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Effects of ultrasound on perovskite phase developments, microstructures, and dielectric properties of sol-gel-processed $PbTiO_3$ thin films

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$PbTiO_3$ thin films were prepared by spin coating of untreated and sonicated sol (from Pb–Ti stock solution) on Si substrates. The films were fired at different temperatures and were analyzed by scanning electron microscopy, X-ray diffraction and atomic force microscopy. Dried gel and thin films prepared through the two different processing routes were compared in terms of phase developments, microstructures, and dielectric properties. Films prepared from the sonicated sol were found to be superior than those from the untreated sol. *© 2000 Kluwer Academic Publishers*

1. Introduction

Perovskite-type ferroelectric materials have been applied to many electronic and optical devices. $PbTiO_3$ (PT) is a good candidate material for applications such as IR detectors, capacitors, piezoelectric actuators and integrated non-volatile memories due to the large pyroelectric coefficient, high dielectric constant and high electro-mechanical coupling factor [1–4]. PT has a tetragonal perovskite structure at room temperature [5] and readily forms a series of perovskite solid solutions, e.g., $(Pb,La)TiO_3$ [6], $Pb(Zr,Ti)O_3$ [7], $(Pb,La)(Zr,Ti)O_3$ [8], etc.

Sol-gel process is a chemical technique which is well suited to obtain powders, ceramics and thin films. The process offers several advantages, such as low processing temperature, low cost, high purity and homogeneity of the products, and a wide range of obtainable compositions. The sol-gel process involves preparation of a polymerizable solution which is diluted and partially hydrolyzed. Polymeric gel is formed when the sol is applied by spin coating. Dried product of the amorphous bulk is then heat treated to remove the organic residuals and to develop crystalline structures.

Ultrasound wave is transmitted through a medium, while alternately compressing and stretching the molecular structures. Average distance between the molecules in a liquid will then vary as the molecules oscillate about their mean position. If a sufficiently large negative pressure is acoustically applied to the liquid so that distance between the molecules exceeds the average value, the liquid will break down and voids (cavitation bubbles) will be created. In succeeding compression cycles, these cavities can collapse violently and release large amounts of energy in and around the microbubbles. The 'hot-spot' theory suggests that temperatures of up to 5000 K and pressures of several thousand atmospheres are produced during this collapse [9]. The action of ultrasound will undoubtedly enhance atomization and provoke alcohol release, which in turn will accelerate the homogenization process [10].

In the present study, PT thin films were prepared on Si-wafer(100) from untreated and sonicated sol. Ultrasound effects on the sol were investigated by examining crystallization behaviors. Microstructure evolutions and dielectric properties of the films were also studied.

2. Experimental procedure

Lead acetate trihydrate and titanium isopropoxide were used as starting materials for coating sol and 2-methoxyethanol was used as solvent. Lead acetate trihydrate was dissolved at 80°C and water was eliminated at 124°C, evaporation temperature of the solvent. Titanium isopropoxide was added to the prepared solution in a glove box (nitrogen atmosphere) to prevent the reaction with water. Water was then added into the solution for hydrolysis of complex alkoxide, while ethylene glycol was added to prevent cleavage of thin films. To prepare final coating sol, the solution was refluxed and divided into two groups: one for sonication and the other for comparison. Sonication process was carried out in an ultrasonic bath for 3 h (Fig. 1). Optical absorption contents of the sol were estimated by way of using a particle size analyzer, on the assumption that the absorption content of the 2-methoxyethanol solvent be zero. Prepared gel powders were dried at 150°C for 24 h and were analyzed with FT-IR to observe the change of bonding in the coating sol after sonication.

Each sol was dropped on Si wafers and are rotated at 3000 rpm for 30 s. After the spin coating process,

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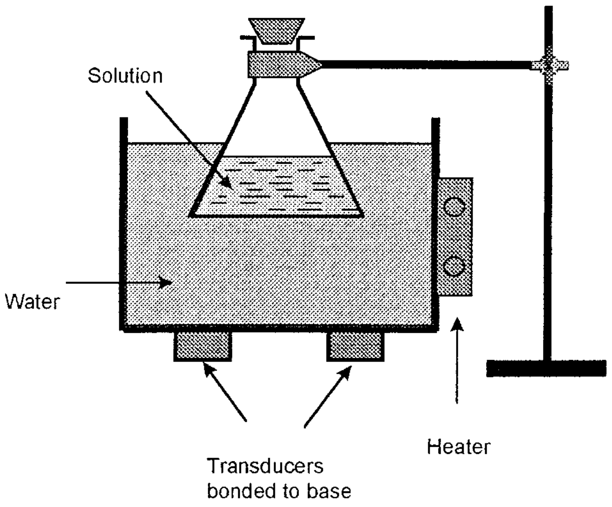

Figure 1 Schematic diagram of a setup for sonication.

the films were heated at 350°C for 5 min over a hot plate. The coating and drying procedures were repeated seven more times until desired thickness were obtained. The films were then fired at 350–650°C (with regular intervals of 50°C) for 1 h by directly inserting to a chamber preheated to desired temperatures, followed by X-ray diffractometer (XRD) analyses for monitoring perovskite structure developments. Film surface morphologies and particle sizes were examined by scanning electron microscopy (SEM). Surface roughness was evaluated by atomic force microscopy (AFM) on areas of 6×6 μm^2 for both films fired at 600°C for 1 h. For electrical measurements, PT films were spin-coated on oxidized and platinized Si-wafers and were fired at 600°C for 30 min, with evaporated aluminum top electrode. Room temperature dielectric constants and losses of the films were measured at several spots with an impedance analyzer at frequencies in the range from 10 kHz to 1 MHz.

3. Results and discussion

In Fig. 2 are FT-IR analysis results of PT gels from the two kinds of sol. An O–H oscillation peak was observed near 3300 cm^{-1} for both spectra. Other oscillation peaks corresponding to C–H and C=O bondings were observable at 2800 and 1300, and 1600 cm^{-1}, respectively. Meanwhile, an M–O peak was also observable in the range of 500–700 cm^{-1}, indicating the initiation of polymerization. By the results, it seems that the sonication process does not influence on the nature of bonding, as little changes of peak developments/disappearances were detectable.

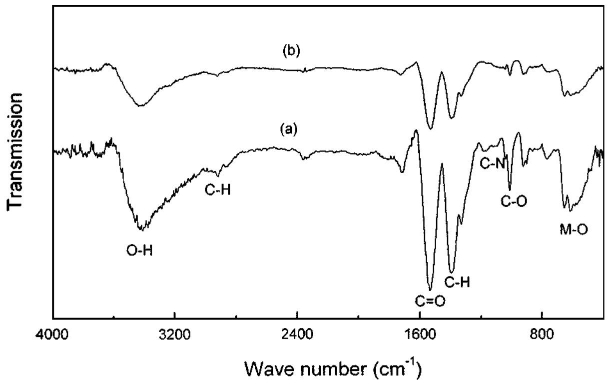

Figure 2 FT-IR spectra of PT gels dried at 150°C from (a) untreated and (b) sonicated sol.

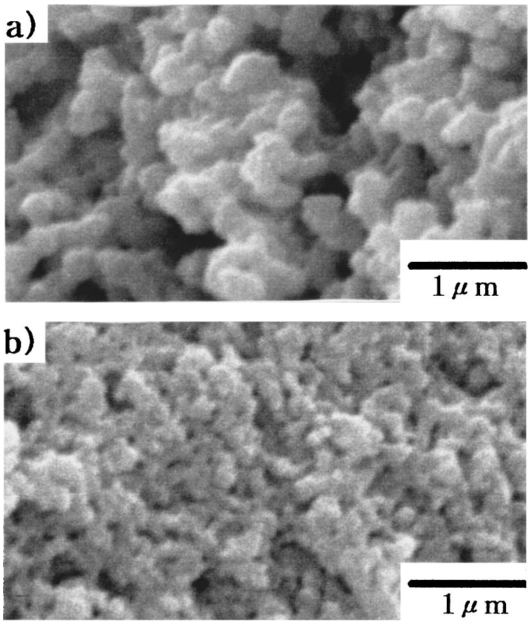

Figure 3 Scanning electron micrographs of PT gels from (a) untreated and (b) sonicated sol (Drying condition: 1 h in air and 48 h at 90°C in an oven).

Optical absorption contents of the sol before and after sonication were estimated to be 0.9 and 2.1 (relative scale). It is well known that the more the number of particles in a solution, the higher the absorption content. Therefore, the present results are thought to be due to rupture of polymer molecules, as ultrasound-induced mechanical stress on a polymer molecule is the primary cause of bond rupture. Polymer molecules become distorted and stretched as they enter the high velocity-gradient area, generated by collapsing cavitation bubbles. At the final stage of collapse, the shock wave radiated from the cavity is expected to generate sufficient stresses within the polymer and is responsible for bond cleavage [11].

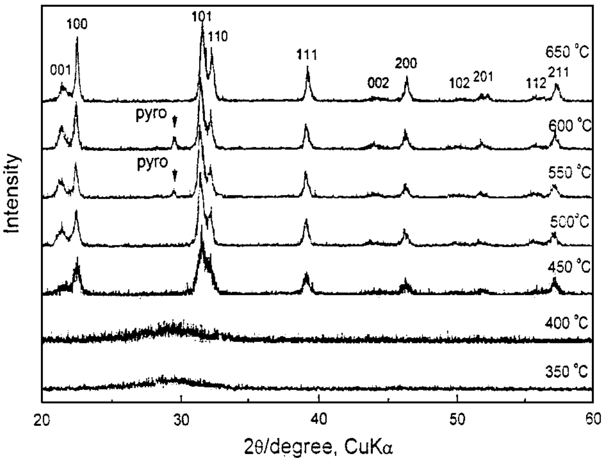

Figure 4 XRD patterns of PT films coated with untreated sol, after firing at different temperatures.

Fig. 3 shows SEM photomicrographs of gel powders dried at 90°C for 48 h in an oven after drying in air for 1 h. Particle sizes of the gel powder from untreated sol were ∼0.3 μm, while those after sonication were ∼0.15 μm, half as small. In consistent with the results of optical absorption content measurement, it is believed that the sonication process decreased the particle size of the gel powder by the rupture of polymer molecules. Consequently, it is expected that films prepared from sonicated sol would have lower phase formation temperatures, as the finer the particle size, the larger the surface area and the greater the driving force. Sintering temperatures are also expected to be lowered and densification could be promoted by using the sonicated sol, which would lead to even-surfaced films with fine- and uniform-sized particles. To examine this, PT thin films were prepared from untreated and sonicated sol, and were characterized.

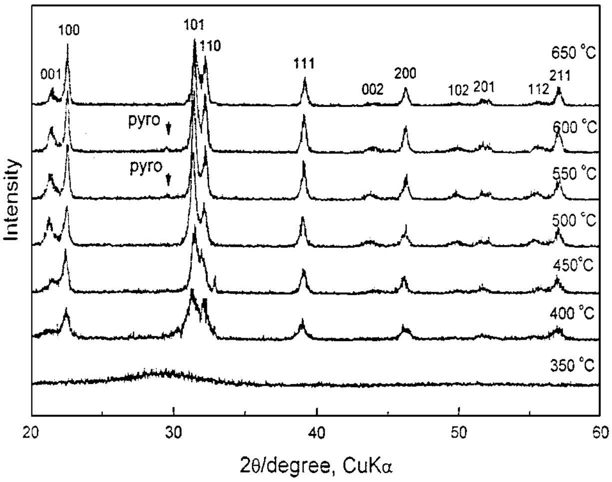

Figure 5 XRD patterns of PT films coated with sonicated sol, after firing at different temperatures.

Structure developments on heat treatments of PT films prepared from the untreated sol are presented in Fig. 4, where characteristic broad diffraction peaks of amorphous state are observable at up to 400°C. At 450°C, a perovskite structure emerged from the amorphous state. The phase developments proceeded with increasing temperatures and increases in peak intensities followed. In the range of 550–600°C, a pyrochlore structure was also detected, but a well-defined pyrochlore-free perovskite phase could finally be obtained at 650°C. Meanwhile, crystallization tendency in the sonicated sol was somewhat different, Fig. 5, where the perovskite phase started to develop at 400°C. The pyrochlore structure was also observed at 550–600°C, but with a much lower intensity than the case of untreated sol. The differences between the two results (Figs 3 and 4) can be explained by the decreased particle size and increased specific surface area by application of the sonication process, as discussed earlier.

Microstructure evolutions of the films prepared from the untreated sol are shown in Fig. 6. Similar to the

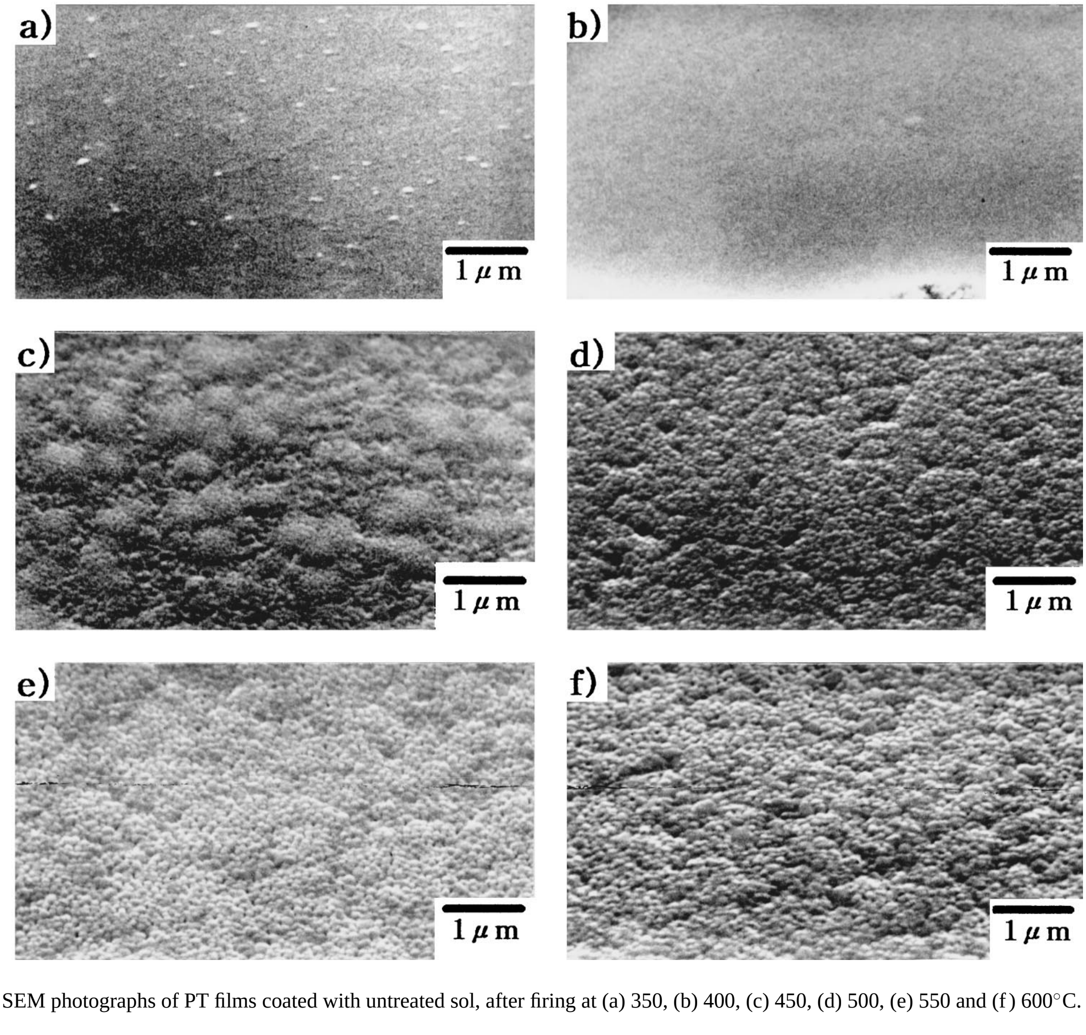

Figure 6 SEM photographs of PT films coated with untreated sol, after firing at (a) 350, (b) 400, (c) 450, (d) 500, (e) 550 and (f) 600°C.

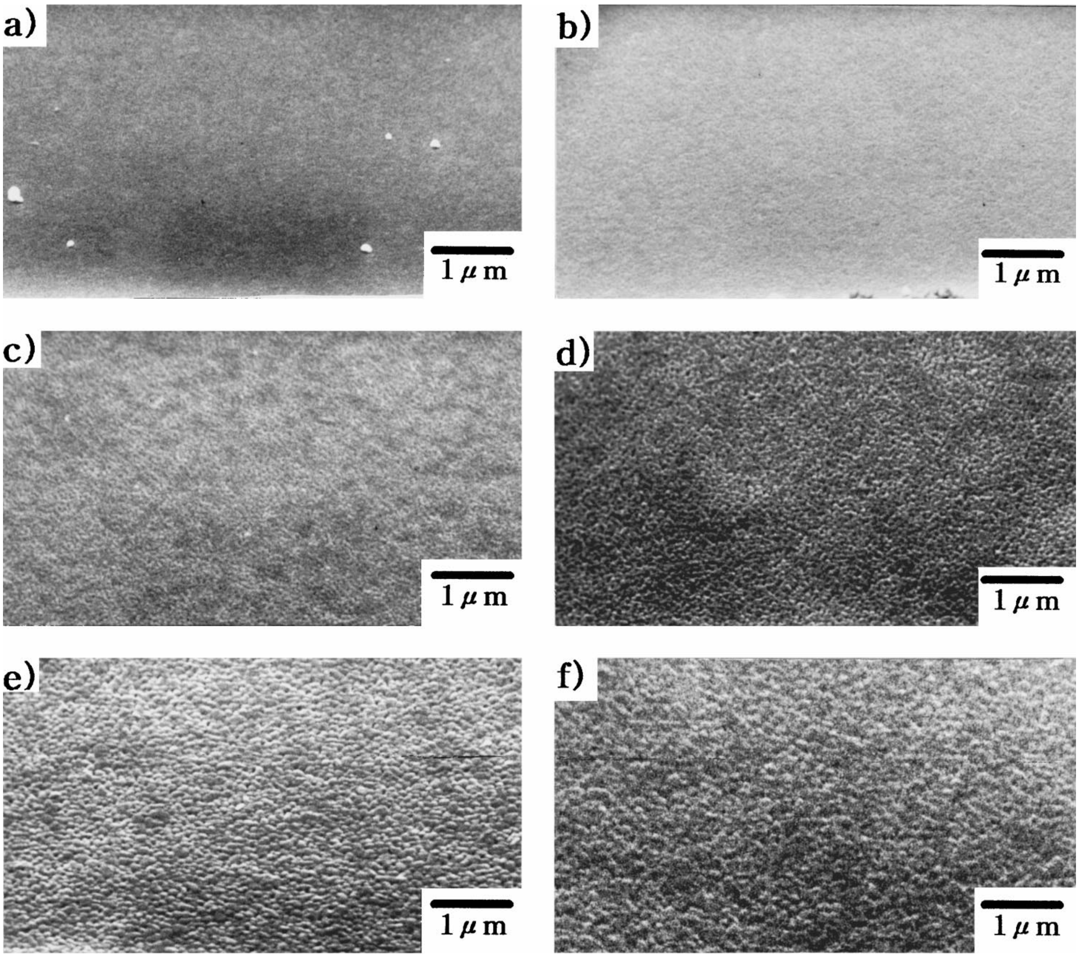

Figure 7 SEM photographs of PT films coated with sonicated sol, after firing at (a) 350, (b) 400, (c) 450, (d) 500, (e) 550 and (f) 600°C.

XRD results, no specific features were observed at up to 400°C, whereas surface irregularities (associated with the initiation of crystallization process) were observable from 450°C and grain growths proceeded with increasing heat treatment temperatures. Microstructures of the films were not uniform, though. In comparison, structure evolutions were observable from 400°C in the case of the sonicated sol (Fig. 7). Grain sizes of the sonicated sol also increased with increasing temperatures, but were much more uniform, so the films looked denser and smoother. Average roughness of the film (fired at 600°C) was 28.6 nm in case of the untreated sol, whilst that from the sonicated sol was only 9.8 nm.

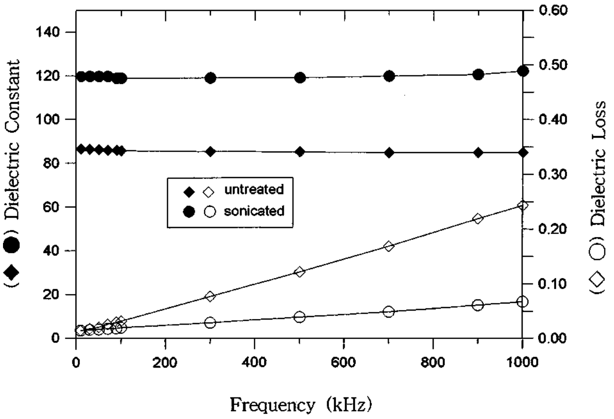

Figure 8 Frequency dependence of relative dielectric constant and loss of PT thin films, prepared from untreated and sonicated sol (Firing temperatures = 600°C).

Variations of the room temperature dielectric constant and loss of the PT thin films with frequency change are plotted in Fig. 8. Dielectric constants of the films prepared from the untreated and sonicated sol were 87 and 120 (10 kHz), and 85 and 122 (1 MHz). Meanwhile, the losses changed from 0.016 (10 kHz) to 0.24 (1 MHz) and from 0.015 (10 kHz) to 0.067 (1 MHz) in the cases of untreated and sonicated sol, respectively. The results indicated that by the sonication process, the dielectric constants were increased appreciably across the whole frequency range, while dielectric losses were decreased preferably at higher frequencies.

4. Conclusion

$PbTiO_3$ thin films were prepared from untreated and sonicated sol. FT-IR analyses on the two kinds of gel were not much different, but optical absorption content of untreated sol was 0.9, whereas that of sonicated sol was 2.1. SEM micrographs of the gel powders revealed that particle size of the sonicated sol was finer. In the films prepared from the sonicated sol, crystallization initiated at a lower temperature with a less degree of pyrochlore formation during heat treatments. Furthermore, denser and even-surfaced films could be obtained by the sonication process. Average roughness of the films prepared from the sonicated sol was 9.8 nm, much lower than 28.6 nm in the case from untreated sol. Dielectric constants and losses of the films prepared from untreated and sonicated sol were ∼85 vs. ∼122 and ∼0.24 vs. ∼0.067 at 1 MHz, respectively. The dielectric constants were found to be rather insensitive to the change of measuring frequency, whereas the losses changed monotonously with the frequency change.

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