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Processing of $Sr_{0.3}Ba_{0.7}Nb_2O_6$ thin film by sol-gel-casting

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$Sr_xBa_{1-x}Nb_2O_6$ (SBN100x) ceramics have been attracting attention because of their electrooptic , pyroelectric and piezoelectric properties. In this paper , SBN30 thin film with good dielectric property was deposited with a novel process of sol-gel-casting. This process includes preparation of precursor solution or sol followed by the dispersion of oxide powder to obtain a good slurry. Precursor film was spin-coated on the $Pt/Ti/SiO_2/Si$ substrate from this slurry. Precursor film was formed by the gelation of precursor sol. Ceramic film was deposited by annealing the precursor film at relatively low temperature where the precursor gel was crystallized. This paper described the optimum condition for the sol-gel-casting of SBN30 thin film.

Key words: $Sr_{0.3}Ba_{0.7}Nb_2O_6$, thin film , sol-gel-casting, dielectric property

1 . Introduction

Strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$; SBN100x) ceramics have been investigated widely because of their electrooptic, pyroelectric and piezoelectric properties. These properties of SBN single crystals are compared with other ferroelectric ceramics, which are consisted of a lead and other oxides. However, large and pure SBN single crystals are difficult to prepare because they melt incongruently. On the other hand, SBN ceramics are promising for various applications because of their low cost and easy fabrication. SBN ceramics have been prepared by sintering the oxide powders at about 1400 ℃. Nishiwaki et al. prepared SBN30 ceramic which was promising for an infrared sensor by a conventional sintering process with a sintering aid of V_2O_5 at relatively low temperature of 1200℃[1,2]. In addition, the recent demand for thin film processing has been increasing, because thin films show superior properties compared with the bulk ceramics. Therefore, various techniques, including sol-gel method, pulsed laser deposition and so on, have been investigated for a deposition of SBN thin films[3,4]. However, the compositions of the SBN thin films prepared in the previous papers were in the range from SBN50 to SBN60. These compositions are difficult to apply in a practical use because of their low curie temperatures. In addition, SBN30 thin film with large grain size and good electrical properties is very difficult to deposite, especially below 1000 ℃.

In this paper, SBN30 thin film which shows a high curie temperature of about 180 ℃ and therefor is promising for a infrared sensor, is deposited by a new method of sol-gel-casting. Sol-gel-casting is a novel process for a low − temperature deposition of oxide thin film which includes preparation of a well-dispersed slurry of fine powders in a sol-gel derived precursor solution followed by the casting and annealing of the precursor film. This process is suitable, especially for the SBN thin films, because large grain size is essential to obtain SBN30 film with good electrical properties[2]. This paper describes the effect of preparation conditions and V_2O_5 addition on the crystallization behavior and dielectric properties of the SBN30 thin film with a sol-gel-casting.

2 . Experimental Procedure

SBN30 oxide powder used for a slurry was prepared by a conventional solid-solid reaction. Strontium carbonate, barium carbonate and niobium pentaoxide were used as starting materials. These raw materials were mixed for 24h by ball-milling using zirconia ball (2mm) and ethanol as a solvent. This mixed powder was calcined at 1100℃ for 6h followed by a ball-milling for 72h to mix the sintering aid of V_2O_5 up to 3 mol%. The resultant powder had average particle size of 0.6 μ m.

Precursor solution of SBN30 was prepared from strontium and barium metal, and niobium

chloride. 2-metoxyethanol was used as a solvent. At first, niobium chloride was dissolved in 2-metoxyethanol and refluxed for 1h with ammonia gas flowing to prepare a niobium precursor solution. On the other hand, Sr－Ba precursor solution was prepared by refluxing the Sr and Ba metal for 1h in a 2-methoxyetanol under a dry nitrogen gas atmosphere. SBN30 precursor solution was prepared by mixing and refluxing the Nb precursor solution and Sr － Ba precursor solution. SBN30 precursor solution with 0.1M or 0.2M concentration was used after the filtration to remove NH_4Cl.

SBN30 slurry was prepared by dispersing the SBN30 powder ultrasonically into a SBN30 precursor solution. Precursor film was spin-coated onto a Pt(111)/Ti/SiO_2/Si substrate (2500 rpm for 30 seconds) from SBN30 slurry. The deposited films were dried for 30 min. at room temperature in an air, followed by the pre-annealing at 350℃ for 15 min. with heating rate of 10℃/min. This process was repeated 5 times to increase the film thickness. After 5 layers deposition, the films were sintered at 900℃ for 8 or 12h with heating rate of 10℃/min(Fig.1).

The effect of slurry preparation condition was estimated by oxide powder concentration and oxide powder ratio, described by the following equations:

$$\text{Oxide powder concentration} = (A+B)/C \quad (kg/dm^3)$$

$$\text{Oxide powder ratio} = A/(A+B) \quad (wt\%)$$

where, A is oxide powder weight used for a slurry preparation, B is oxide powder weight derived from precursor solution and C is slurry volume, respectively.

4 types of slurries were prepared with different oxide powder concentration and/or ratio [(0.27 kg/dm^3) and 73.2 (wt%), 0.23 (kg/dm^3) and 83.2 (wt%), 0.45 (kg/dm^3) and 83.2 (wt%), 0.41(kg/dm^3) and 90.2 (wt%)] . The deposited films were characterized by X-ray diffractometry (XRD) using Cu-k α radiation. Film thickness and surface morphology were observed by SEM. The dielectric properties of the films were measured by LCR meter (HP － 4284) at room temperature using gold as a top electrode.

3 . Results and Discussion

3.1 Crystallization behavior and thickness

Fig.2 shows XRD patterns for SBN30 oxide powder used for a slurry preparation and the precursor powder derived from SBN30 precursor solution, calcined at 800℃ for 2h. SBN30 oxide powder was mainly consisted of SBN30 phase with a faint amount of $BaNb_2O_6$(BN) phase. On the other hand, SBN30 precursor powder crystallized into single phase SBN30 at 800℃.

The resultant films sintered at 900 ℃ showed different film thickness, depending on the preparation condition of slurries. Thickness for the film with different oxide powder concentration of 0.23 (kg/dm^3) , 0.27(kg/dm^3) , 0.41(kg/dm^3) and 0.45 (kg/dm^3) was 2.7 μm, 2.9 μm, 3.3 μm and 4.5 μm, respectively.

3.2 Sol-gel-casting with no additive

XRD patterns for the resultant films were almost same as that for the oxide powder used for a slurry preparation. This result indicates that no BN phase was formed during sintering. In addition, dielectric properties of these films could not be measured except for the film with a oxide powder concentration of 0.45kg/dm^3 and a oxide powder ratio of 83.2 wt%, sintered at 900℃ for 8h. This result suggests that the low oxide powder concentration for the slurry resulted in the low green density of the precursor film, leading to the insufficient densification of the resultant films. On the other hand, relatively dense film was obtained for the precursor film with a low oxide powder ratio if the oxide powder concentrations were high enough because sol-gel derived particles were precipitated at the interstitial sites of the oxide powders, leading to the higher density of the precursor film. However, the electrical properties were very poor (ε_r=29.4 and $\tan\theta$=0.151) even for this film. This ascribed to the poor sinterability for the precursor films below 900℃. Therefore, addition of sintering aid was essential for the low-temperature processing of the SBN30 film.

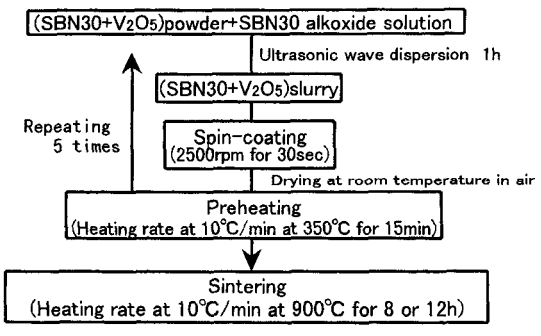


Fig.1 Flow chart for film deposition by sol-gel casting

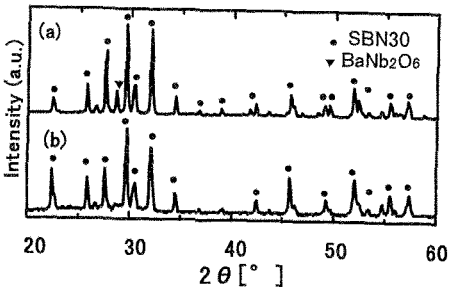


Fig.2 XRD patterns for (a)SBN30 oxide powder and (b)SBN30 aikoxide derived oxide powder calcined at 800℃

3.3 Sol-gel-casting with V_2O_5 additive

Figures 3 and 4 show the effect of soaking time on the grain growth of the resultant films sintered at 900 ℃. Namely, change in the longitudinal particle size and aspect ratio with soaking time were shown in Fig.3 and 4, respectively. In these figures, the particle size and aspect ratio were postulated as 0.6 μm and 1, respectively, corresponding to the calcined oxide powder.

Figure 3 shows that grain growth occurs if the oxide concentration is high. However, the grain growth hardly occurred when the precursor film had low oxide powder concentration (0.23 and 0.27kg/dm^3). This ascribed to the lower green density for the precursor film, whereas the maximum of the aspect ratio in Fig.4 could not be explained.

Figure 5 shows XRD patterns for the films deposited from different slurries with 3mol% V_2O_5, sintered at 900℃ for 12h. This figure indicated that a new BN phase was formed at low oxide powder concentration and low oxide powder ratio. Newly formed BN phase could be ascribed to the inhomogeniety of the composition due to the liquid phase formed during sintering. On the other hand, BN phase was not formed in the films with higher oxide powder concentration because almost all sol-gel derived particle might be consumed for the grain growth of SBN30 oxide powder.

Table I Dielectric properties for SBN30 films sintered at 900℃ with 3mol% V_2O_5 sintering aid

Oxide powder concentration(kg/dm^3)		0.28	0.24	0.48	0.44
Oxide powder ratio (wt%)		71.2	83.2		90.8
8h	dielectric constant	—	—	257	—
	dielectric loss	—	—	0.099	—
12h	dielectric constant	—	—	264	166
	dielectric loss	—	—	0.064	0.206

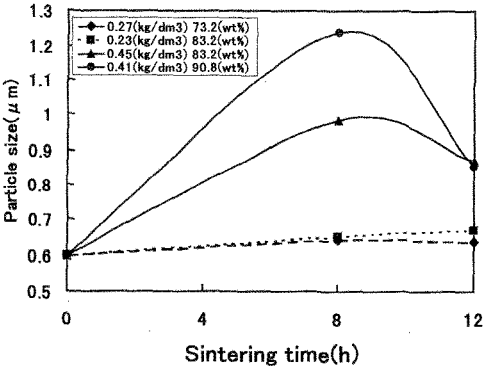


Fig.3 Chage in longitudinal particle size with sintering time

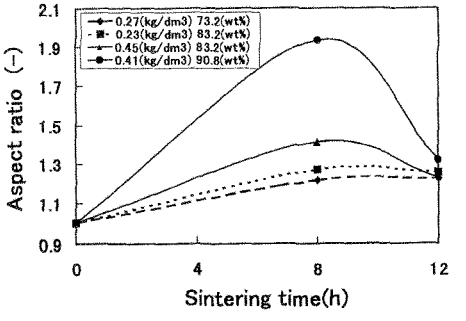


Fig.4 Change in aspect ratio with sintering time

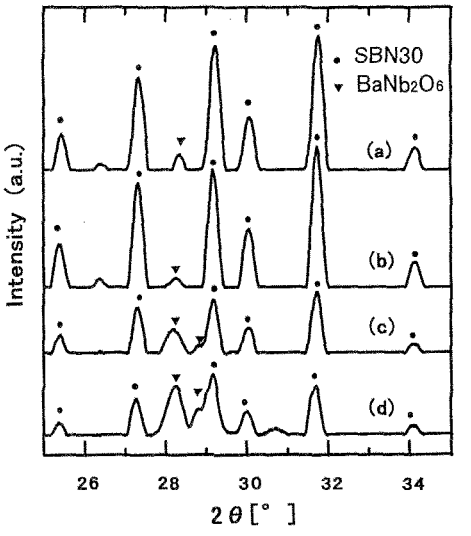
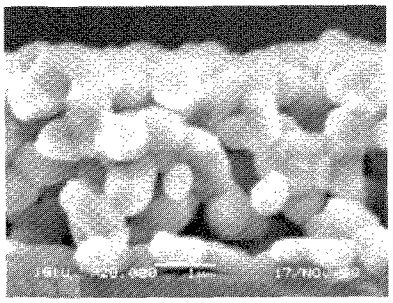


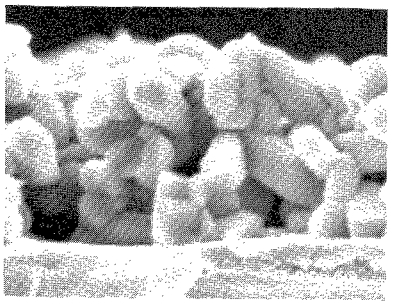
Fig.5 XRD patterns for films deposited from different slurries with 3 mol% V_2O_5 sintered at 900℃ for 12h. Oxide powder concentration and ratio for each films was (a)0.41kg/dm^3 90.8wt%, (b)0.45kg/dm^3 83.2wt%, (c)0.23kg/dm^3 83.2wt%, (d)0.27kg/dm^3 71.2wt%.

Table I lists the dielectric properties of the resultant films. From this table, it was obvious that the dielectric properties of films with low oxide powder concentration could not be measured even though the 3 mol% V_2O_5 addition. This also may

be ascribed to the lower green density of the precursor films, as well as the increased amount of the BN phase in the film. On the other hand, SBN30 films with high oxide powder concentration exhibited relatively good dielectric properties. This suggested that V_2O_5 additive improved the sinterability of the SBN30 films to obtain dense films with the good electrical properties. In addition, higher dielectric constant for the films with oxide powder concentration of 83.2 wt% was ascribed to the large grain size of the resultant films.(Figs. 3 and 4).



(a)0.45(kg/dm^3)、83.2(wt%)、
sintered at 900℃ for 12h



(b) 0.41(kg/dm^3)、90.8(wt%)、
sintered at 900℃ for 8h

Fig.6 SEM images for cross sections of SBN30 films

Figure. 6 shows the cross sections of SEM images for the SBN30 films. Fig.6 (a) is for the image of film with oxide powder concentration of 0.45 (kg/dm^3) and oxide powder ratio of 83.2 (wt. %) sintered at 900℃ for 12h, corresponding to the highest dielectric constant. On the other hand, Fig. 6 (b) is for image of the film with oxide powder concentration of 0.41 (kg/dm^3) and oxide powder ratio of 90.8 (wt. %), sintered at 900℃ for 8h, corresponding to the film of which dielectric property could not be measured because of the leakage current. From these images, large aspect ratio of the film resulted in the lower density, leading to the lower film quality. As a result, the electrical properties of the SBN30 films prepared by the sol-gel-casting were largely affected by the preparation conditions for the slurry and the amount of V_2O_5 additive.

4. Conclusions

In this paper, effects of preparation conditions for slurry and the addition of sintering aid on the densification and dielectric properties of SBN30 films which were deposited by the sol-gel-casting. As a result, followings were concluded:

(1) For the SBN30 films without sintering aid, oxide powder concentration and ratio had large effect on the densification of the resultant films. Relatively dense films were obtained if the oxide powder concentration was high and oxide powder ratio was low.

(2) The dielectric properties of the SBN30 films without sintering aid were very poor, showing that sintering aid was essential for the dense SBN30 film with good electrical properties.

(3) For the SBN30 films with 3mol% V_2O_5, dense SBN30 films with relatively good electrical properties were deposited if the oxide powder concentration was high and oxide powder ratio was low. Prolonged sintering was effective for the grain growth and lower aspect ratio, leading to the improved dielectric properties of the resultant films.

(4) Dense SBN30 film with good dielectric properties of $\varepsilon_r = 265$ and $\tan\delta = 0.066$ was successfully deposited at 900℃ for 12h from precursor film with oxide powder concentration of 0.45(kg/dm^3) and oxide powder ratio of 83.2(wt%)

This paper showed that a new process of sol-gel-casting is very promising for a low-temperature processing of ceramic thin film with thickness below 10 μm but above 1 μm, which is very difficult by the conventional film deposition method. However, further improvement of slurry preparation condition is essential for the low-temperature processing of SBN30 film.

Reference

[1]S. Nishiwaki , J. Takahashi and K. Kodaira , Jpn. J. Appl. Phys.,33,5447－5481(1994)

[2] S. Nishiwaki , J. Takahashi and K. Kodaira, J.Ceram.Soc.Jpn., 103, 1246－1250(1995)

[3]M. Nakano, H. Tabata, K. Tanaka, Y. Katayama and T. Kawai, Jpn. J. Appl. Phys.,36, 1331－1332(1997)

[4]W. Sakamoto, T. Yogo, K. Kikuta, K. Ogiso, A. Kawase, and S. Hirano, J. Am. Ceram. Soc.,79, 2283－2288(1996)

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