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Low-temperature crystallization of sol–gel-derived lead zirconate titanate thin films using 2.45 GHz microwaves

Ankam Bhaskar [a,*], T.H. Chang [a], H.Y. Chang [b], S.Y. Cheng [c]

[a] Department of Physics, National Tsing Hua University, Hsinchu, Taiwan
[b] Department of Marine Engineering, National Taiwan Ocean University, Keelung, Taiwan
[c] Material and Chemical Research Laboratories, Industrial Technology Research Institute, Chutung 31060, Hsinchu, Taiwan

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Abstract

Lead zirconate titanate (PZT) thin films of thickness 420 nm were deposited on Pt/Ti/SiO_2/Si substrate using a spin coating sol–gel precursor solution, and then annealed using 2.45 GHz microwaves at a temperature of 450 °C for 30 min. The film has a high perovskite content and high crystallinity with a full width at half maximum of 0.35°. The surface roughness of the PZT thin film was 1.63 nm. Well-saturated ferroelectric properties were obtained with a remanent polarization of 46.86 μC/cm^2 and coercive field of 86.25 kV/cm. The film also exhibited excellent dielectric properties with a dielectric constant of 1140 and a dissipation factor of 0.03. These properties are superior to those obtained by conventional annealing at a temperature of 700 °C for 30 min.

Keywords: Microwave annealing; Surface roughness; Dielectric properties; Hysteresis loops; Lead zirconate titanate

1. Introduction

Thin films of ferroelectric materials can be used in a variety of applications in the microelectronics industry, for example non-volatile memories, high-frequency capacitor applications, pyroelectric detectors, sensors, actuators, and transducers. One of the most useful materials for thin films is Pb (Zr_xTi_{1-x}) O_3 (PZT), because it has excellent piezoelectric, pyroelectric, and dielectric properties. The formation of the ferroelectric perovskite phase in PZT thin films generally occurs above 600 °C. These high temperatures often cause problems of PZT diffusion between layers, and make the PZT thin films unsuitable for high-density devices [1]. Therefore, reducing the processing temperature for the ferroelectric thin films has been the goal of researchers. Many groups are attempting to prepare PZT thin films at low-temperatures by various techniques such as electrophoretic deposition [2], hydrothermal synthesis [3], radio frequency (rf) sputtering [4], sol–gel process [5], CO_2 laser annealing [6], metal-organic chemical vapor deposition [7], and millimeter wave annealing [8].

Microwave processing of ceramics has attracted considerable attention in recent years [9,10]. The advantages of microwave heating over conventional heating are that the heat is generated uniformly throughout the material, resulting in a uniform sintering of the material, lower required sintering temperature and time, a suppression of grain growth, and very rapid heating rates [11]. Microwaves have been utilized for both the synthesis and in the sintering of a wide variety of materials, especially oxides [12,13]. Microwave processing has been adopted to anneal films [14,15]. Song et al. [15], using a multimode cavity of 2.45 GHz microwaves, completed the formation of perovskite-phase PZT thin films at a lower temperature (600 °C) than that of conventionally annealed PZT thin films (700 °C). However, low-temperature processing (<500 °C) of PZT thin films using 2.45 GHz microwaves has not been reported.

This study reports the low-temperature processing of PZT thin films deposited on Pt/Ti/SiO_2/Si substrate using a single-mode cavity of 2.45 GHz microwaves, to obtain good dielectric, and ferroelectric properties. The crystal structure, the surface morphology, and the electrical properties of PZT thin films were investigated. Based on experimental results, the effect of 2.45 GHz microwaves on PZT thin films is discussed; and compared to the effect of conventional annealing of PZT thin films.

* Corresponding author. Tel.: +886 3 574 2560x13; fax: +886 3 572 3052.
E-mail address: ankambhaskar@gmail.com (A. Bhaskar).

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2. Experiment

PZT thin films were prepared by the sol–gel method. The lead acetate trihydrate was dissolved in 2-methoxyethanol; the solutions were heated to 110 °C, and then refluxed for 2 h. The solutions were cooled to 90 °C before the required quantities of zirconium-*n*-propoxide and 2-methoxyethanol were added sequentially and refluxed for 1 h. Isopropyl-orthotitanate was added to the same as zirconium-*n*-propoxide processing for 2 h. Clear light yellow PZT stock was obtained by air-cooling to room temperature. The solution was stable and no crystallite formed for several months. The concentration of the final solution can be adjusted to 0.2 M by adding or distilling an appropriate quantity of solvent. The precursor solution was entirely prepared in an ambient atmosphere. The nominal composition of the solution was Pb: Zr: Ti = 1.1: 0.53: 0.47. Pt/Ti/SiO_2/Si substrates, which provide nucleation sites for the perovskite phase because of good lattice matching, were selected [16]. The precursor solution was deposited on Pt/Ti/SiO_2/Si substrates by spin coating at 500 rpm for 1 s and at 3000 rpm for 15 s. The as-deposited layer was dried on a hot plate in air at 150 °C for 5 min and decomposed at 400 °C for 10 min to evaporate alcohol and organics. The decomposition temperature was established by the thermo gravimetric analysis, which indicates that at 400 °C, most of the organics evaporated and decomposed from the PZT thin films. The spin coating and drying process were repeated ten times, to obtain the desired thickness of 420 nm.

The PZT thin film was placed in a casket, which was thermally insulated. The casket was located at the center of the highest electric field in the applicator. SiC rods are used as susceptors because PZT does not absorb 2.45 GHz microwaves at room temperature [17]. The microwave energy initially heated the SiC rods, which, in turn, transferred heat to the insulation and eventually to the thin film [18]. As the temperature of the PZT thin film increased, it more effectively coupled with the microwave energy, promoting direct heating. The microwave frequency was 2.45 GHz and the power was adjusted 350 ± 50 W, to a maintained annealing temperature of 450 °C. The temperature was controlled to within ±1 °C by continuously adjusting. The temperature was measured using a thermocouple (Pt and 87%Pt–13%Rh) with an alumina sheath, which was in contact with the surface of film. The PZT thin films were annealed by 2.45 GHz microwaves at 450 °C for 30 min, and the conventionally annealed at 700° for 30 min.

Fig. 1 compares the time–temperature profile of the conventional annealing and the microwave annealing of PZT thin films. The microwave annealing was conducted at 450 °C for 30 min with an average ramp rate of 25 °C/min. The total cycle time was 48 min, excluding the period of cooling. For comparison, conventional annealing was also conducted at 700 °C for 30 min with an average ramp rate of 5 °C/min. Cooling at 5 °C/min to 300 °C was followed by natural cooling. Excluding the cooling period, it took about 2 h 45 min, which was much longer (1 h 55 min) than the microwave annealing time (50 min). The advantage of processing temperature, energy, and time efficiency of microwave annealing over conventional annealing is unambiguously shown.

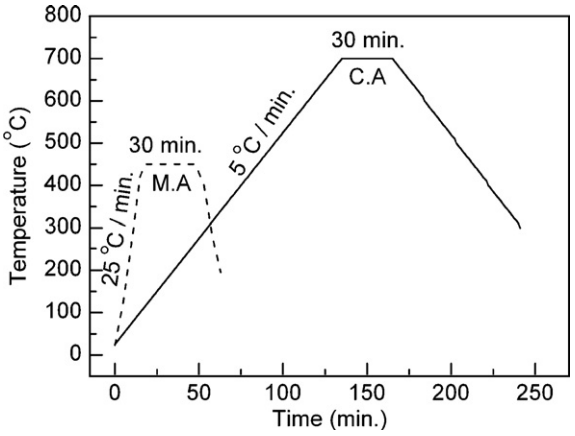

Fig. 1. Comparison of time–temperature profiles of conventionally (C.A) and microwave (M.A) annealed PZT thin films.

The crystalline structures of the PZT thin films were examined by X-ray diffraction (XRD) (Rigaku D/MAX-IIB, Cu Kα radiation wavelength $\lambda = 1.5405$ Å, scan speed of 2° per min.). The film thickness, surface morphologies, and cross-sections of the PZT thin films were examined under field emission scanning electron microscope (FE-SEM) (JSM-6500F). The surface roughness of PZT thin films was characterized using a Seiko Instruments (Inc. SPI3800N) atomic force microscope (AFM) system. Au electrodes were deposited by rf sputtering on the top surface of PZT thin films through a shadow mask with a diameter of 1 mm for electrical measurements. This deposition was conducted at room temperature. The dielectric properties were measured at room temperature in the frequency range 1 kHz to 1 MHz using an impedance analyzer (HP impedance/gain analyzer 4194A). The polarization-electric (P-E) hysteresis loops were measured using a Radiant Technologies RT-66A ferroelectric test system by applying triangular voltages at a frequency of 1 kHz.

3. Results and discussion

Fig. 2a shows that the conventional annealing of PZT thin films at 450 °C yields a broad diffraction peak of (2 2 2) planes of the pyrochlore phase. No peak of the perovskite phase was detected in the thin film because the temperature of the PZT thin film was not high enough for the reaction to occur among the Pb, Ti, Zr, and O. The microwave-annealed PZT thin film (450 °C) yields a prominent diffraction peak of the perovskite phase (1 1 0) planes, and no peak of the pyrochlore phase was detected in this film. The conventionally annealed PZT thin film at 700 °C yielded an XRD pattern that was similar to that of the PZT thin film annealed using 2.45 GHz microwaves. The peak with the highest intensity in the X-ray diffraction pattern of the PZT thin film was indexed as (1 1 0) planes, indicating that the thin film was mostly randomly oriented. The full width at half maximum (FWHM) of the perovskite phase peak (1 1 0) was considered in evaluating the quality of the PZT thin film. In all of the XRD patterns (Fig. 2a), a peak at around $2\theta = 30.6$–$31.8°$ was observed, corresponding to the

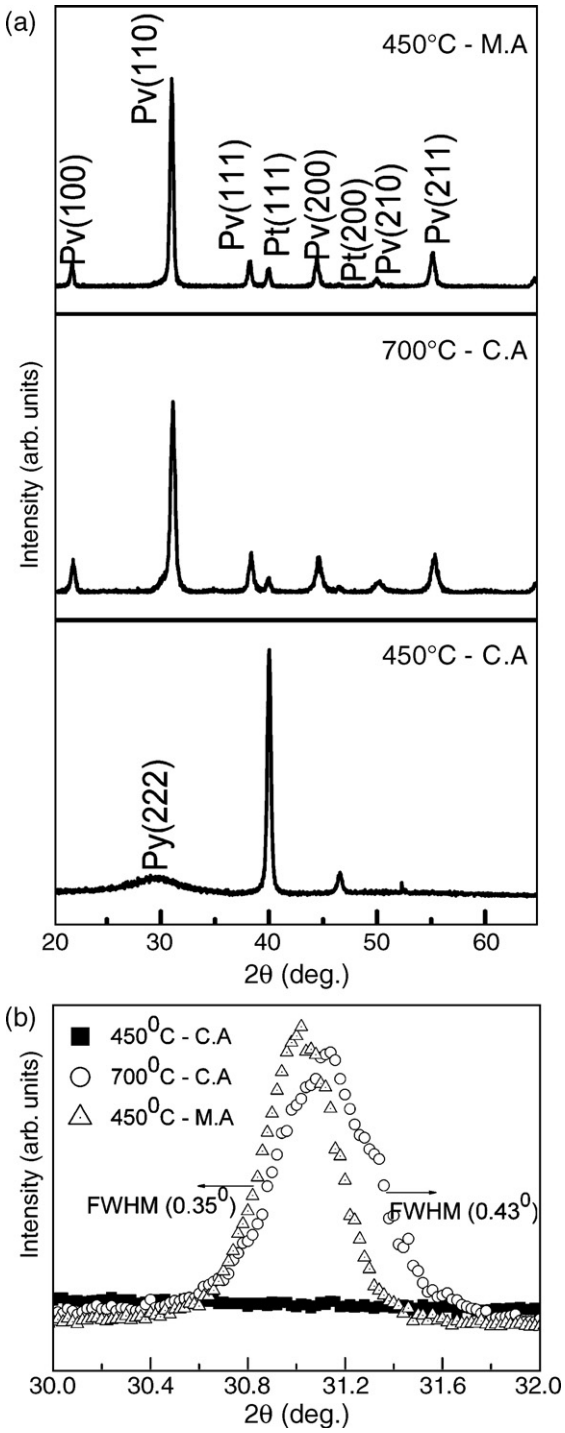

Fig. 2. (a) XRD patterns of PZT thin films annealed by microwave annealing (M.A), and conventional annealing (C.A) (b) The peak at $2\theta = 30.6–31.8°$ in the XRD pattern (Fig. 1a) redrawn on an expanded scale to emphasize the intensity and FWHM of the perovskite phase peak (1 1 0).

(1 1 0) perovskite plane. This peak was redrawn on an expanded scale in Fig. 2b. The conventionally annealed PZT thin film at 450 °C does not yield any peak. The microwave-annealed PZT thin film (450 °C) yielded a higher (1 1 0) perovskite phase peak, whose FWHM (0.35°) was narrower than that of the FWHM (0.43°) of the conventionally annealed PZT thin film at 700 °C. The microwave-annealed PZT thin film (450 °C) exhibits better crystallinity and higher thin film quality than that of the conventionally annealed PZT thin film at 700 °C. The processing temperature of the microwave annealing was much lower (250 °C) than that of the conventional annealing. Similar trends have also been reported for the micro/millimeter wave processing of ferroelectric thin films. Song et al. [15] formed a PZT thin film containing only a perovskite phase using a multimode cavity of 2.45 GHz microwaves at a lower temperature (600°C) than used in the conventional annealing of PZT thin films (700 °C). The presently reporting microwave-annealed PZT thin film is 150 °C lower than above reported value, perhaps because the cavity was single-mode or the mode of precursor method. The multimode cavity of 2.45 GHz microwaves has a critical drawback since the electromagnetic field in the cavity was not uniform; resulting in inhomogeneous heating and the unavoidable formation of hot spots [9]. Wang et al. [8] reported the PZT thin film crystallization at 480 °C using 28 GHz microwave irradiation, at a temperature 120 °C lower than the conventionally annealed PZT thin film (600 °C). Mastsumoto et al. [19] conducted research on the mm-wave (28 GHz) processing of $SrTiO_3$ thin films and compared the results with those of conventional processing; they have reported that the millimeter wave processing reduced the annealing temperature by more than 90 °C, probably because mm-wave irradiation enhances the diffusion of atoms. Many researchers in the field of sintering have reported that ceramics were densified at

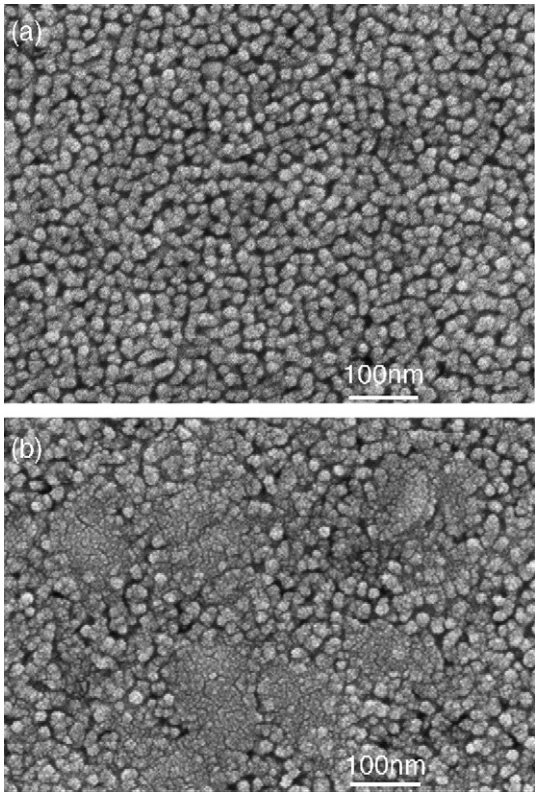

Fig. 3. FE-SEM image of PZT thin films annealed by microwaves (a) and conventionally (b).

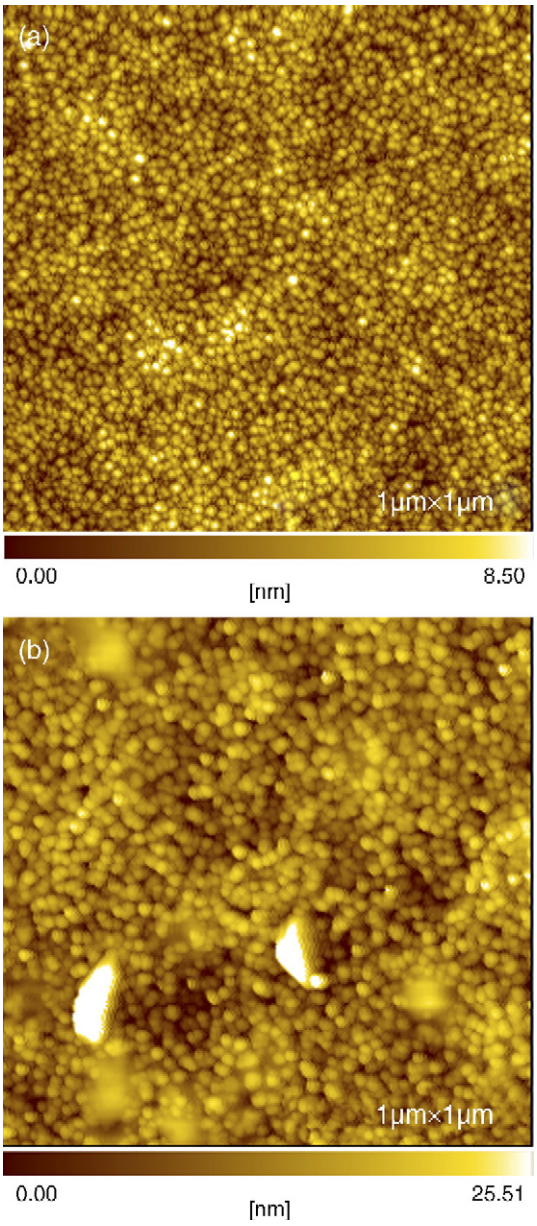

Fig. 4. AFM two-dimensional images of PZT thin films annealed by microwaves (a) and conventionally (b).

lower temperature by the microwave heating due to the enhanced diffusion [20,21].

The surface morphologies of PZT thin films were examined by FE-SEM. The microwave annealing of PZT thin film (450 °C) yields dense and fine grains, uniform and without cracks, with an average grains size of (~27 nm) (Fig. 3a). The conventional annealing of PZT thin film yields both large and small grains, which were not uniform, and had an average grain size of ~90 nm (Fig. 3b). The conventionally annealed of PZT thin film at 700 °C has larger grains than the microwave-annealed PZT thin film, perhaps because of the difference between the rise ramp rates of the annealing temperatures, as indicated in Fig. 1. The Laser-Induced Phase transformation Technique (LIPT) of PZT thin films yielded similar trend results. Lu et al. [22] reported that the grain sizes of PZT thin films with LIPT were much smaller than those of the films annealed in an oven. They attributed this result to the difference between the slow rate of rise of temperature in oven annealing and fast rate of rise associated with the LIPT process.

The surface roughness was examined by AFM. Fig. 4 shows the two-dimensional image of PZT thin films that were annealed by microwaves and conventionally. The microwave annealing of PZT thin film yields small grains, which are more uniformly distributed than those in the conventionally annealed PZT thin film. The microwave-annealed PZT thin film had a smoother surface, with a root mean square (rms) roughness of 1.63 nm, than the conventionally annealed PZT thin film, which had an rms roughness of 5.11 nm. The roughening was interpreted as a result of grain agglomeration and enlargement of grains. The uniformity of the PZT thin film was improved with microwave annealing because with shorter sintering cycles and reduced thermal gradients, finer grains were obtained and the grains were more uniformly sized.

Fig. 5 shows the cross-sectional FESEM image of microwave-annealed and conventionally annealed PZT thin film multilayer (PZT, Pt, Ti, SiO_2, Si) structures, as well as the interface between the PZT film and the bottom electrode (Pt). The thickness of the PZT thin films was 420 nm. The microwave annealing of PZT films yields a clear interface between the film and the bottom electrode. The conventional annealing of PZT thin films yields the same interface as the

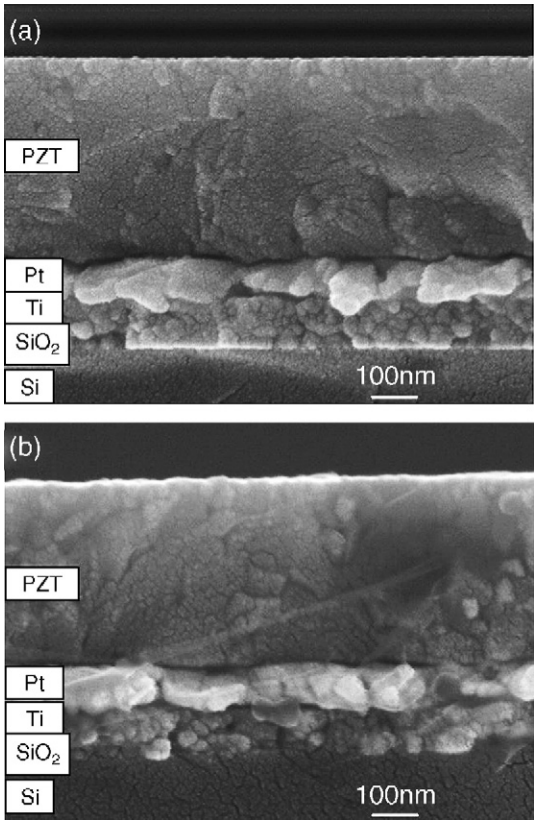

Fig. 5. FE-SEM cross-sectional image of PZT thin films annealed by microwaves (a) and conventionally (b).

microwave annealing. However, more work must be performed to elucidate further details of the interaction between the microwaves and the PZT thin films.

The dielectric properties of PZT thin films were measured in term of the dielectric constant and the dissipation factor. Fig. 6 exhibits the dielectric properties of the PZT thin films annealed by microwaves and conventionally at various frequencies. The microwave annealing of PZT thin film yields a higher dielectric constant and a lower dissipation factor than the conventional annealing. Microwave-enhanced diffusion probably enables the PZT thin film to crystallize at a lower temperature and produce better crystallinity than achieved by conventional annealing. The dielectric properties of microwave-annealed PZT thin films were higher than the reported [15].

Fig. 7 shows the P-E hysteresis loops of microwave and conventionally annealed PZT thin films. The microwave-annealed PZT thin film (450 °C) has a square hysteresis loop, a remanent polarization P_r of 46.86 μC/cm^2 and a coercive field E_c of 86.25 kV/cm. An attempt was also made to measure the hysteresis loop of a PZT thin film conventionally annealed at 450 °C, but no hysteresis loop was obtained, since it contained only the pyrochlore phase, as revealed by the XRD pattern (Fig. 2a). The PZT thin film conventionally annealed at 700 °C exhibits a reasonably square hysteresis loop; the value of P_r is lower about 39.40 μC/cm^2; E_c is 101.21 kV/cm, higher 250 °C than that of the microwave-annealed PZT thin film. Microwave-sintered PZT ceramics yielded similar results. Sharma et al. [17] studied the effect of 2.45 GHz microwaves on PZT ceramics using a multimode cavity, and compared it to the conventionally sintered PZT ceramics. They reported that microwave-sintered PZT ceramic has higher P_r, and lower E_c than conventionally sintered PZT ceramics. The shape of the hysteresis loop reflected the difference between the crystallinity of the PZT thin films. Notably the low value of E_c is an advantage in device applications, since the power losses are minimized and the switching voltages reduced. Hence, microwave-annealed PZT thin films are better than conventionally annealed PZT thin films. The P_r for this film was higher than the reported values for microwave-annealed thin films [15].

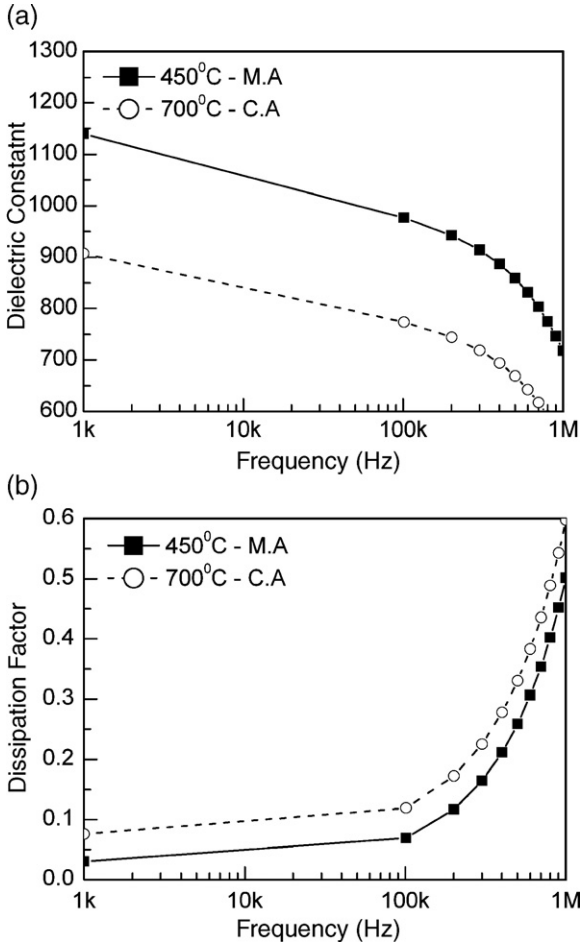

Fig. 6. Dielectric properties of PZT thin films annealed by microwave annealing (M.A) and conventional annealing (C.A).

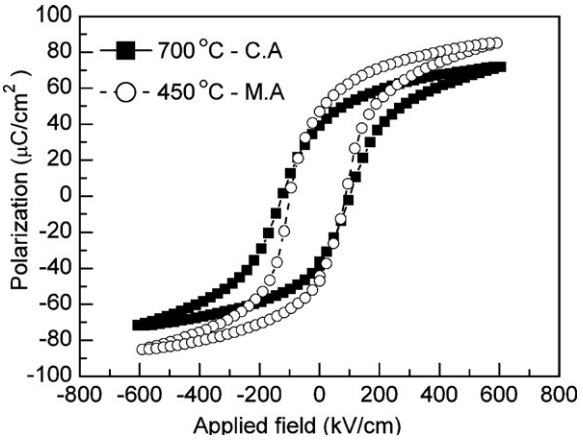

Fig. 7. Polarization-electric field hysteresis loops of PZT thin films annealed by microwaves (M.A) and conventionally (C.A).

4. Conclusions

This work demonstrates that microwave annealing can yield highly crystalline sol–gel derived ferroelectric Pb (Zr_xTi_{1-x}) O_3 (x=0.53) thin films on Pt/Ti/SiO_2/Si substrate. The (1 1 0) perovskite phase peak of the microwave-annealed PZT thin film (450 °C) was higher and its FWHM was lower than those of the peak of the conventionally annealed PZT thin film at 700 °C. The microwave-annealed PZT thin film has smaller grains than the conventionally annealed PZT thin film. The microwave-annealed PZT thin film exhibits better dielectric and ferroelectric properties than those of the conventionally annealed PZT thin film.

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