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Structural Characterization of AD-PZT Films annealed with Millimeter-wave Heating

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Structural characterization of AD-PZT films before and after millimeter-wave(MM) post-annealing was performed by glancing angle XRD(GAXRD), XPS and Raman scattering methods and the difference between MM and conventional heating methods was examined. From GAXRD analysis, the existence of small amount of lead dioxide (or Pb_3O_4) was indicated in the conventionally-annealed PZT film, while the existence of lead dioxide (or Pb_3O_4) was scarcely detected in the MM-annealed PZT films. Two different states of oxygen in the surface layer of annealed PZT films were detected by XPS analysis and these oxygen states were assigned to lattice oxygen and adsorbed oxygen, respectively. Effective removal of adsorbed oxygen was observed in the MM-annealed PZT films. Additional Raman peak near 800cm^{-1}, which suggests the proceeding of interfacial reaction with the substrate steel, was observed in the both annealed PZT films. However, difference was not so remarkably detected on account of fairly thick film as observed in thin films.

1. INTRODUCTION

Aerosol deposition (AD) method has attracted much interests as a new technology for synthesizing various functional thin ceramics and alloys in the fabrication of functional devices and new microelectronic mechanical systems[1]. It is necessary in these fabrications to deposit thin films ranging several μm to several hundreds μm onto various substrate materials in a versatile shape. However, there occur various problems such as weak interfacial strength, generation of cracks and low productivity in deposition of fairly thick films by conventional methods. Accordingly, instead of the conventional methods, AD method is now promising for versatile deposition of such fairly thick films[2]. Successful synthesis of several ceramics by AD method have been reported[3-5]. Following advantages are indicated in comparison with the conventional methods [3];

1) high crystallinity and stoichiometry of raw powder material,
2) high densification due to impact pressure,
3) fine pattern of film in versatile shape.

High crystallinity leads to the lowering of 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.

Because structural disordering with small energy difference such as incoherency in grain boundary should be selectively recovered without perturbing main structure, post-annealing by low energy electromagnetic radiation is suitable for improving such microstructure problems. In comparison with various post-annealing method based on electromagnetic radiation, the microwave heating is very preferable for elaborately modifying microstructure, because the microwave energy is fairly lower than that of lattice vibration and thereby controllable energy transfer be allowed. Among microwaves 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 strong temperature dependence of dielectric loss, that is, 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(MM) heating enables 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 our previous study[13], it has been found that the strain in the AD-PZT films decreases by MM post-annealing, with suppressing the crystallite growth. It has indicated that interfacial reaction between PZT film and substrate stainless steel can also be suppressed in the MM post-annealing. In the present study, further examination of surface state and microstructure of AD-PZT films before and after MM annealing has been performed by glancing angle XRD, XPS and Raman scattering methods for the purpose of verifying the capability of MM heating as an elaborate post-annealing of ceramics thin films.

2. EXPERIMENTAL PROCEDURES

PZT raw powder (Sakai Chemical Co. Ltd.) with the average size of 0.3μm was used. The ratios of Pb to (Ti+Zr) and of Zr to Ti were 1.003 and 0.517/0.483, respectively. The powder was deposited onto stainless steel substrate (1.0mm thickness) using aerosol deposition (AD) method. Carrier He gas was supplied at the flow rate of 4.0ℓ /min. Post-annealing was done at 400°C, 500°C or 600°C by conventional or millimeter-wave (MM) heating method, respectively. A 28GHz gyrotron generator and multi-mode applicator (Fuji Denpa Kogyo, FGS-10-28) was used for MM post-annealing[14]. Details on AD conditions are described elsewhere[13]. Glancing angle XRD (GAXRD), XPS and Raman scattering spectroscopy were performed for structural analysis of AD-PZT films before and after post-annealing. GAXRD patterns were measured at the glancing angle of 5 degree, 1 degree or 0.2 degree using a spectrometer of RINT 2000 type(Rigaku Co. Ltd.) with Cu Kα radiation. X-ray photoelectron spectra of O(1s), Ti(2p), Zr(3d) and Pb(4f) electrons were measured using a spectrometer of S-Probe ESCA(Surface Science Instrument Co. Ltd.) with Al Kα radiation. Raman scattering spectra of PZT films were measured using He-Ne 633nm laser (LabLam HR-800type, Horiba Co. Ltd.) with micro-focusing method.

3. RESULTS AND DISCUSSION

Figs. 1 and 2 show XRD patterns of PZT films measured with glancing angle method. In the as-deposited film, a shoulder was observed at the smaller angle position than that of {110} peak of PZT. The shoulder becomes clearer with decreasing the glancing angle and it almost disappeared after post-annealing with both conventional and MM heating methods. Remarkable difference in the post-annealing with both conventional and MM heating methods was detected in the XRD patterns of PZT films annealed at 500°C measured at the glancing angle of 0.2 degree. As shown in Figs.1 and 2, two small but clear XRD peaks appeared near 2θ=26 degree and 2θ=34 degree in the PZT film post-annealed at 500°C with conventional method, while these peaks were not observed in the PZT film post-annealed at 500°C with MM method, though the XRD peak near 2θ=34 degree was observed very slightly. These peaks are probably assigned to (110) and (101) due to lead dioxide. However, some possibility of assigning these peaks to Pb_3O_4 should be also considered. According to the previous paper, it has indicated that the formation of lead dioxide is attributed to the sufficient amount of oxygen due to surface absorption and/or hydroxyl. Accordingly, it is interpreted that the additional oxygen in the surface of PZT films is effectively removed in the annealing with MM heating. In other words, no formation of highly oxidized state of lead suggests the reduction effect of millimeter-wave radiation.

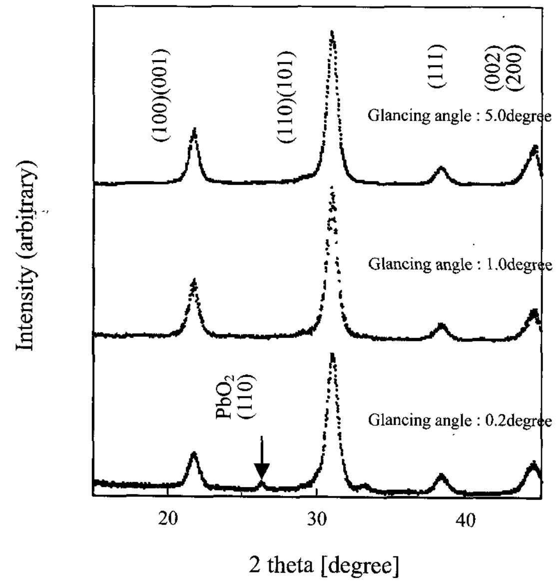

Fig.1 Glancing angle XRD patterns of AD-PZT films annealed at 500°C with conventional heating method.(Main indices of PZT are shown.)

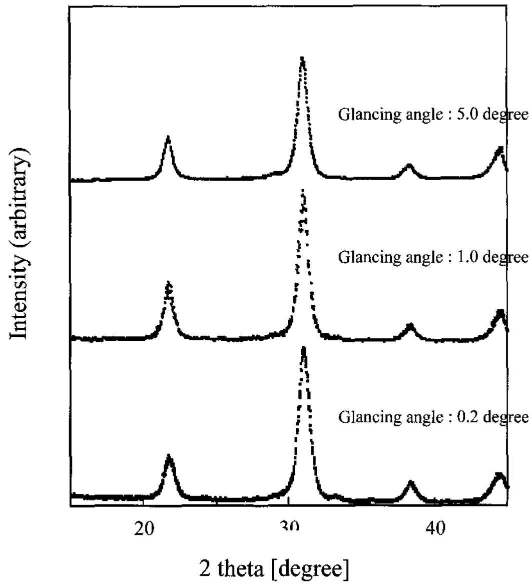

Fig.2 Glancing angle XRD patterns of AD-PZT films annealed at 500°C with millimeter-wave heating method

Subsequently, Fig.3 shows Raman scattering spectra obtained from PZT films post-annealed at 500°C or 600°C with conventional or MM heating method, respectively, together with that for the as-deposited PZT film. Improvement of crystalline state of PZT film by both annealing was clearly observed in the Raman spectra. Clearer appearance of a new Raman peak near 800cm^{-1} was indicated in the PZT films annealed at higher temperature, that is, at 600°C. Further, the peak

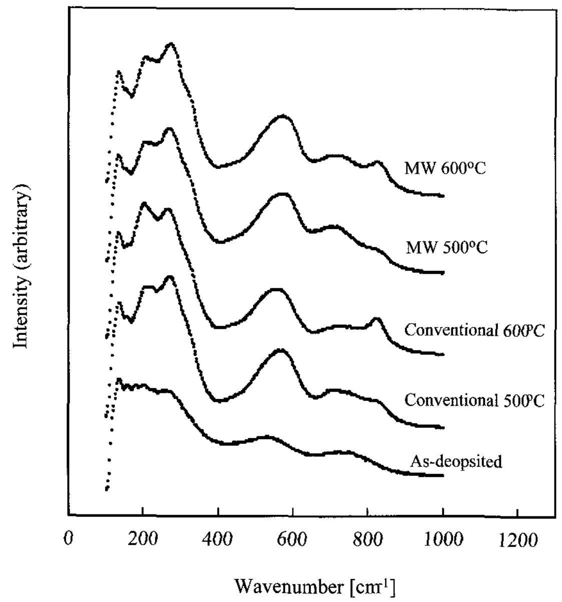

Fig.3 Raman scattering spectra of AD-PZT films annealed at 500°C or 600°C with conventional or millimeter-wave heating method. The spectrum of as-deposited AD-PZT film is also shown for comparison.

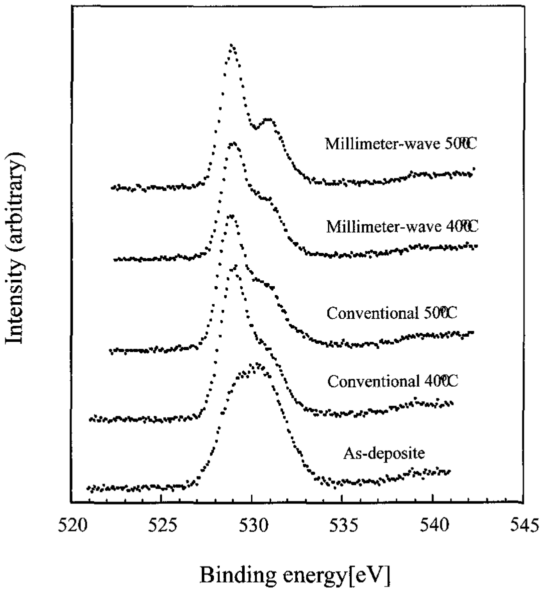

Fig.4 O(1s) XPS spectra of AD-PZT films annealed at 400°C or 500°C with conventional or millimeter-wave heating method. The spectrum of as-deposited AD-PZT film is also shown for comparison.

has assigned to A_1(3LO) mode in the tetragonal PZT and the generation of the mode of the tetragonal PZT is attributed to the interfacial reaction with substrate stainless steel[15]. As reported in our previous paper[13], the new Raman peak near 800cm^{-1} is observed more clearly in the annealed PZT films with thinner thickness, indicating clear evidence of the interfacial reaction of PZT film with substrate stainless steel. Further, it has also indicated that the interfacial reaction is suppressed in the MM-annealed PZT films on account of selective heating of millimeter-wave. Because thickness of PZT films in the present study ranges from 15μm to 25μm, it is found that the difference in the intensity of the Raman peak near 800cm^{-1} is not so clearly observed as in the annealed PZT films with several μm in thickness. As shown in Fig.3, however, slightly intense peak is observed in the PZT films annealed at 500°C and 600°C with conventional method, respectively. Further, it should be noted that strong fluorescence occurs in the PZT films annealed at 400°C and clear Raman spectra were not measured in these specimens.

In order to examine the electronic states in the surface of PZT film, x-ray photoelectron spectra of O(1s), Pb(4f), Ti(2p), Zr(3d) electrons were measured in the PZT films annealed at 400°C and 500°C, respectively. x-ray photoelectron spectra in the shallow energy range less than 40eV were also measured for examining the valence state. Fig.4 shows XPS spectra of O(1s) obtained from the PZT films as-deposited and annealed at 400°C and 500°C. A broad spectrum of O(1s) electron was observed in the as-deposited PZT film. The broad spectrum was resolved into two peaks by post-annealing and the resolution became better with the increase of annealing temperature. Further, better resolution was obtained in the MM-annealed PZT film, compared with the conventionally-annealed film.

According to the previous reports on XPS analysis of PZT[16-18], O(1s) XPS spectrum has been resolved into three peaks that appear at around 529.2eV, 530.7eV and 532.2eV, respectively, and these peaks has been assigned to the lattice oxygen, surface adsorbed oxygen and hydroxyl, respectively[16]. Therefore, change of O(1s) spectrum before and after annealing indicates that hydroxyl in the surface layer of PZT film can be effectively removed with the millimeter-wave annealing. Influence of the existence of lead dioxide on the O(1s) spectra was not observed though the O(1s) peak due to lead dioxide appears in the range from 530eV to 531eV. This is attributed to the relatively small amount of lead dioxide. Slight shift was observed in the spectra of Pb(4f), Ti(2p), Zr(3d) electrons, respectively. Detailed results on these spectra will be reported in another paper for lack of space.

SUMMARY

Post-annealing effect on the structural change of AD-PZT films was investigated by using GAXRD, XPS and Raman scattering methods. GAXRD results indicated that small amount of lead dioxide (or Pb_3O_4) was formed in the surface layer of the AD-PZT film annealed at 500°C conventionally, while scarce formation of lead dioxide (or Pb_3O_4) was suggested in the AD-PZT film annealed at 500°C with millimeter-wave heating method, suggesting the reduction effect under millimeter-wave radiation.

From XPS analysis of 1s electronic state of oxygen, removal of adsorbed oxygen in the surface layer was progressed effectively with millimeter-wave heating. However, significant difference was not found in the oxygen state due to the existence of lead dioxide on account of its small amount.

Characteristic peak near 800cm^{-1} was observed in the PZT films annealed with both annealing methods and slight difference was only detected because fairly thick PZT films were analyzed in the present study. The result agree with the predominant existence of the phase with the origin of 800cm^{-1} peak in the interfacial region of AD-PZT films.

In further investigation, detailed analysis of surface state of PZT film and interfacial region between PZT film and substrate steel and interfacial reaction will verified by XPS and cross-sectional Raman scattering methods.

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