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Effect of auxiliary on hysteresis property of ferroelectric film by aerosol deposition

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Concerning the ferroelectric films produced by AD method, the effects by adding auxiliary agents to injection powder and the effects by grain size were investigated for the purpose of realizing higher ferroelectric property. Ferroelectricity of AD film was found to be improved by adding low melting point auxiliary agents and using calcined powder, and was also found to depend on the grain size of injection powder, and to be improved by increasing the size to an appropriate value. By optimizing the conditions, good ferroelectricity was realized; such as Pr = 25.4 μC/cm^2 in the heat treatment at 600°C (63% of sintered film, calcined powder added with low melting point glass) and Pr = 38.0 μC/cm^2 in the heat treatment at 700°C (95% of sintered film, calcined powder added with Bi_2O_3-ZnO).
Key words: aerosol deposition, ferroelectric, calcination powder, auxiliary, grain size

1 Introduction

As electronic parts become smaller and more integrated, thick film forming technologies have been actively developed for the functional films on various substrates. As for the piezoelectric substances (ferroelectric substances), in particular, various developments go on for actuators, ultrasonic sensors, etc. For the method of forming piezoelectric film on substrate, generally, screen printing method and thin film method (including sol-gel method and CVD method, etc.) are used. The former is not applied to wide variety of substrates because it requires burning at around 1000°C for high density while the latter is not appropriate for forming thick films because the film-forming rate is low (50-200nm/min). Aerosol deposition (AD) method, on the other hand, is characterized by films very dense at room temperature and high film-forming rates (10-30μm/min), and the development activities became very active recently. If PZT thick film is formed on SUS substrate by AD method, it is reported that characteristics equivalent to or more than other film-forming methods are realized; such as the piezoelectric constant of -d31 = 80 - 100 pm/V in heat treatment at 600°C which is roughly as low as a half of sintered substance.[1,2] This is because large amounts of lattice distortion or defects are included due to plastic deformation of particles in the asdepo film because AD method is a film-forming method by impact solidification, and because such modification is insufficient in the heat treatment at around 800°C or lower.

Therefore, the purpose of this report was specified as the production of AD films free of lattice distortion or defect in the heat treatment at lower temperatures and as the realization of higher ferroelectricity. As a measure for such purpose, addition of auxiliary agents to injection powder was studied, which is thought to promote the modification of lattice distortion or defect in heat treatment. Also in order to suppress the introduction of lattice distortion or defects in film forming, optimization of grain size of injection powder was also studied.

2. Powder Production & Experiment Methods

2.1 Powder Production Method

For the ferroelectric substances, 0.15 Pb (Zn, Nb) O_3-0.85 Pb (Zr, Ti) O_3 (hereinafter shown as "PZN-PZT") was used. Powder was produced in the solid phase reaction method by the procedure shown below. The materials PbO, ZnO, Nb_2O_5, ZrO_2 and TiO_2 were measured to the specified amounts so that the total weight may be 200g, and were wet-blended by ball mill. Conditions of ball mill are shown in Table 1. After drying, the blended powder was calcined at 900°C, and wet-crushed by ball mill. Ferroelectric powder was obtained after drying. For the auxiliary agents on the other hand, two types were discussed, such as Bi_2O_3-ZnO[3] and lead zinc borosilicate low melting point glass (IWF-9598 made by AGC). Respective melting points are 751°C and 648°C. For Bi_2O_3-ZnO, $Bi2O_3$ and ZnO were measured to specified amounts, wet-blended by ball mill, and crushed to the grain size of 0.5 μm after being calcined at 750°C. Low melting

Table 1 ball mill condition

apparatus	ball mill amount
pot diameter and volume	φ 140mm / 1ℓ
ball diameter and material	φ 5-YSZ ball
ball weight	2kg
disperse media and weight	water / 300g
mixed time	40 hours
mixed time (after calcined)	5-12 hours

point glass was also wet-crushed so that grain size may be 0.5 μm. 1.0 wt% of auxiliary agent was added to PZN-PZT.

2.2 Auxiliary agent adding method

Powder added with auxiliary agent was prepared in two ways; such as the blended powder made by mixing PZN-PZT with auxiliary agent by ball mill and the calcined powder crushed by calcination at the specified temperature after mixing. Calcinating temperatures was 850°C in the addition of Bi_2O_3-ZnO, and 600°C, 700°C, 800°C, 900°C and 1200°C in the addition of low melting point glass. The keep time at calcinating temperature was 2 hours.

2.3 AD film production method[4]

Powder obtained was used as injection powder, and films were formed by AD film-forming equipment. For the substrate, YSZ substrate was used. As for the electrodes, Pt was formed by screen printing, and heat-treated at 1310°C, thus realizing the thickness of 5 μm. On this substrate, thick film of 5 - 6 μm was formed as an AD film. Film-forming conditions at the time are shown in Table 2. Heat treatment temperature after forming film were 600°C, 700°C and 800°C. Max temperature was kept for 2 hours. Heat treatment was performed at 600°C by printing Au electrode after heat treatment. Size of electrode was 0.8mm x 0.5 mm.

Table 2 Condition of film forming

Carrier Gas	high purity Air
Size of Nozzle Orifice	10×0.5～10×1.2mm^2
Working Pressure	80～2000Pa
Working Distance	5mm
Consumption of carrier gas	6L / min
Deposition Temperature	Room Temperature
Nozzle speed	1.25mm/s

2.4 Evaluation of Powder and AD Films

Grain size distribution of powder produced was measured by laser diffraction particle size distribution analyzer (HORIBA; LA-700). Micro structure of AD film was observed by using SEM (JEOL; JSM6390LA). Average grain sizes of film were calculated from SEM images. Crystallinity of AD films was evaluated by X-ray diffraction using Cu-Kα line. The remanent polarization value (Pr) and coercive electric field (Ec) as the characteristic values showing ferroelectricity were to be evaluated, and was obtained from the hysteresis curve when adding 100 Hz of triangle wave of max +/- 200 kV/cm to films.

3. Experiment Results and Evaluation

3.1 Effects by adding auxiliary agent: Bi_2O_3-ZnO

Micro structure of formed AD film is shown in Fig. 1. In the heat treatment at 700°C, there were no large differences among PZN-PZT powder, mixed powder and calcined powder. Film grain size at the time was 100 nm or so. In the heat treatment at 800°C, however, grains grew largely by calcined powder, and the film grain size became 280 nm.

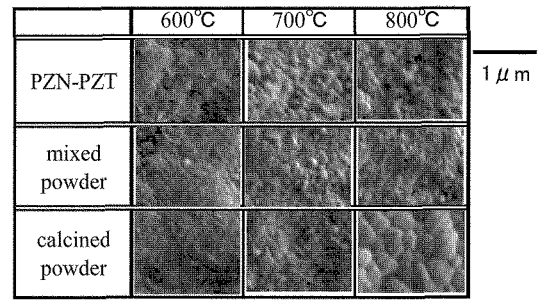
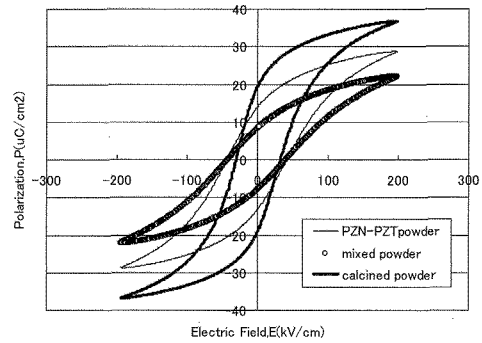


Fig.1 Micro structure of formed AD film



	Heat treatment	PZN-PZTpowder	mixed powder	calcined powder
Pr [uC/cm^2]	600℃	9	5.5	11
	700℃	14	8	20
	800℃	26	25	38
Ec [kV/cm]	600℃	43	46	37
	700℃	40	42	32
	800℃	39	40	24

Fig2.Hysteresis curve in heat treatment 700℃ and various of Pr and Ec

Fig. 2 shows the hysteresis curve of AD film heat-treated at 700°C and the changes of Pr. For calcined powder, Pr improved 22% as compared with PZN-PZT powder in heat treatment at 600°C, 43% in heat treatment at 700°C and 46% in heat treatment at 800°C. Ec was also found to drop as heat treatment temperature rose. As compared with sintered film (burned at 1200°C; Pr=42.0 μC/cm^2, Ec=11kV/cm), however, Pr remained as low as 50% in heat treatment at 700°C. Ferroelectricity of AD films improved when using the calcined powder to which auxiliary agent was added, and such effects were more remarkable as the heat treatment temperature was higher. In the mixed powders, characteristics dropped. Factors of these results were evaluated as shown below. In the observation of condition inside the films, no difference was seen in density. In the analysis of composition by EPMA, a segregation of Bi_2O_3-ZnO components was detected in the AD film using mixed powder, and remained even after the heat treatment at 800°C. No sufficient voltage was applied to ferroelectric substance due to the presence of this segregation as a low dielectric constant phase, thus seemingly reducing the value of Pr. In the asdepo film using calcined powder and AD films heat-treated at 800°C, on the other hand, such a segregation in the film as when using mixed powder was not found. Result obtained from XRD of calcined powder also showed that

Bi_2O_3-ZnO was sufficiently diffused. We estimated the values of Pr had been improved by a sufficient diffusion of substances even in such a dense film as AD by heat treatment and a promotion of growth of film grain, by forming films with injection powder in which auxiliary agent is sufficiently diffused.

3.2 Effects by Auxiliary Agent: Low melting point glass

Fig. 3 shows the cross-sectional micro structure of AD film. In the powder calcined by mixed powder and at 700°C or lower, dense film was not available. These powders strongly showed the hallow derived from glass component in XRD, and it was found that the low melting point glass particles were not sufficiently melted or diffused. When forming films with glass only, dense film was not available. Judging from this, small amount of glass powder present in the injection grain was suspected to interfere with the plastic deformation and micro crystallization in forming films, thus disabling the formation of dense film.

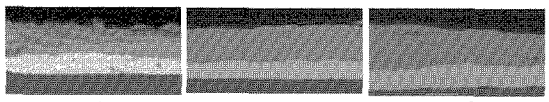


Fig.3 the cross-sectional micro structure of AD film using calcined powder at 600-1200℃

In the calcined powder at 800°C or higher, in the meantime, dense film was available. XRD also shows these powders have small hallow, and that low melting point glass was sufficiently diffused in the primary grain of PZN-PZT or grain. Fig. 4 shows the micro structure of film surface. Growth of grain was found to have developed in the heat treatment at 600°C lower than that of Bi_2O_3-ZnO.

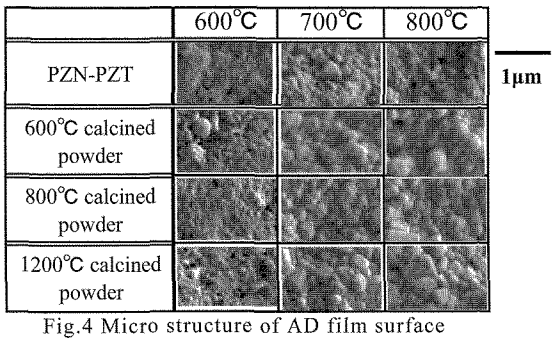


Fig.4 Micro structure of AD film surface

This is because the melting point of glass is lower than that of Bi_2O_3-ZnO. It can be said that the diffusion of substances started at lower temperatures, and the growth of grain was promoted. Fig. 5 shows Pr of AD film using each calcined powder heat-treated at 600℃ and 700°C and the changes of Pr. Pr was the highest in the film using the calcined powder at 800°C, and was improved by 26% in the heat treatment at 600°C, and by 48% in the heat treatment at 700°C as compared with PZN-PZT powder. In the heat treatment at 700°C, such an improvement was 51 % as compared with sintered film (burned at 1200°C). In the calcined powder at 900°C or higher, on the other hand, the value of Pr dropped slightly. This result was evaluated as shown below. In the XRD of calcined powder at 900°C or higher, peak derived from the components of low melting point glass, peak of ZnO and $ZnSiO_4$ in particular, was observed remarkably. Also in the film's EPMA, segregation of Zn was seen. This made us estimate that deposition of ZnO had occurred as a different phase derived from glass components if calcined at 900°C or higher, and was present in the film as a phase of low dielectric constant, thus lowering the ferroelectric properties.

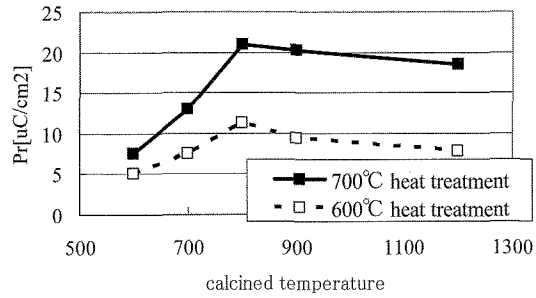


Fig.5 Pr of AD film using each calcined powder

3.3 Effects by Powder Grain Size

We have investigated how ferroelectricity changed, by increasing the grain size in the calcined powder added with both additives. Grain size of powder was adjusted according to the ball mill crush time after calcination, and the grain sizes 0.5, 1.0, 1.8 and 2.6 μm were obtained. Using these powders, AD films were formed and heat-treated. In the powder of 2.6 μm, it was hard to realize the required film thickness. Then, films were formed by changing the conditions (including change of nozzle diameter). However, only thing given was the thickness of about 3 μm.

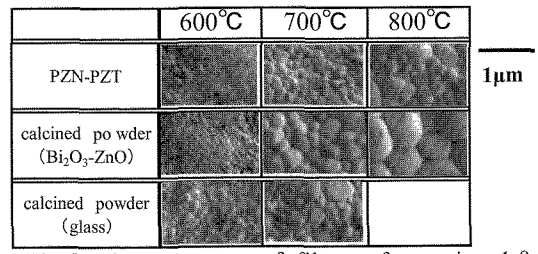
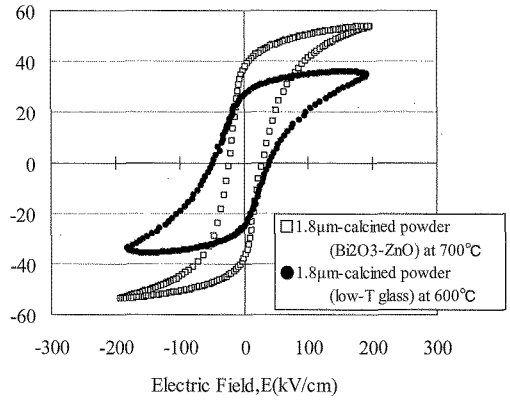


Fig.6 Micro structure of film surface using 1.8μm powder

Observation of cross-sectional micro structure of films enabled us to ensure that dense films were seen in powders of all grain sizes. Fig. 6 shows the micro structure of film surface using 1.8μm powder and Fig. 7 shows hysteresis curve. Table 3 shows relation of injection size and film grain size and Pr. Up to 1.8 μm in both calcined powders, grain size of film after heat treatment increased as the grain size of powder increased, thus increasing the value of Pr. High values of Pr were obtained, such as 38.0 μC/cm2 (95% of sintered

film) in 700°C heat treatment in grain size of 1.8 μm of Bi_2O_3-ZnO calcined powder, and 25.4 μC/cm2 (63% of sintered film) in 600°C heat treatment in grain size of 1.8 μm of low melting point glass calcined powder. If powder of grain size of 2.6 μm is used, in the meantime, grain size



of film decreased, Pr dropped, and Ec increased.
Fig.7 Hysteresis curve using 1.8μm injection powder

Table 3 Influence of injection powder size

		600℃ heat treatment		700℃ heat treatment	
	injection powder size	grain size [nm]	Pr [μC/cm2]	grain size [nm]	Pr [μC/cm2]
PZN-PZT	0.5μm	100	9	100	14
	2μm	100	15	180	34
Bi_2O_3-ZnO calcined	0.5μm	100	11	100	20
	1.0μm	110	14	190	29
	1.8μm	120	20	240	38
	2.6μm	100	16	210	34
low-T glass calcined	0.5μm	100	12	200	21
	1.1μm	100	16	210	26
	1.8μm	150	26	270	36

We have also examined, from X ray analysis, the fact that Pr value has a peak according to the grain size of powder to be used. Since the film produced by AD method is accompanied by the plastic deformation or crush of grain in forming films, irregular strains are suspected to occur. In the scope of the half breadth, therefore, effects by crystal's irregular strains are included in addition to the crystallite size. Then, we calculated the crystallite sizes and irregular strains respectively in the asdepo film and heat-treated film by using the formula of Hall. Formula of Hall may be as shown below.

$$\beta\cos\theta/\lambda = 2\eta\sin\theta/\lambda + 1/\varepsilon$$

Where, β: half breadth, θ: diffraction angle, 2η: crystalline strain, λ: wavelength of X ray, ε: crystallite size.

By this formula, it is possible to calculate the crystallite size and irregular strain separately. Results were shown in Table 4. There is very small change in crystallite size in time of asdepo according to the grain size of powder. Irregular strain does change on the other hand, and it was shown that, up to 1.8 μm, strain decreased as injection grain size increased. However, it was shown in 2.6 μm that strain increased to the contrary. In 2.8 μm, films are thought to have been damaged heavily because it was hard to form films. In the area of 1.8 μm or less, in the meantime, it was found that films of less strain could be obtained by increasing the grain size. Comparison of these results with the film grain size after heat treatment brought the result that the grain growth is promoted after heat treatment in the asdepo films with less strain. It was also shown that the crystallite size after heat treatment is related to the grain size of film. This made us think that area of less strain in film formation worked as a core under heat treatment, thus promoting the crystallite size and grain growth.

Table 4.Crystallite size and irregular strain by formula of Hall

0.5μm size	ε [nm]		η	
heat treatment	asdepo	600℃	asdepo	600℃
PZN-PZT	7.1	8.2	3.8	2.8
BZ calcination	6.5	9.1	3.1	2.4
PZBS calcination	6.7	9.7	3.1	2.4

1.8μm size	ε [nm]		η	
heat treatment	asdepo	600℃	asdepo	600℃
PZN-PZT	6.8	10.1	3.2	1.6
BZ calcination	8.6	13.0	2.5	1.1
PZBS calcination	9.2	20.1	2.5	0.7

2.6μm size	ε [nm]		η	
heat treatment	asdepo	600℃	asdepo	600℃
PZN-PZT	-	-	-	-
BZ calcination	7.8	11.3	2.6	1.6
PZBS calcination	7.5	13.1	2.8	1.8

4. Conclusion

For the purpose of realizing superior ferroelectric properties with less strain and defect on lattice in the heat treatment at lower temperatures in the production of ferroelectric thick films by AD method, we studied the effects by adding auxiliary agents to injection powder and the effects by grain sizes. As a result, ferroelectricity of AD films was found to improve by adding low melting point auxiliary agents and using the powders calcined at appropriate temperatures. It was also found to improve by increasing the grain size of injection powder to an appropriate level. Optimized conditions brought about good ferroelectric properties; such as 25.4 μC/cm2 (63% of sintered film, calcined powder added with low melting point glass) of Pr in the heat treatment at 600°C, and 38.0 μC/cm2 (95% of sintered film, calcined powder added with Bi_2O_3-ZnO) of Pr in the heat treatment at 700°C.

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