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Low-temperature processing of sol-gel derived $Pb(Zr,Ti)O_3$ thick films using CO_2 laser annealing

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Abstract Fabrication of ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thick films on a $Pt/Ti/SiO_2/Si$ substrate using powder-mixing sol-gel spin coating and continuous wave CO_2 laser annealing technique to treat the specimens with at a relatively low temperature was investigated in the present work. PZT fine powders were prepared by drying and pyrolysis of sol-gel solutions and calcined at temperatures from 400 to 750°C. After fine powder-containing sol-gel solutions were spin-coated on a substrate and pyrolyzed, CO_2 laser annealing was carried out to heat treat the specimens. The results show that laser annealing provides an extremely efficient way to crystallize the materials, but an amorphous phase may also form in the case of overheating. Thicker films absorb laser energy more effectively and therefore melt at shorter periods, implying a significant volume effect. A film with thickness of 1 μm shows cracks and rough surface morphology and it was difficult to obtain acceptable electrical properties, indicating importance of controlling interfacial stress and choosing appropriate size of the mixing powders. On the other hand, a thick film of 5 μm annealed at 100 W/cm^2 for 15 s exhibits excellent properties ($P_r = 36.1$ μC/cm^2, $E_c = 19.66$ kV/cm). Films of 10 μm form a melting zone at the surface and a non-crystallized bottom layer easily at an energy density of 100 W/cm^2, showing poor electrical properties. Besides, porosity and electrical properties of thick films can be controlled using appropriate processing parameters, suggesting that CO_2 laser annealing of modified sol-gel films is suitable for fabricating films of low dielectric constants and high crystallinity.

Keywords Laser annealing · Sol-gel · Ferroelectric · $PbZrTiO_3$ · Thick films

1 Introduction

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) is one of the most promising ferroelectric materials for nonvolatile memory devices, sensors, actuators and microelectromechanical systems due to its high remanent polarization and high piezoelectric constants [1–3].

Most device developments have centered on silicon micro-machined structures. Combining micromachined silicon with ferroelectric films has resulted in several novel microdevices, such as membrane sensors [4] and accelerometers [5]. These devices are generally based upon thin film materials with thickness less than 1 μm. However, the application of devices using PZT films is not limited to the microdevices. Many applications require film thickness of 1 to 30 μm and geometries of μm^2 to cm^2, such as optical fiber modulator [6], ultrasonic high frequency transducer for eye examination [7], self-controlled vibrational damping systems [8] etc. The film thickness and device geometry required for those applications is difficult to be achieved by conventional thin film preparation processes, such as sputtering, sol-gel, or chemical vapor depositions.

Fabrication of a PZT thin film of 1 μm has however been achieved in conventional sol-gel method, but the spin coating cycle has to be repeated many times to attain desired thickness in order to produce thick films [8, 9]. This fabrication procedure is clearly time-consuming and other problems, such as crack development after films was grown over a critical thickness, ordinarily less than 1 μm, due to mechanical

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stress building up during processing. Philips et al. [10] introduced a novel diol-based sol-gel method to fabricate thicker films up to 5 μm with a single deposition of about 1 μm. Several methods have been proposed by different research groups [11–16] to fabricate PZT films with thickness to several 10 μm. Akedo and Lebedev [11, 12] fabricated thick PZT films with high density at high deposition rate by using aerosol deposition method at low processing temperatures. Yasuda et al. [13] have prepared PZT films that have good crystallinity as to that of thin films by using Arc-Discharged Reactive Ion-plating method. However, these kinds of gas deposition methods generally require complicated set-up and expensive apparatus. Alternatively, modified sol-gel coating techniques are relatively simple [14–16]. Trurumi et al. [14] have prepared PZT films of 10–50 μm using an interfacial polymerization technique. Sayer and Barrow et al. [15] have introduced a 0-3 composite process in which a piezoelectric coating is produced by spin coating a suspension of PZT powder in a PZT sol-gel solution. Wu et al. [16] have introduced different seeding techniques which used a seeding layer of $PbTiO_3$ before coating PZT on substrate. Wang et al. [17] adopted sol-gel based nano-composite process to fabricate dense PZT thick films at a sintering temperature of 700 to 800°C and the ferroelectric properties are comparable to that of bulk PZT ceramics.

The atomic inter-diffusions among the heterostructures and deterioration of electrical properties might occur when the growth condition of PZT films is at a substrate temperature of 600°C or above under an oxygen reaction atmosphere. From this viewpoint, a low-temperature process for growth of PZT films is therefore required for yielding a reliable integrated device with superior performance. Calzada et al. [18] employed UV irradiation assisted RTP process to develop a low temperature processing method for ferroelectric thin films, compatible with silicon integrated circuit technology. Park et al. [19] introduced the low-temperature processing of PZT thin films and they uses RF and microwave oxygen-plasma treatment successfully to anneal PZT films. Kwok and Desu was the first group to use seeding particles in the sol (sols containing powders) for decreasing the crystallisation temperature of the films, and they employed seeding layers of $PbTiO_3$ produced by a sol-gel method to reduce the pyrochlore-to-perovskie transformation temperature [20]. However, the thick films prepared by this technique showed poor mechanical properties due to their porous or cracked microstructure [21]. Electrical properties of PZT thin films grown by sol-gel and PLD techniques using a seeding layer were also reported and compared [22].

Donohue et al. [23] have shown a low temperature process using a pulse-extended excimer laser to treat the ferroelectric thin film on a low thermal budget substrate. However, properties of the films were not revealed. Lai et al. employed extended-pulse excimer laser annealing to PZT films on a $LaNiO_3$ electrode, and a 50% improvement in remanent polarization was observed. However, the value is still low compared to properties of bulk PZT [24]. We have reported that the laser annealing processes may be an alternative low-temperature process for fabricating high quality PZT thin films [25, 26]. The continuous CO_2 laser can be successfully applied to anneal PZT thin films with much better electrical properties than those processed by an excimer laser for a specimen with thickness higher than 0.4 μm [25–27]. Homogenous microstructures, good ferroelectric properties and well crystallinity of PZT thin films could be obtained after CO_2 laser irradiation at room temperatures. But an amorphous layer can be observed at the bottom part of a specimen treated by an excimer laser [28]. Kholkin et al. [26] fabricate thick PZT films using sedimentation of the PZT powder onto Pt-coated Si substrates with a subsequent multiple infiltration of powder coatings with PZT sol-gel solution. PZT films with a thickness range of 1–20 μm can be fabricated at a temperature as low as 550°C.

In this work, a modified sol-gel route with fine-grain containing sol-gel solutions were employed to prepare PZT thick films. The spin-coated PZT thick films were sequentially irradiated by the CO_2 laser for crystallization and sintering. Change of surface morphology, crystal structure and microstructural evolution and electrical properties of the laser annealed PZT thick films were investigated to evaluate CO_2 laser annealing process for PZT thick film fabrication, which was carried out at temperatures less than 400°C.

2 Experimentals

Flow chart of preparing the stock solution of $Pb(Zr_{0.52}Ti_{0.48})O_3$ is shown in Fig. 1. The lead acetate $[Pb(CH_3COO)_2{\cdot}3H_2O]$, zirconium n-butoxide $[Zr(OC_4H_9)_4]$, and titanium n-butoxide $[Ti(OC_4H_9)_4]$ were used as the starting materials for synthesis of $Pb(Zr_{0.52}Ti_{0.48})O_3$ precursor solution. Lead acetate was firstly dissolved in 1.2-propanediol and then a stoichiometric amount of titanium n-butoxide and zirconium n-butoxide was added under a steady-state stirring to produce a 0.3 M-PZT complex solution. 10 mol% excess lead acetate for the precursor was added to the PZT solution, in order to compensate PbO evaporation, and 10 vol% formamide was also added to control the wetting angle. PZT powder was prepared by drying PZT precursor at 200°C for 30 min and pyrolyzed at 400°C for 24 h and calcined at a temperature from 400 to 750°C for 30 min. The dried sol-gel pyrolyzed powders were ball-milled using methanol as media to a particle size at around 0.4 μm and powders using an oxide-mixing method calcined at 870°C 4 h and ball-milled were also prepared for comparison.

Coating of PZT thick films onto Pt(1500 nm)/Ti(1000 nm)/SiO_2(1500 nm)/Si (abbreviated as Pt(Si)) was carried out by spin-coating the powder-containing sol-gel precursor, and the wet films were dehydrated at 200°C for 30 min, followed by pyrolysis at 400°C for 30 min. The spin-coating and heating process was repeated several times until the desired thickness was attained. The crystallization of PZT thick films was achieved by a CO_2 laser irradiation (wavelength is 10.6 μm, laser beam area is 2.89 cm^2) under different radiation periods and fluence. The radius of laser beam which applied to heat treat the ferroelectric layers was 9.6 mm. The thickness of PZT films could be controlled pretty well and the thickness was measured by scanning electron microscopy (SEM) to be around 1.0 μm for each layer.

The pyrolysis behavior was analyzed using a thermal-gravimetric-analyzer (TGA). The crystalline phases of the PZT/Pt(Si) films were determined using an X-ray diffractometer (XRD) and the morphology of the films were examined using an SEM. Au electrodes with an area of 1×10^{-4} cm^2 were sputtered on top of the PZT films as a Au/PZT/Pt(Si) configuration for electrical measurements, and the hysteresis loops were determined with a commercial ferroelectric tester (Radiant, Precision Workstation).

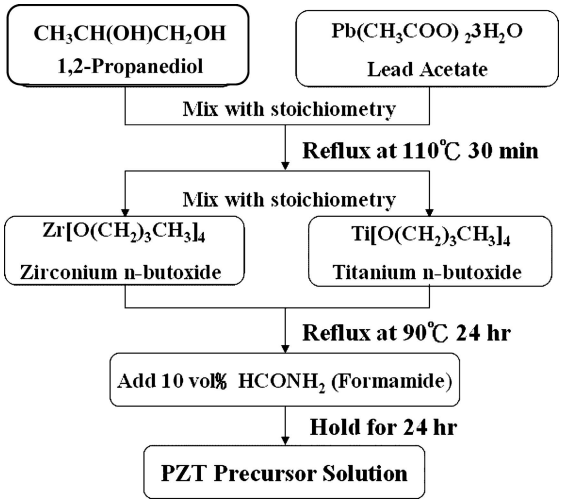

Fig. 1 Flow chart of sol-gel precursor preparation

3 Results and discussion

PZT powders were prepared by a sol-gel pyrolysis method and an oxide-mixing method was also adopted for comparison. Using oxide mixing method and ball milling, the powders were prepared to an average particle size of around 2.0 μm. On the other hand, finer powders were prepared by pyrolysis of sol-gel solution and ball milled to a size of around 0.4 μm. Figure 2 shows the SEM micrographs and the particle size analyses of the sol-gel derived powders, which

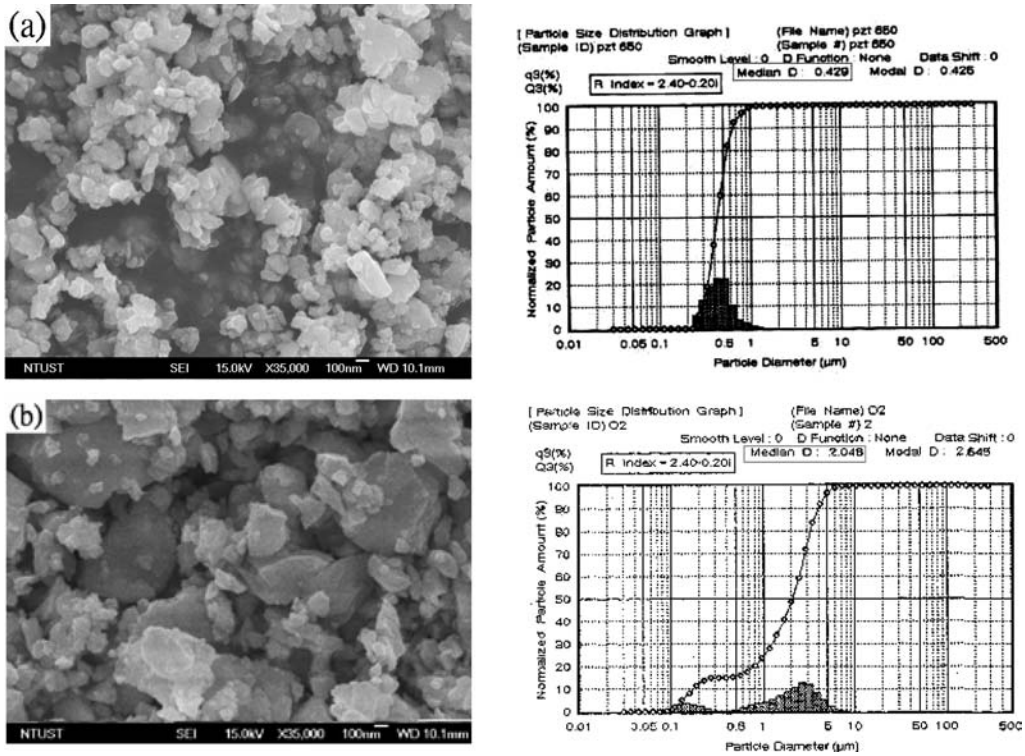

Fig. 2 Scanning electron micrograph and size distribution of PZT powders prepared by (a) a sol-gel process; (b) an oxide mixing method. The sol-gel solution was pyrolyzed at 400°C (24 h) and crystallized at 650°C for 30 min. The average particle size of the PZT powder is about 0.429 μm. On the other hand, particle size of oxide-mixing method shows an average particle of 2.048 μm

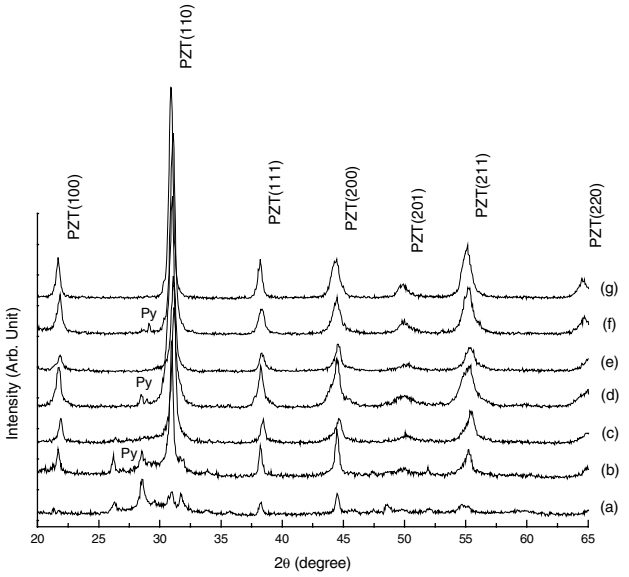

Fig. 3 X-ray diffraction patterns of sol-gel derived PZT powders calcined at different temperatures. (a) 400°C; (b) 500°C; (c) 550°C; (d) 600°C; (e) 650°C; (f) 700°C; (g) 750°C

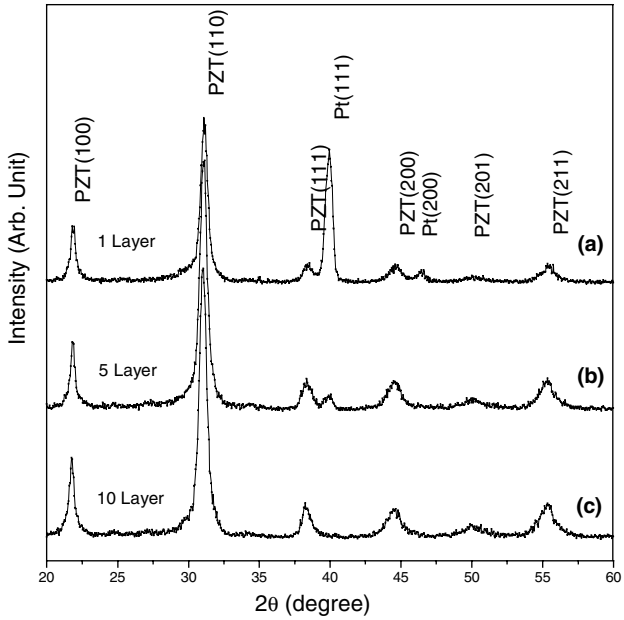

Fig. 4 X-ray diffraction patterns of PZT thick films prepared by spin-coating and dried at 140°C (10 min), pyrolyzed at 400°C (30 min), repeated various times to obtain different thickness and laser annealed under 100 W/cm^2, (a) 1; (b) 5; (c)10 layers

was pyrolyzed at 400°C (24 h) and crystallized at 650°C for 30 min, and the oxide mixing powders, calcined at 870°C for 4 h. The average particle sizes of the PZT powders are about 0.429 μm and 2.048 μm respectively. Finer particle can be obtained if crystallized at lower temperatures and well ball-milled.

Figure 3 shows X-ray diffraction patterns of sol-gel derived PZT powders calcined at different temperatures as (a) 400°C; (b) 500°C; (c) 550°C; (d) 600°C; (e) 650°C; (f) 700°C; (g) 750°C. Pyrochlore phase was often observed in powder preparation using pyrolysis of sol-gel solutions. More pyrochlore phase was found at lower annealing temperatures and lower crystallinity was obtained, but this does not influence the perovskite phase formation during thick film fabrication using laser annealing.

Figure 4 shows the X-ray diffraction patterns of PZT thick films prepared by spin-coating of powder-containing sol-gel solutions. The as-coated specimens were dried at 140°C for 10 min, and pyrolysed at 400°C for 30 min each layer. The coating process could be repeated for various times to obtain different thickness and laser annealed at a power density of 100 W/cm^2 was carried out. The pyrochlore phase was not observed in thick film specimens, even when the PZT powders may show some. There is no big difference in the diffraction patterns of thick films of 1, 5, and 10 layers, if the specimens were not overheated and melted, implying crystallization of the thick films using laser annealing is fast and efficient. The PZT particles in sol-gel solutions work as nucleation sites or they trigger crystallization of amorphous ingredients of a 0-3 composite arrangement in the present case.

Scanning electron microscopy provides direct microstructural information of specimens. Figure 5 shows cross-sections of PZT films under laser annealing at 100 W/cm^2 for different periods. If the specimens absorbed too much laser energy, thermal run-away, similar to microwave sintering of some materials, may occur. Temperature of the treated specimen booms up at a certain point and the specimen melts. One-layer specimen can be annealed for 25 s at an energy density of 100 W/cm^2 without melting; 5-layer specimens stand for 15 s; 10-layer specimens melt when annealed over 8 s. The results suggest a significant volume effect of a laser annealing process. Besides, the one-layer specimen exhibit a quite rough surface, implying that the particle size of adding PZT powders should be controlled well. Appropriate processing parameters, such as mixing particle properties, laser power, cooling rate control were employed to process specimens. It is possible to control specimen density and microstructures, and hence obtain required electrical properties. A specimen treated by conventional furnace annealing at 650°C for 30 min were also shown for comparison. It appears that conventional furnace annealing is more difficult to produce dense thick films, unless nano-sized powders were employed [20].

Figure 6 shows P-E curves for PZT thick films prepared by spin-coating of powder-containing sol-gel solutions and heat treated using a CO_2 laser annealing (LA). The PZT powders mixed into sol-gel precursor were prepared using oxide mixing method and the average particle size is around 2.0 μm. A 5-layer PZT thick films using oxide mixing powders and treated by LA (100 W/cm^2, 15 s) shows a typical shape of a hysteresis loop, but the remenant

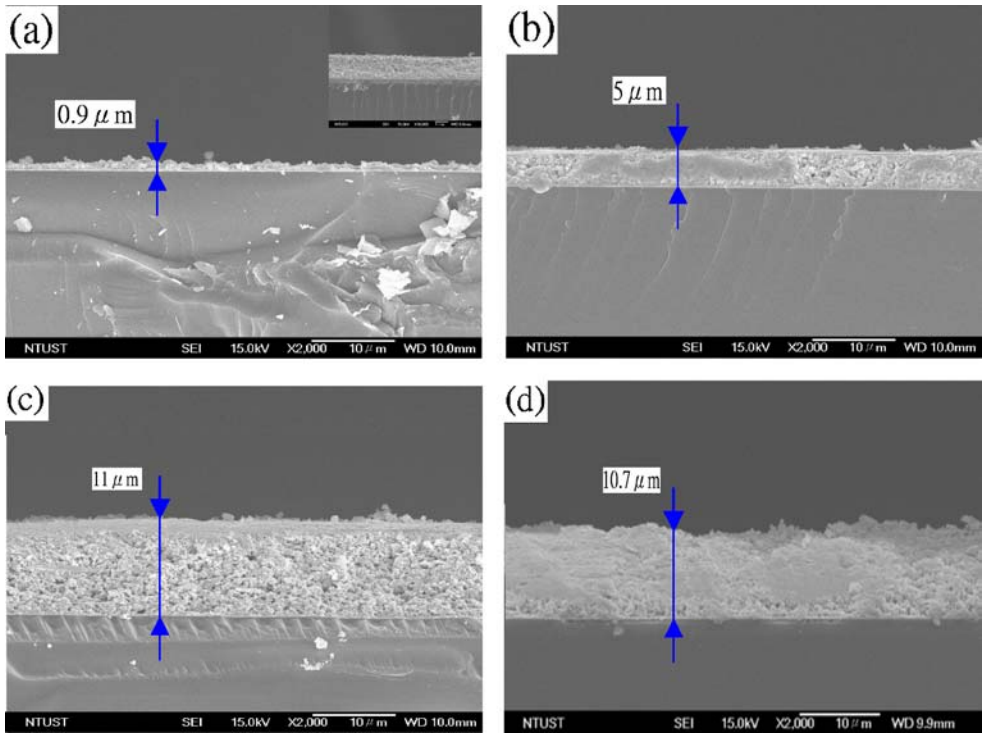

Fig. 5 Cross-sections of PZT films under laser annealing at 100 W/cm^2; (a) 1 layer annealed for 25 s; (b) 5 layers (15 s); (c)10 layers (5 s); (d) 10 layers using furnace annealing at 650°C, 30 min

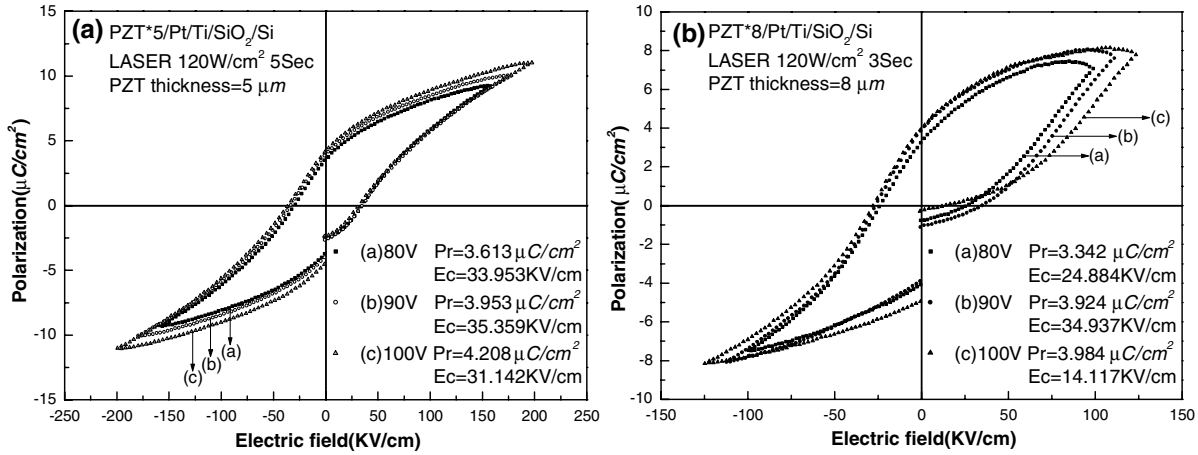

Fig. 6 *P-E* curves for PZT thick film prepared by powder-containing sol-gel spin-coating using laser annealing (LA). (a) 5-layers PZT, LA (120 W/cm^2, 5 s); (b) 8-layers PZT, LA (120 W/cm^2, 3 s). PZT powders were prepared by an oxide mixing method and ball milling to a size of 2 μm

polarization was low, probably due to large particle size of the PZT powder mixed into the sol-gel precursor. A 8-layer PZT thick films treated by LA (100 W/cm^2, 15 s) exhibits a non-symmetric hysteresis loop, implying a possibility of the non-uniform distribution of the crystallinity of the film along the thickness direction and asymmetric interfacial condition for upper and bottom electrodes using laser annealing.

To improve material performance, PZT thick films prepared by spin-coating of powder-containing sol-gel solutions and heat treated using Laser annealing (LA) were investigated using PZT powders prepared from the sol-gel precursor and the average particle size is around 0.4 μm. Figure 7 shows P-E curves for a 5-layer PZT thick film with smaller adding particles heat treated using continuous CO_2 Laser annealing (LA) and conventional furnace annealing (FA). Figure 7(a) presents a P-E curve of a 5-layer PZT treated by LA(100 W/cm^2, 15 s) and a corresponding P-E curve of 5-layer PZT using FA (650°C, 30 min) was observed in Fig. 7(b). The laser annealed thick film exhibits much better ferroelectric properties than the FA specimen

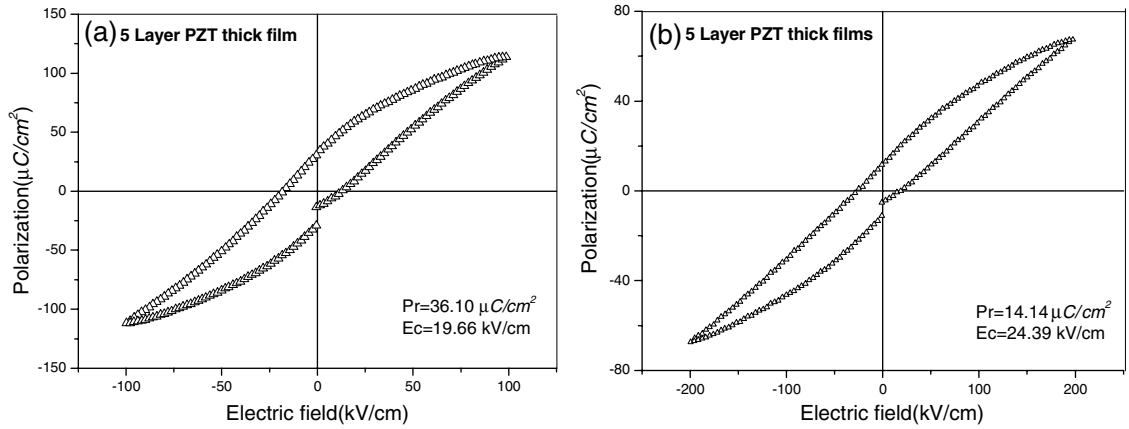

Fig. 7 *P-E* curves for 5-layer PZT thick film using laser annealing (LA) and conventional furnace annealing (FA). (a) LA (100 W/cm^2, 15 s); (b) FA (650°C, 30 min)

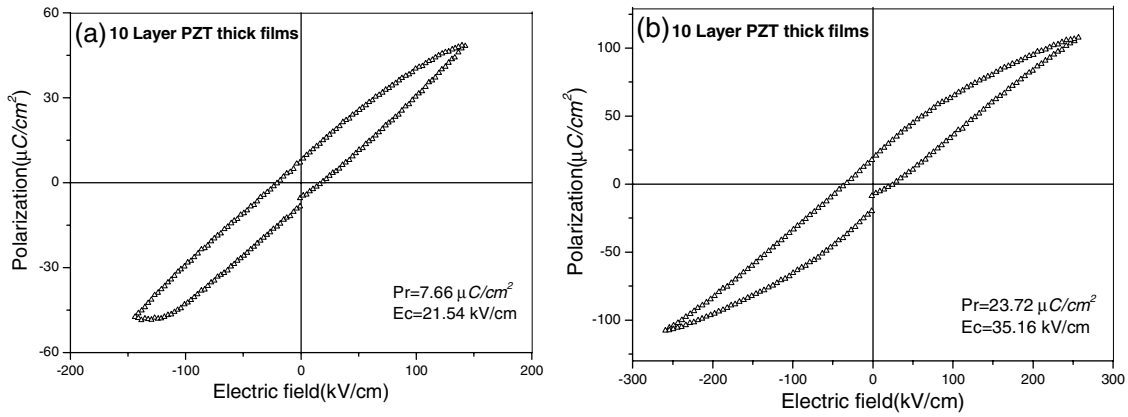

Fig. 8 *P-E* curves for 10-layer PZT thick film using laser annealing (LA) and conventional furnace annealing (FA). (a) LA (100 W/cm^2, 5 s); (b) FA (650°C, 30 min)

(P_r = 36.10 μC/cm^2, E_c = 19.66 kV/cm for the LA specimen; P_r = 14.14 μC/cm^2, E_c = 24.39 kV/cm, for the FA specimen), indicating an intriguing energy absorbing mechanism for laser annealing. Due to localized heating of ceramics using laser annealing, the crystallinity of PZT films is obviously higher than that by conventional sintering and therefore exhibits better electrical properties.

On the other hand, Fig. 8 shows P-E curves for a 10-layer PZT thick films with adding particles of 0.429 μm heat treated using continuous CO_2 Laser annealing (LA) and conventional furnace annealing (FA). Figure 8(a) shows the ferroelectric properties of 10-layer PZT, LA (100 W/cm^2, 5 s) with P_r = 7.66 μC/cm^2 and E_c = 21.54 kV/cm and Fig. 8(b) exhibits the P_r and E_c of the 10-layer PZT thick film using conventional furnace annealing (650°C, 30 min) as 23.72 μC/cm^2 and 35.16 kV/cm, respectively. The ferroelectric properties of the FA specimen shows a better result than that of a LA sample in a 10-layer thick films, indicating a certain reason induces deterioration of electrical properties of laser annealed specimens.

Figure 9 shows SEM micrographs of surface morphology and cross section of a PZT 10-layer thick film annealed at 140 W/cm^2 for 4 s, indicating melting surface and non-conversion bottom layer. The results imply that laser energy was absorbed by the specimens as a function of thickness. If the ferroelectric layer is thin, the laser beam transmits the whole thickness and is reflected by the bottom electrode and heat treats thin ferroelectric again. If the ferroelectric film is thick, the absorption of the laser energy is significant and specimen heat up quickly on surface. The hotter the surface is, the more effective the energy is absorbed. Therefore, the surface layer melts, even if the bottom layer has not been fully crystallized. Once the films were over heat-treated and melted, the electrical properties of films will be deteriorated. We also notice that lower power density and longer annealing time produce better results due to easier controlled processing.

One may notice that the P-E hysteresis loop of thick film such as Fig. 7(a) show rather large saturated polarization (Ps) value, but it is not saturated well. The reason why the thin

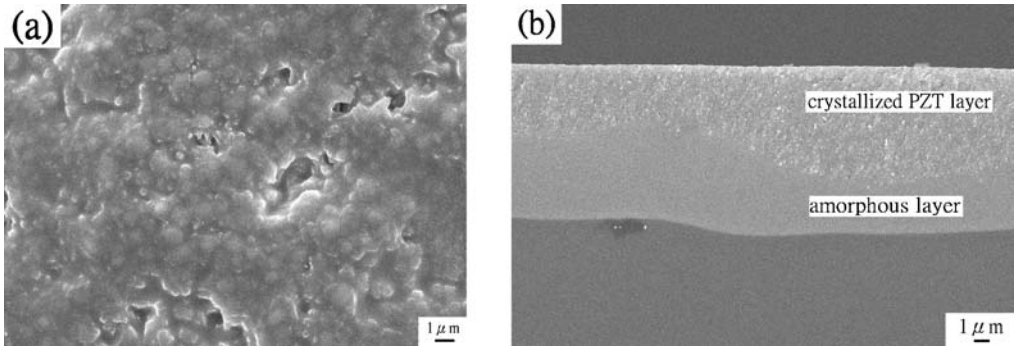

Fig. 9 SEM micrographs showing (a) surface morphology, (b) cross section of a PZT 10-layer thick films annealed at 140 W/cm^2 for 4 s, showing melting surface and non-conversion bottom layer

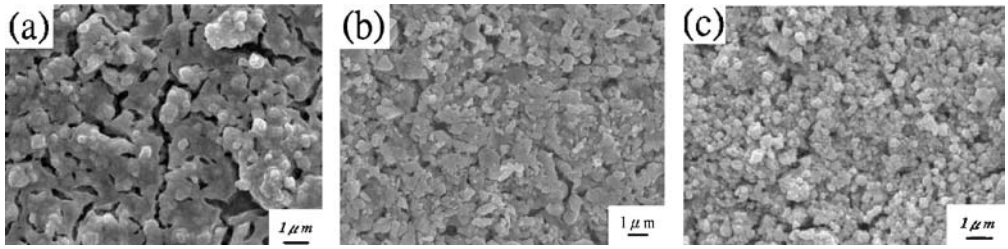

Fig. 10 SEM micrographs showing surface morphology of PZT thick films laser treated using power density of 100 W/cm^2. (a) 1 layer annealed for 25 s; (b) 5 layers (15 s); (c)10 layers (5 s)

film exhibiting large Ps value implies that the polarization vectors switch under the applied electric field and the amount of switchable polarizations is large. Considering microstructures in the materials, this indicates that if the specimens show higher Ps value, the domain boundaries are easier to move, and fewer switching barriers occur in the specimens. Generally, the specimens show better crystallinity, more homogeneous composition or less pinning sites for domain boundaries. This suggests that the LA processing enhances composition homogeneity and higher domain switchability effectively. If electric field was unloaded from a high voltage, some polarizations may switch back due to internal stress, and the remanent polarization (Pr) was obtained. Higher quality films may show larger Pr and Ps. However, if the leakage of the specimen is significant, the specimen may exhibit a false value of the remanent polarization.

The dielectric constant and the dielectric loss of the specimens prepared by adding sol-gel pyrolyzed powers were measured, and the results show that thicker specimens exhibit higher dielectric constant, for instance, at 1 kHz, $\varepsilon_r =$ 400(1 layer), $\varepsilon_r = 2070$ (5 layers) and $\varepsilon_r = 2900$ (10 layers). Tangent loss for thicker specimens show smaller value, but become saturated after specimen thickness reaches a certain value. The tangent loss is around 0.2% at 1 kHz for one layer film, and the loss values are smaller than 0.05% at 1 kHz for 5-layer and 10-layer specimens. The results imply that 5-layer specimens processed by CO_2 laser annealing exhibit high quality films, if the processing parameters were appropriately chosen.

Figure 10 shows SEM micrographs of the surface morphology of the PZT thick films laser treated using power density of 100 W/cm^2. Figure 10(a) is a film of 1 layer annealed for 25 s, and we observed cracks and rough particles on surface morphology, indicating a better interfacial design to reduce processing interfacial stress need to be considered in this case. Smaller or nano-sized particles can be employed in order to obtain flatter surfaces. Figure 10(b) shows top view of a 5-layer film annealed for 15 s and Fig. 10(c) is the surface morphology of a 10-layer film specimen annealed for 5 s. The specimens exhibit porous microstructures at the present mixing particle size and processing parameters. However, it is also possible to obtain dense thick films, if appropriate processing conditions were adopted, as shown in Fig. 9(b). Controlling mixing particle size, we are able to obtain various film density and porosity, and therefore dielectric constants of specimens. As we can see that laser annealed ferroelectric thick films can possess good crystallinity if they were not overheated, Fig. 4, and therefore preserve excellent electrical properties, Fig. 7(a). Therefore, we expect the current thick film processing parameters provide opportunities to fabricate ferroelectric thick films with high polarization and low dielectric constants, which may be appropriate for pyroelectric applications. Moreover, we also found that if one repeats applying laser-annealed 5-layer PZT films using appropriate processing parameters, it is possible to fabricate films with excellent properties thicker than 20 μm using the present powder-mixing sol-gel spin coating method.

4 Conclusions

It was demonstrated that the CO_2 laser annealing technique is successfully employed to obtain well crystallized, sol-gel derived ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$ thick films on $Pt/Ti/SiO_2/Si$ substrates.

PZT films coated on $Pt/Ti/SiO_2/Si$ substrates exhibit well-crystallized features with polycrystalline perovskite structures, and suggests that the crystallization of PZT films was successfully obtained by CO_2 laser annealing at room temperatures. The remanent polarization of a PZT film increases with an increment in the irradiation fluence, and can be explained by crystallinity improvement and larger grain size of the thin films. Laser annealing provides an extremely efficient way to heat treat the samples. Thicker films absorb laser energy more effectively and therefore melt at shorter periods, implying a significant volume effect. Once the films were over heat treated and melted, the electric properties of films will be deteriorated.

Both conventional furnace annealing and laser annealing of PZT thick films prepared by spin-coating of powder-containing sol-gel solutions at the present processing parameters produce porous films. However, laser annealing samples provide much better crystallinity as well as electric properties. It is also possible to fabricate thick films with various density or porosity using CO_2 laser annealing by adjusting appropriate powder properties, laser power density, and/or cooling rate. The current thick film processing parameters provide opportunities to fabricate thick ferroelectric films of good quality.

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