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Millimeter-wave Post-annealing of Aerosol-deposited PZT Films

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Post-annealing effect of 28GHz millimeter-wave heating on aerosol-deposited PZT films was investigated from structural standpoint, compared with the conventional heating method. From strain analysis based on XRD measurement, it was found that millimeter-wave post-annealing enables to decrease the strain in PZT films with suppressing the growth of crystallite. From Raman scattering analysis, suppression of interfacial reaction between PZT and substrate stainless steel was also observed in the PZT films post-annealed by millimeter-wave heating, indicating the effect due to selective heating under millimeter-wave irradiation.

(Keywords) Millimeter-wave, Aerosol-deposition, PZT, Post-annealing, Selective heating

1. INTRODUCTION

Recently, aerosol deposition (AD) method has attracted much interests as a new technology for synthesizing various functional thin ceramics and alloys in the fabrication of new micromechanical systems[1]. In these fabrications, it is required to deposit thin films ranging 1μm to 100μm onto various substrate materials in a versatile shape. The fairly thick films deposited by conventional methods encounter various problems such as generation of cracks, weak interfacial strength and low productivity. Instead of the conventional methods, aerosol deposition (AD) method is now promising for versatile deposition of such fairly thick films[2]. According to recent papers, several ceramics such as alumina and PZT with several 10μm thickness have successfully synthesized by AD method[3-5]. Comparing with the conventional methods, many advantages can be indicated as follows[3];

1) high crystallinity attributed to the preservation of the crystal structure and stoichiometry of raw powder material,
2) high densification due to impact pressure,
3) finely patterning of film in versatile shape.

Especially, high crystallinity enables to lower the post-annealing temperature of deposited films. However, removal of stress in AD-synthesized films is an important factor for improving their various characteristics and the existence of finer crystallite becomes also troublesome in some functions such as dielectric properties.

In order to improve such microstructure problems, selective post-annealing by low energy electromagnetic radiation is preferable because structural disordering with small energy difference such as incoherency in grain boundary can be selectively recovered without perturbing main structure. Comparing with various post-annealing method based on electromagnetic radiation, the microwave heating is very preferable for elaborate modification of microstructure, because the microwave energy is fairly lower than that of lattice vibration and thereby controllable energy transfer can be allowed. Among microwave with various frequencies, 2.45GHz centimeter-wave is most popular and easily available but the microwave is not so suitable heat source for elaborate post-annealing of dielectric materials on account of low controllable character due to so-called "thermal run-away"[6]. On the other hand, millimeter-wave is much more controllable as the post-annealing for elaborate improvement of microstructure on account of suppression of "thermal run-away"[7-9]. For example, millimeter-wave heating enable to densify alumina rapidly at a lower temperature compared with 2.45GHz centimeter-wave heating[10] and the elaborate control of grain boundary structure has been attained in the aluminum nitride with high thermal conductivity[11,12].

In the present study, for the purpose of examining the capability of millimeter-wave heating as an elaborate post-annealing of ceramics thin films, delicate control of microstructure and removal of stress in PZT films prepared by AD method were verified by XRD and Raman scattering methods.

2. EXPERIMENTAL PROCEDURES

Raw powder of PZT (Sakai Chemical Co.Ltd.) with the ratio of Pb/(Zr+Ti)=1.003 and Zr/Ti=0.517/0.483 was used. Using aerosol deposition (AD) method, the powder was deposited onto stainless steel substrate(0.2mm thickness) under the experimental conditions described in Table 1. Details are referred elsewhere[1,4]. PZT films prepared by AD method were post-annealed by the millimeter-wave heating equipment, which consists of a 28GHz gyrotron generator and multi-mode applicator (Fuji Denpa Kogyo, FGS-10-28)[13]. Post-annealing of the PZT films with a conventional method was done using an electric furnace. The post-annealing of all samples were made at 500°C for 60min in air. The heating rate was fixed at 20°C/min. XRD patterns were measured using a spectrometer of RINT 2000 type (Rigaku Co. Ltd.) with Cu Kα radiation for verifying microstructure difference, crystallite size and strain in the PZT films

before and after post-annealing. The numerical values of crystallite size and strain were calculated by Hall-Wilson method. Raman scattering spectra of PZT films with or without post-annealing were measured using He-Ne 633nm laser (LabLam HR-800 type, Horiba Co. Ltd.) with micro-focusing method.

Table 1 Experimental conditions

Pressure of the film-deposition chamber	0.55 Torr
Gas and flow rate	He . 3.0λ/min
Substrate temperature	room temp
Average particle size	0.3 um
Film thickness	1.4 um. 3 um and 14 um
Structure of powder	perovskite

3.RESULTS AND DISCUSSION

XRD patterns of as-deposited, millimeter-wave-annealed and conventionally-annealed PZT films with 3μm and 14μm thickness are shown in Fig. 1 and 2. Similar XRD patterns were obtained in the PZT films with 1.4μm. Decrease of the intensity in the tail of the peak near 2θ=31 degree (corresponding to (110) and (101) PZT peaks) is observed after post-annealing. Remarkable difference between the post-annealed PZT films with 14μm is observed in the XRD peaks near 2θ=44 degree. Peak separation is not clearly observed in the conventionally-annealed film. While, in all PZT films, except for the conventionally-annealed film with 14mm, clear separation is observed between the two peaks, which are assigned to (002) and (200) peaks of tetragonal PZT. In the samples of PZT thin films, appearance of XRD peak due to substrate SUS 304 should be considered because its strongest peak is detected at the angle of 2θ=43.6 degree. However, two peaks with similar intensity are observed near 2θ=44 degree irrespective of thickness. Accordingly, the observation of no clear separation between (002) and (200) peaks may not be attributable to the interfacial region but to the bulk region in the thick PZT film annealed by conventional heating.

Subsequently, the relation between crystallite size and strain examined by Hall-Wilson method is shown in Fig.3. Crystallite size of as-deposited films ranges from 22nm to 29nm and crystallite size is inclined to increase with increasing the film thickness. With increasing the crystallite size, the strain in the film also increases in the as-deposited and millimeter-wave-annealed films, though no clear dependence of the strain on the crystallite size is observed in the conventionally-annealed films. Further, remarkable difference was observed between the PZT films annealed by millimeter-wave and conventional methods, compared with the values of strain in the as-deposited films. That is, post-annealing by millimeter-wave heating decreased the strain by 10% to 20% of the value in as-deposited film. While, the strain was not decreased in the films post-annealed by conventional method. Thus millimeter-wave heating enables to decrease strain without changing crystallite size significantly, indicating that millimeter-wave heating can remove strain in the film without change of microstructure.

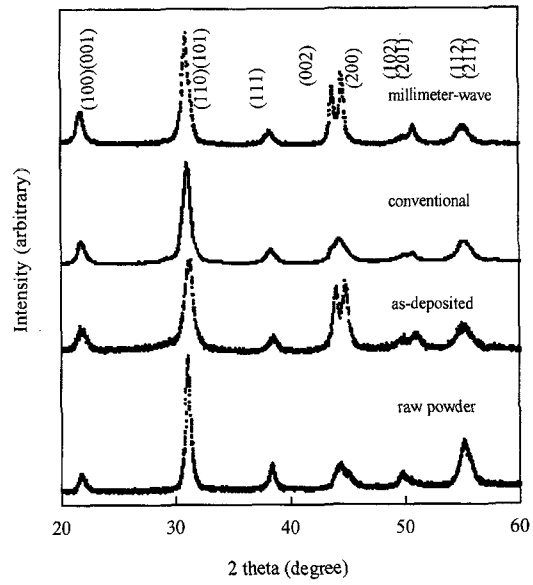

Fig.1 XRD patterns of raw powder, as-deposited, conventionally- and millimeter-wave-heated PZT films with 14μm thickness.

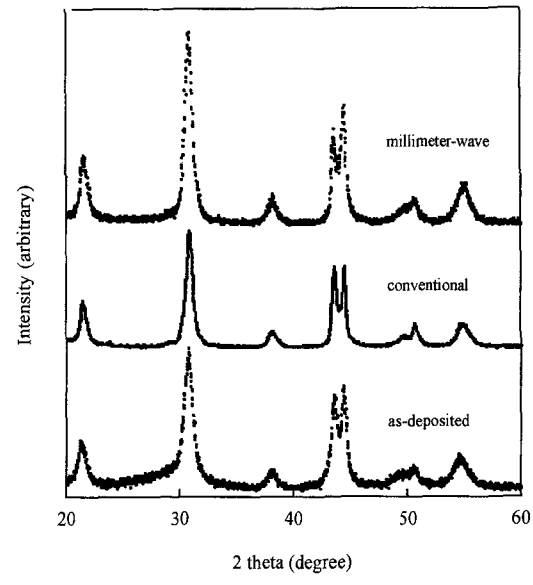

Fig.2 XRD patterns of as-deposited, conventionally- and millimeter-wave-heated PZT films with 3μm thickness.

Raman scattering spectra of raw PZT powder, as-deposited and post-annealed PZT films were measured for the purpose of examining the change of PZT lattice characteristics due to the post-annealing. These spectra are shown in Figs.4, 5 and 6. Raw PZT powder shows Raman peaks near 130cm^{-1}, 200cm^{-1}, 300cm^{-1}, 550cm^{-1} and 750cm^{-1}, respectively. According to the previous papers[14,15], the Raman peaks near 200cm^{-1}, 300cm^{-1}, 550cm^{-1} are assigned to E(2TO), B1+E and E(3TO) modes of tetragonal PZT, respectively. The Raman peak

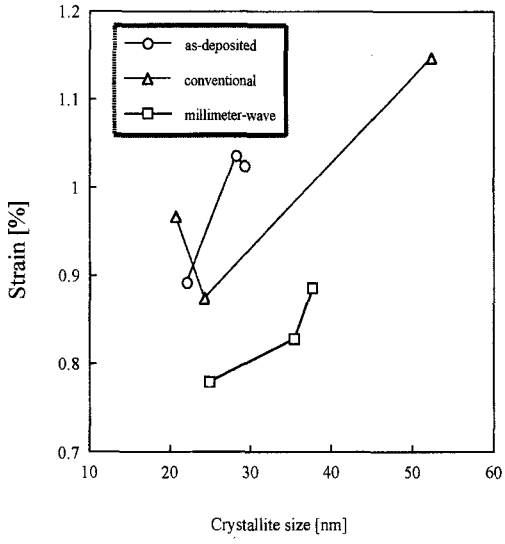

Fig.3 Relation between strain and crystallite size in the PZT films before and after post-annealing

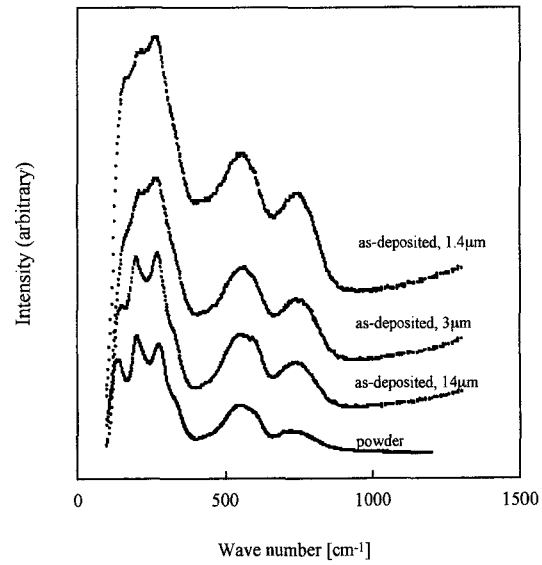

Fig.4 Raman scattering spectra of PZT powder and as-deposited PZT films .

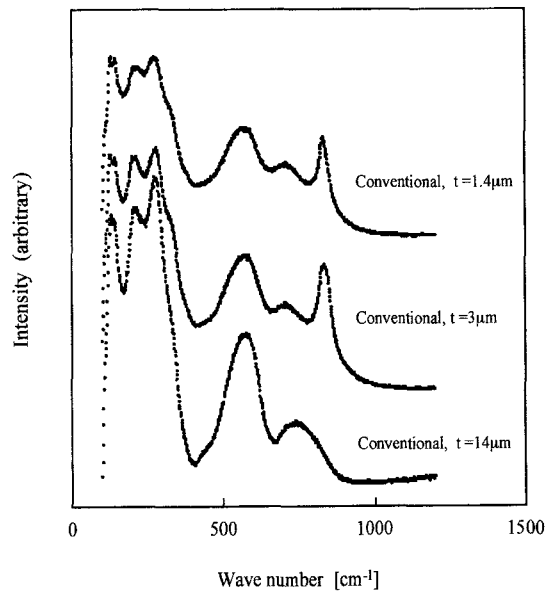

Fig.5 Raman scattering spectra of PZT films post-annealed by the conventional heating method.

near 130cm^{-1} is assigned to A_1(1TO) and E(1LO) of tetragonal PZT but, in some cases, the assignment to$PbTiO_3$ or PbO is suggested[16]. As shown in Figs. 5 and 6, comparing with the spectra of as-deposited films, the clear difference is the appearance of a new Raman peak near 800cm^{-1} after post-annealing by both millimeter-wave and conventional heating. The Raman peak appeared in the post-annealed thinner films with 3μm and 1.4μm and was not observed in the post-annealed thick films with 14μm. Further, the Raman peak was observed more intensely in the conventionally-annealed films. According to the previous result, the Raman peak near 800cm^{-1} is assigned to A_1(3LO) mode in the tetragonal PZT and it has indicated that the peak appears in the PZT film on stainless steel which is annealed in air at 650°C by conventional heating. Considering that the Raman peak near 800cm^{-1} was intensely observed in the thinner PZT films, the peak is the attributed to the generation of A_1(3LO) mode of tetragonal PZT near the interface to stainless steel. However, remarkable discrepancy in the intensity of the peak has been indicated in the previous results. According to the H.Zhang et al.[14], the peak is very weak and broad and no observation of the peak in $PbTiO_3$ and PZT is attributed to its weak intensity and high background. While, the strong and fairly sharp peak was observed by Czakaj et al. [15]. Though the observation of the fairly sharp peak was not explained by them, an important factor may be attributed to substrate material. In this experiment, stainless steel was used as substrate similar to the case by Czakaj et al., so that the appearance of the Raman peak due to A_1(3LO) mode of tetragonal PZT may be due to the same origin to the result by Czakaj et al.. Although the reason for the appearance of the Raman peak near 800cm^{-1} remains unclear, weakness in the Raman peak shows that the effect of annealing in the interfacial region is suppressed in the millimeter-wave heating, indicating clear evidence of heating PZT film selectively in the millimeter-wave post-annealing. Comparing Raman spectra with XRD results, assignment of the Raman peak near 800cm^{-1} may be inconsistent with the appearance of (002) and (200) XRD peaks assigned to tetragonal phase because the Raman peak was not observed or very weak in the PZT films with 3mm and 1.4mm post-annealed by millimeter-wave heating. However, the inconsistency seems to be attributed to the shallow detection depth in Raman scattering spectrometry. Accordingly, depth analysis should be required in the further investigation.

4.SUMMARY

Post-annealing of aerosol-deposited PZT films was

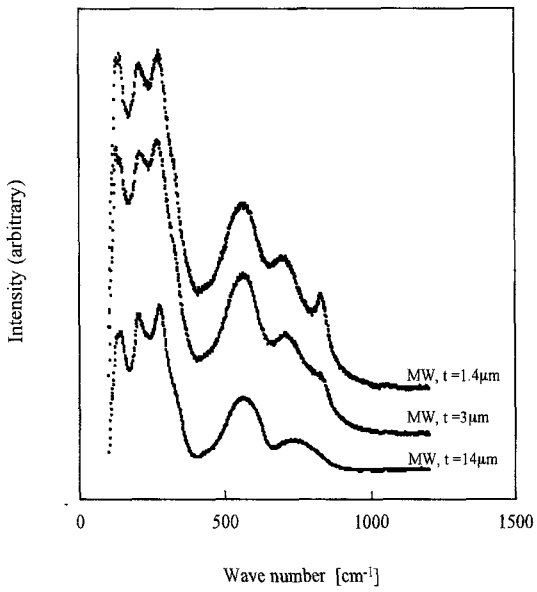

Fig.6 Raman scattering spectra of PZT films post-annealed by millimeter-wave heating method.

performed by 28GHz millimeter-wave and conventional heating methods and structural difference in these post-annealed PZT films was examined by structural analysis based on XRD and Raman scattering methods. Dependence of strain on crystallite size indicates that the post-annealing by millimeter-wave heating can release the strain of AD-PZT films with controlling the crystallite growth of PZT. From Raman scattering analysis, suppression of interfacial reaction between PZT and substrate stainless steel was also observed in the PZT films post-annealed by millimeter-wave heating, indicating the effect due to selective heating under millimeter-wave irradiation.

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References

1) J.Akedo, M.Ichiki, K.Kikuchi and R.Maeda; Proc. IEEE the 10th Ann. Int. Workshop on Micro Electro Mechanical Systems '97, Nagoya, Japan, Jan. 26-30, p135(1997).
2) H.Adachi, Y.Kuroda, T.Imahashi and K.Yanagisawa; Jpn. J. Appl. Phys., 36 (1998) 1159- .
3) M.Ichiki, J.Akedo, A.Schroth, R.Maeda and Y.Ishikawa; Jpn. J. Appl. Phys., 36 (1997)5815-5819.
4) M.Lebedev, J.Akedo and T.Ito; J. Crystal Growth, 275(2005)1301-1306.
5) A.Iwata and J.Akedo; J. Crystal Growth, 275(2005)1269-1273.
6) W.H.Sutton; Am. Ceram. Soc. Bull., 68(1989)376-386.
7) W.H.Sutton; Mater. Res. Soc. Proc., 269(1992)3-20
8)Y.Makino and S.Miyake; J. High Temperature, 29(2003)3-12(in Japanese).
9) S.Miyake and Y.Makino; IEICE Trans. on Electronics, E86-C(2003)2365-2370.
10) H.D.Kimrey, J.O.Kiggans, M.A.Janney and R.L.Beatty; Mater. Res. Soc. Proc., 189 (1991)243-255, (Microwave Processing of Materials II, ed. by W.B.Snyder et al.).
11) T.Yoshioka, Y.Makino and S.Miyake; J. Jpn. Soc. Powder Powder Metallurgy, 50 (2003)916-920.
12) T.Yoshioka, Y.Makino, S.Miyake and H.Mori; J. Alloys and Compounds, in press.
13) T.Saji; New Ceramics, 8(1995)21-30 (in Japanses).
14) H.Zhang, S.Leppävuori and P.Karjalainen; J. Appl. Phys., 77(1995)2691-2696.
15) D.Czekaj, M.J.Gomes, M.Vasilevskiy, M.Pereira and M.P.Dos Santos; J. European Ceramic Soc., 19(1999) 1489-1492.
16) H.Zhang, A.Uusimäki, S.Leppävuori and P.Karjalainen; J. Appl. Phys., 77(1995) 2691-2696.

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