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Influence of mm-wave annealing on ferroelectrics properties of PZT films fabricated by AD method

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Lead zirconate titanate (PZT) films with thickness of 3μm were deposited on $Pt/Ti/SiO_2/Si$ substrate by using aerosol deposition (AD) method. Microstructure and ferroelectric properties of these PZT films were investigated with XRD, SEM, ferroelectric tester, and LCR meter. Difference between millimeter wave and conventional heating methods was compared by examining the change in the microstructure and ferroelectric properties.

Influence of mm-wave heating on ferroelectric properties was evaluated by the difference of microstructure and ferroelectric properties annealed at same conditions by the both method. The dielectric constant of the as-deposited PZT film at 1kHz was 200, and increased with increasing annealing temperature in both methods. The vale of PZT films annealed at 873K reached about 1000 for mm-wave heating and about 800 for conventional method, respectively. The dielectric constant of the PZT film was improved with mm-wave heating method.

Key words: millimeter-wave heating, aerosol deposition (AD) method, ferroelectric properties, microstructure, PZT film

1. INTRODUCTION

Lead zirconate titanate (PZT) films are very promising for the applications to various devices such as piezoelectric actuator and ultrasound transducers [1-3]. In recent years, it is necessary to produce dense PZT film with thickness in the range of 1 to 100μm structured on Si and stainless steel substrates. There are some reports of the fabrication of PZT thick films by sol-gel, sputtering or hydrothermal synthesis method. These are several problems such as crack occurrence and peel off from substrate in these PZT films.

On the other hand, PZT films thicker than 10μm can be fabricated easily by aerosol deposition (AD) method with high deposition rate and good adherence to substrate show high density [4,5]. However, post annealing at about 873K is required in the as-deposited PZT films as similar in PZT films in other methods, in order to improve its crystallinity and dielectric properties.

Recently, millimeter-wave (mm-wave) heating method has being paid much attention a promising novel method, instead of conventional heating, since the decrease of densification temperature and well-controllable heating can be expected by weak temperature dependence of dielectric loss of ceramics and enhancement of mass transfer due to high-frequency electromagnetic field. Several successful results have been reported on the sintering of ceramics and their composites by mm-wave heating preparation [6-8].

The objective of this study was obtained to basic knowledge on decreasing annealing temperature to recover the ferroelectric properties of PZT ceramics. Millimeter-wave heating was applied to annealing of PZT ceramics fabricated by AD method. Influence of mm-wave heating on ferroelectric properties was evaluated by the variation of the *P-E* hysteresis loop, dielectric constant, and dielectric loss tangent as function of annealing temperature.

2. EXPERIMENTAL

2.1 Fabrication of PZT film using AD method

The PZT films were deposited by AD method on $Pt/Ti/SiO_2/Si$ substrate at room temperature. Schematic of AD apparatus was shown in Fig.1. AD apparatus was constructed of aerosol chamber, processing chamber and vacuum system.

A PZT powder was filled into aerosol chamber and these chambers were vacuumed to 80Pa. After the pressure of this chamber was evacuated to 0.8Pa and N_2 gas was introduce to the chamber. The PZT powder was deposited on the substrate by using ultra-fine grain beam. Distance from nozzle to substrate was fixed at about 10mm. The conditions of deposition were shown in Table I. The as-deposited films were annealed in the range of 773K to 873K for 1.8ks by mm-wave and conventional heating method.

2.2 PZT films annealed by mm-wave heating method

The films were annealed with mm-wave and conventional heating methods. The annealing was done in air in the range of 773K to 873K for 1.8ks. Heating rate was fixed at 20K/min. A high power 28GHz gyrotron generator combined with multi-mode applicator (Fuji Denpa Kogyo, FSS-10-28) was used for mm-wave annealing. In the mm-wave annealing, temperature of the films was measured by contacting a thermocouple of Type-K on the surface. Conventional annealing of the films was made with the same conditions by mean of an electric-furnace.

2.3 Evaluation of ferroelectrics properties

Thickness of the films was measured with thicknessmeter. Microstructure of the as-deposited and annealed films were analyzed with X-ray diffraction (XRD, Rigaku Miniflex), and observed with scanning electron microscope (SEM, JEOL-6320).

Au electrode was formed on the surface of the films for electric tests by using ion-sputtering apparatus (JEOL, JFC-1100E). *P-E* hysteresis loops were measured using ferroelectrics tester (Radiant technology, Precision LC) with high voltage interface (Radiant technology, HVA-2000). Dielectric constant and dielectric loss tangent were determined with LCR Hi-tester (HIOKI, 3532-50) by setting the oscillation level at 1V.

3. RESULTS AND DISCUSSION

3.1 PZT films fabricated by AD method

Surface morphology of the PZT film with thickness 3μm was shown in Fig.2. All deposited PZT film on substrate showed gray color. After polishing the deposited PZT films, metallic luster was obtained, indicating high density and small surface roughness.

Relationship between the deposition time and thickness of the films is shown in Fig.3. The deposition time was changed in the range of 30s to 240s. Thickness of the films increased with increasing deposition time. The deposition rate with this AD apparatus was determined to be 3μm/min from dependence of the film thickness on deposition time. This value is very high, compared with other deposition method such as sputtering and sol-gel method. The film with thickness of 3μm was used for annealing tests, and evaluations of microstructure and ferroelectric properties.

XRD patterns of PZT powder and as-deposited PZT film are shown in Fig.4. The structure of as-deposited PZT film still maintained after deposition at room temperature. As-deposited films were not orientated like the sputtered PZT thin film. It is found that the films are dense from the observation of cross section by using SEM and microstructure of the films is similar to bulk PZT ceramics.

The variation of XRD angles and half-value width are evaluated after deposition. The diffraction angles shifted from the PZT powder and half-value width increased. Occurring of residual stress and decrease of grain size are suggested from the XRD results.

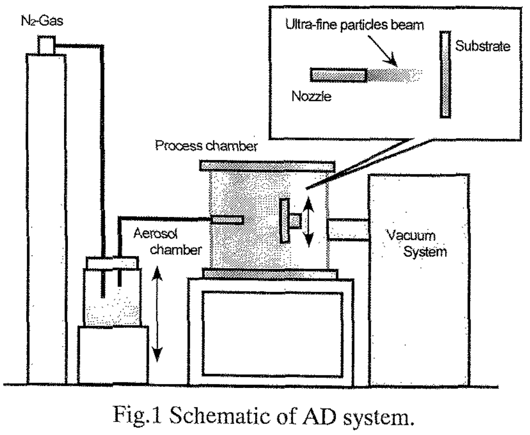

Fig.1 Schematic of AD system.

Table I Deposition conditions of AD method.

Pressure in process chamber	80-150Pa
Deposition time	20-240s
Carrier gas	N_2
Distance	10mm

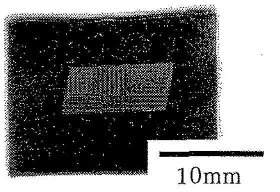

Fig.2 Surface morphology of PZT film on substrate with thickness 3μm.

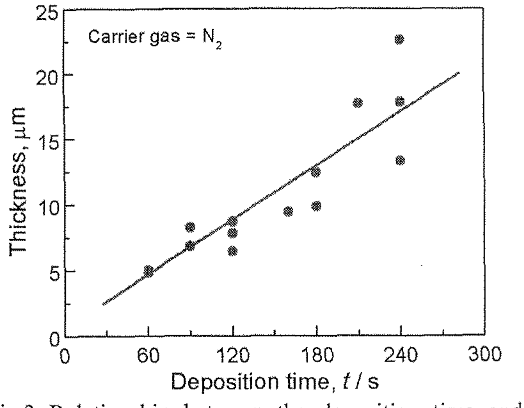

Fig.3 Relationship between the deposition time and thickness of PZT films

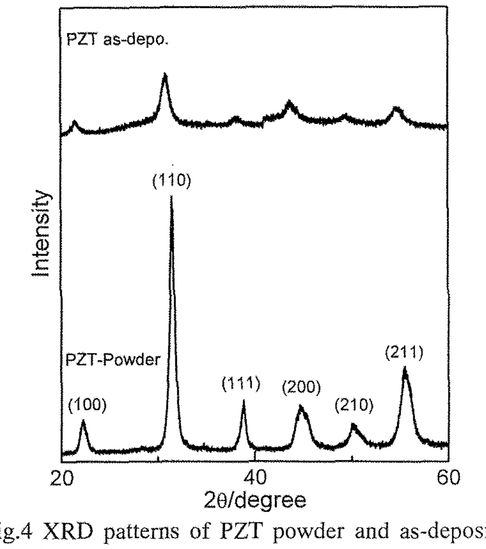

Fig.4 XRD patterns of PZT powder and as-deposited PZT film.

3.2 Variation of ferroelectric properties after annealing

Fig.5 show the change of the hysteresis loop under application of a 300kV/cm external field in the PZT films annealed in range of 773K to 873K for 1.8ks by mm-wave and conventional heating methods. The value of remanent polarization (P_r) and coercive field (V_c) of as-deposited PZT films were 0.82μC/cm^2 and 7.63kV/cm. In both annealing methods, Pr increased with increasing annealing temperature. The Pr and Vc values of PZT films annealed at 873K conventional heating method were 6.0μC/cm² and 10.8kV/cm, respectively. While these in mm-wave heating method were 7.1μC/cm² and 13.2kV/cm, respectively. The value of Vc was improved by mm-wave annealing. However, remarkable improvement on Pr was not found by the mm-wave annealing. No remarkable improvement may be attributed to the leakage of the film.

Variation of the dielectric constant and loss tangent of the PZT films annealed by both heating method are shown in Fig.6. The value of the dielectric constant was calculated from capacitance of the film. For example, the dielectric constant and loss tangent of the as-deposited film measured at 1kHz were 200 and 0.017, respectively. The dielectric constant of the film annealed at 773K by mm-wave and conventional heating measured at 1kHz are 680 and 480, respectively. The higher dielectric constant of mm-wave-annealing PZT films may be attributed to variation of microstructure due to annealing at high temperature. The relationship between microstructure and dielectric relationship are discussed as follow.

The dielectric constant of PZT ceramics can be explained by change the grain size. This increase of grain

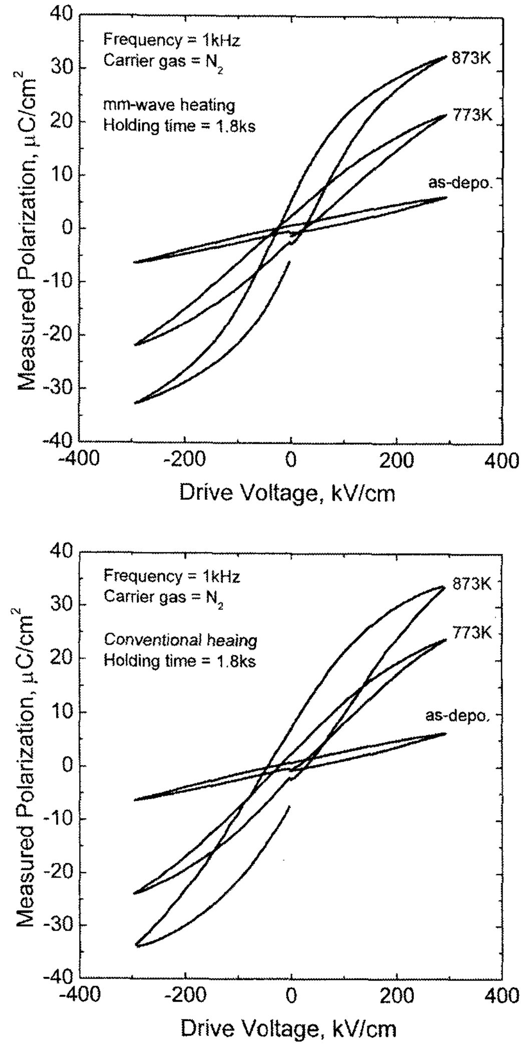

Fig.5 Change of the hysteresis loop in the PZT films annealed in range of 773K to 873K for 1.8ks by mm-wave and conventional heating methods.

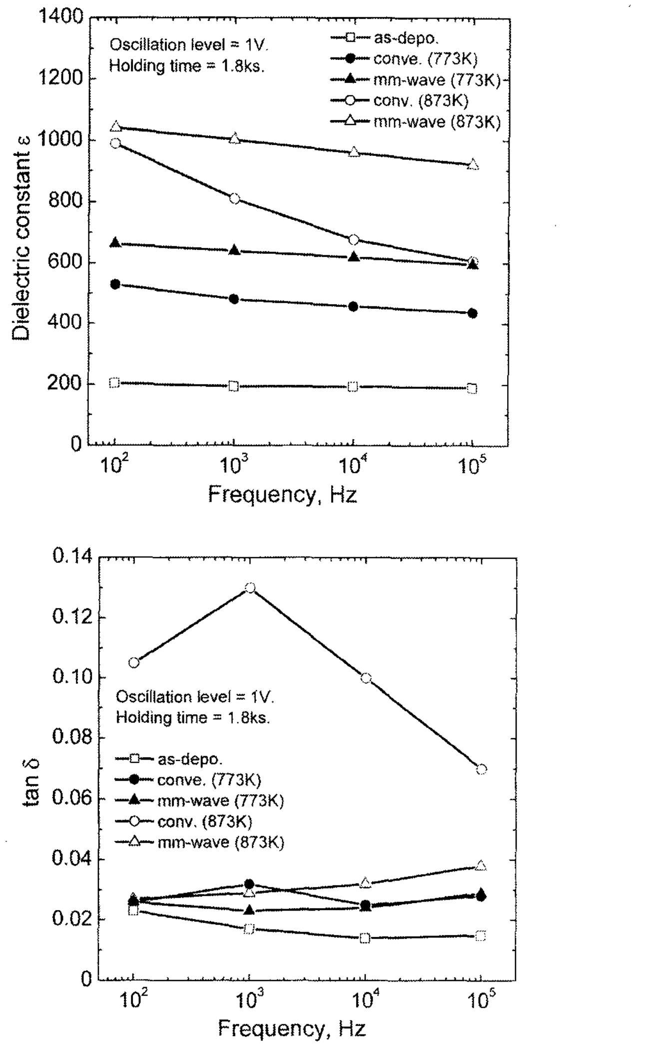

Fig.6 Variation of the dielectric constant and loss tangent of the PZT films annealed by mm-wave and conventional heating methods.

size reduces the volume fraction of grain boundary [8] and the domain density [9,10]. The coupling effect between the grain boundaries and the domain wall, which makes domain reorientation more difficult and severely constrains the domain wall motion, decreases with the increase grain size. Thus, the improvement of the dielectric properties due to grain growth is expected.

It is generally accepted that mass transfer of enhanced diffusion arises from "so-called" microwave effect in the microwave (including millimeter wave) heating. Thus, the grain size of material annealed by mm-wave heating method becomes larger than that by conventional heating method. For example, the influence of 2.45GHz microwave heating method on grain growth was reported in Al_2O_3 [11]. According to the report, the grain sizes of Al_2O_3 sintered at 1573K by microwave and conventional sintering methods were 1.2 and 0.7μm, respectively. Thus, the enhancement of grain growth is respected in the PZT film annealed with mm-wave heating.

Dielectric materials such as ceramics are heated by the electromagnetic filed due to microwave and. The power due to the electromagnetic filed is given by the following equation [12]:

$$P = E^2 \omega \varepsilon_0 \varepsilon_r \tan\delta / 2 \qquad (1)$$

where, E is strength of the electric field by electromagnetic wave, ω is the angular frequency, ε_0 is the dielectric constant, ε_r is the relative permittivity and $\tan\delta$ is the dielectric loss tangent. This relation indicates that the heating efficiency of 28GHz millimeter-wave is much better than 2.45GHz microwave.

It is considered that the difference between dielectric constants of PZT films annealed at same temperature with mm-wave and conventional heating depends on the difference of grain growth and provably of microstructural effect.

4. CONCLUSION

The Ferroelectric properties of PZT films deposited by AD method and the effect of mm-wave-annealing on these PZT films were examined. The conclusions in the present paper are summarized as follows.

1. Deposition rate of AD method using present study was about 3μm/min. This rate is superior to another deposition method. The dielectric constant and dielectric loss tangent of the PZT films annealed by mm-wave and conventional heating method were evaluated.
2. The dielectric constants of the PZT films annealed by mm-wave and conventional heating at 773K measured at 1kHz are 680 and 480, respectively. It is considered that PZT films annealed at same temperature by mm-wave and conventional heating depends on the difference of grain growth and provably of microstructure.

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