysis temperature. No special change was observed for the PZT film pyrolyzed at 450 °C, even though the (100) preferential orientation was formed near that temperature. This result suggests that the orientation has no apparent influence on the leakage current characteristics. The microstructure of the polycrystalline ceramic films, resulting from the different processing conditions, may play an important role in the leakage current property. The residual organics, lead vacancies and micro cracks at the surface region of PZT films are likely to be the key contribution to the variation of the current density.

Fig. 9 shows the degradation of the remnant polarization of the PZT films pyrolyzed at different temperature as a function of number of cycles. As far as the remnant

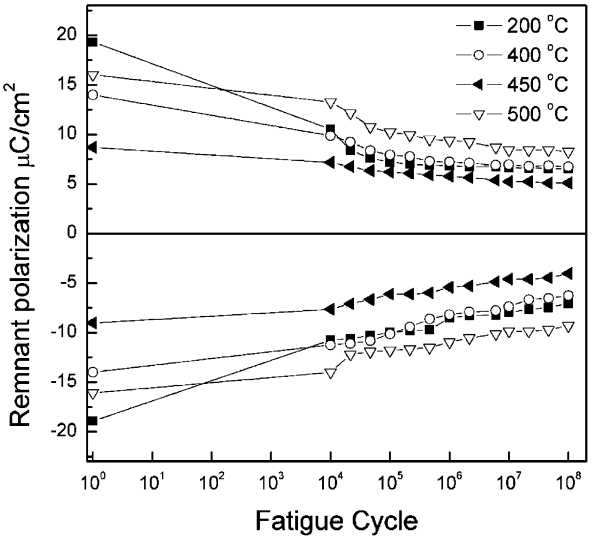

Fig. 9. Remnant polarization of the PZT films pyrolyzed at different temperatures as a function of switching cycle.

polarization is concerned, the PZT pyrolyzed at 200 °C with large initial remnant polarization retained less value after 10^8 fatigue cycles. The remnant polarization was reduced to about 60% after 10^8 fatigue cycles for the specimen pyrolyzed at 200 °C, whereas more than 74% initial remnant polarization was retained after 10^8 fatigue cycles when pyrolyzed at 450 °C. However, the influence of orientation on fatigue property is not certain, because it appears that almost the best fatigue properties can be obtained when the pyrolysis temperature was increased up to 400 °C.

4. Conclusions

Ferroelectric lead zirconate titanate films with MPB composition were deposited on to the Pt(111)/Ti/SiO_2/Si substrate by sol-gel method. XRD and SEM were employed to characterize the polycrystalline structure, preferential orientation and cross-section morphology. The electrical properties of the as-deposited PZT films, including C–V curve, hysteresis loop, leakage current and fatigue, were evaluated through a ferroelectric test.

Pyrolysis temperature is a critical processing condition parameter for preferential orientation and control of electrical properties. Pyrolyzed at 450 °C, the PZT films with MPB composition were strongly (100) oriented. Otherwise, the films tended to take the (111) preferential orientation. Different nucleation mechanics induces different dominant preferential orientation. The nearly (100) oriented films that were pyrolyzed at 450 °C possessed lower dielectric constant as compared with the (111) oriented ones, but it possessed relatively low loss factor as well. The spontaneous polarization and saturation polarization of PZT films intensively depend on the preferential orientation. The saturation polarization and spontaneous polarization of the (111) oriented PZT film pyrolyzed at 200 °C were 33.4 and 28.1 $\mu C/cm^2$, respectively. As the (100) contribution ratio increased, the polarization values decreased to 15.8 $\mu C/cm^2$ (saturation polarization) and 12.1 $\mu C/cm^2$ (spontaneous polarization). Lower leakage current and better fatigue properties were related to high pyrolysis temperature.

Acknowledgements

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