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LOW-TEMPERATURE PROCESSING OF BARIUM TITANATE THIN FILM BY SOL-GEL-CASTING

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This paper focuses on a new class of processing for low-temperature preparation of ceramic thin films. In this study, a ferroelectric barium titanate thin film was successfully prepared at low temperatures above 700 ºC. We proposed a new processing method as "Sol-Gel-Casting" which includes dispersion of fine particles in the alkoxide-derived precursor solutions followed by the casting and annealing at relatively low temperatures. This process resulted in the relatively dense barium titanate thin films with ferroelectricity at above 700 ºC. The dielectric properties of the resultant thin films depended on the processing conditions which controlled the microstructure of the film. The key to deposit ferroelectric thin films at low temperatures was how to control the agglomeration of the particles in the precursor slurry to prepare a slurry with high solid content.
Key words: Sol-Gel-Casting, Barium Titanate, Low-Temperature Processing, Thin Film, Ferroelectricity

I. Introduction

Ceramic thin films with perovskite structure are of renewed interest for microelectronic application, including ferroelectric random access memory (FRAM), dynamic random access memory (DRAM), and capacitors integrated onto a silicon wafer[1]. On the other hand, recent advancement in micromachine requires a high performance microactuator. For this purpose, a new class of processing for low-temperature deposition of piezoelectric ceramic thin films with several micrometer thickness has been expected to be developed. Therefore, this paper focuses on a new class of processing method for ceramic thin films with several micrometer thickness, which includes dispersion of fine particles in the alkoxide-derived precursor solutions followed by the casting on a substrate and annealing at relatively low-temperatures. This new sol-gel based process has been developed by Sayer et al. to prepare thick lead zirconate titanate (PZT) films with ferroelectric and piezoelectric properties[2]. However in their process, relatively high annealing temperatures of above 650 ºC were required to deposit piezoelectric PZT films. We think that the key to prepare the ferroelectric thin film at relatively low temperatures by this process is how to control the agglomeration of the particles in the precursor slurry to prepare a well dispersed slurry with high solid content. Therefore, we proposed to call this process as a "Sol-Gel-Casting" because this process is consisted of, so called, sol-gel process and "Gel-Casting". Gelcasting[3] is a novel method for molding ceramic powder to form a dense green body, leading to the low-temperature sintering of ceramics.

In this paper, a new class of processing method named "Sol-Gel-Casting" for low-temperature deposition of ferroelectric barium titanate thin films with several micrometer thickness were described. Barium titanate is a very important material as a electronic ceramic especially for a capacitor. Barium titanate (BT) thin films have been prepared by sol-gel method[4], hydrothermal-electrochemical method[5], spray pyrolysis[6] and rf-sputtering[7]. All these films have submicrometer thickness and relatively low relative permittivity. In this study, relatively thick BT films with good dielectric and ferroelectric properties were successfully prepared by the Sol-Gel-Casting at relatively low temperature on a Pt(111)/Ti/SiO_2/ Si(100) wafer.

II. Experimental Procedure

(1) Deposition of Film

Figure 1 shows the flowchart for the preparation of a sol-gel precursor solution and a slurry followed by the spin coating for a sol-gel-casting to form ferroelectric BT thin films. BT precursor sol was prepared by adding water to the BT precursor solution. In the case of the sol-gel-casting, precursor sol should be stable to the humidity to avoid gelation of slurry until the precursor film formation. Commercial BT powders (Sakai Chemical Co.Ltd., BT 05 and BT 01) were used as raw materials in this study. Average particle sizes of these powders are 0.5 (BT 05) and 0.1 (BT 01) μ m, respectively. The spin-coated precursor films on the Si wafer were pre-annealed at 350 ºC for 1.5 h to remove the residual organics in the films. Final annealing was carried out up to 900 ºC for 2 h.

(2) Film Characterization

The microstructure of the resultant film was observed by the scanning electron microscope (SEM). Dielectric property of the film was measured by the LCR meter (YHP-4284A). Substrate used in this study was Si(100) wafer with platinum electrode, Ti and SiO_2 buffer layers. Upper electrode used in this study was gold.

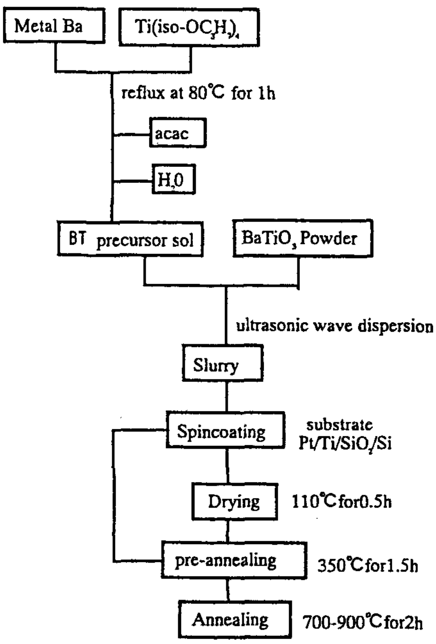

Fig.1. Flowchart for deposition of BT films by Sol-Gel-Casting.

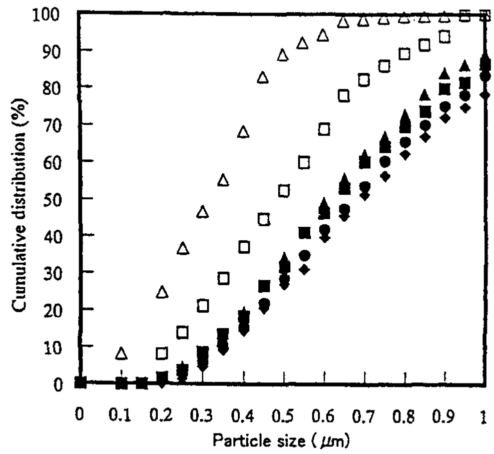

Fig.2. Size distribution ofBTparticles.
(a) after grinding:△, (b)in slurry without dispersant:□, and in slurry with different dispersant of
(c) Polyacrylic Acid (PAA;Mw12000):▲,
(d) PAA(Mw6000):■,
(e) AmmoniumPolyacrylate (PAA/NH4OH):●
(f) SodiumPolyacrylate (PAA/Na):◆

III. Results and Discussion

(1) Characterization of Slurry

As already described, the key to deposit the ferroelectric thin film at relatively low temperatures by the sol-gel-casting is how to control the agglomeration of the particles in the precursor slurry to prepare a well dispersed slurry with high solid content. Therefore, size distribution of the BT 05 powder in the slurry with or without dispersants were measured and shown in figure 2. The solid content for this slurry was 74 weight percent. It is obvious that the 50 % diameter for BT 05 powder after grinding was less than 0.5 μm. However in the slurry, average particle size was about 0.5 μm. This suggested that BT particles in the slurry coagulated with each other. Therefore, different type of dispersants were added to the slurry to obtain well dispersed slurry. As a result, average particle size of the BT particles in the slurry increased by the addition of any kinds of dispersants used in this study (Fig. 2). Accordingly, we did not use the dispersant in this study.

The temperature dependence of relative permittivity for the sol-gel-casted BT films annealed at 700 ºC was measured and shown in figure 3. Relative permittivity of the resultant BT films at room temperature depended upon the film thickness, as shown in the figure 4. In addition, relative permittivity showed maximum at around 110 ºC. This indicated that the sol-gel-casted BT films have curie temperature or ferroelectricity. However, the relative permittivity of the BT film with 4.5 μm thick was only about 450 at room temperature, relatively low compared with the bulk BT ceramic. The dissipation factors of the resultant films were about 0.1 in all case. From the SEM observation of film crosssections, the average thickness for one coating was estimated to be about 0.7 μm. The average film thickness for sol-gel-casting is very thick compared with that for the sol-gel derived thin film. In the case of sol-gel-derived film, the average thickness for one coating is limited to 0.1 μm. We think that the relatively thick film deposition for one coating is the advantage of the sol-gel-casting over the sol-gel processing. We applied hybrid method of sol-gel-casting and sol-gel method to improve the microstructure of the resultant BT film.

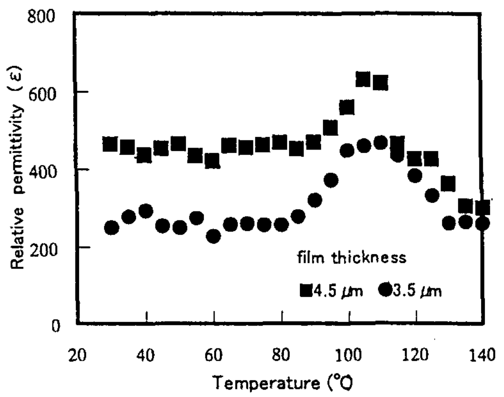

Fig.3. Change in relative permittivity of $BaTiO_3$ films annealed at 700°C with temperature.

(2) Hybrid Method

To increase the film density, hybrid method of sol-gel-casting and sol-gel method have been applied. Figures4 and 5 shows the change in the relative permittivity of the resultant BT films prepared by the hybrid method and annealed at 700 ºC and 800 ºC, respectively. Two types of hybrid methods were applied in this study. One is the hybrid of sol-gel-casting from different slurry consisted of different BT powders with average particle size of 0.1 and 0.5 μ m. This method includes alternative sol-gel-casting from different slurry with 5 coatings for each sol-gel-casting. As a result, film thickness became about 4.5 μ m. The other hybrid method is consisted of sol-gel-casting and sol-gel method. This process also includes alternative sol-gel-casting or sol-gel spin coating with 5 coating for each. In this case, film thickness was about 3.5 μ m, relatively thin compared with that for the hybrid method of sol-gel-casting from different slurry. These results suggested that sol-gel spin coating mainly infiltrated in the pores of the sol-gel-casted film. Therefore, hybrid method of sol-gel-casting and sol-gel method is considered to be better to improve the microstructure of the film. Figure4 confirmed this consideration. Namely, the relative permittivity of the resultant films by the hybrid method was higher than that for the sol-gel-casted BT film with thickness of about 3.0 μ m. In the case of the hybrid film from slurry with different BT particle size, relatively thick film resulted in the increased relative permittivity. On the other hand, hybrid film from sol-gel-casting and sol-gel spin coating also showed increased relative permittivity, even though it had almost same film thickness as that for the sol-gel-casted film from slurry of BT 05 and precursor sol. This showed that the infiltration of sol-gel-casted film by the sol-gel method was very effective to prepare the dense film without increasing film thickness. If the BT films were annealed at 800 ºC, films became more dense to increase the relative permittivity for all case, probably because by the viscous sintering of the residual amorphous sol-gel precursor (Figure 5). High-temperature annealing above 800 ºC leads to the degradation of the substrate, resulting in the reduced dielectric property of the BT film.

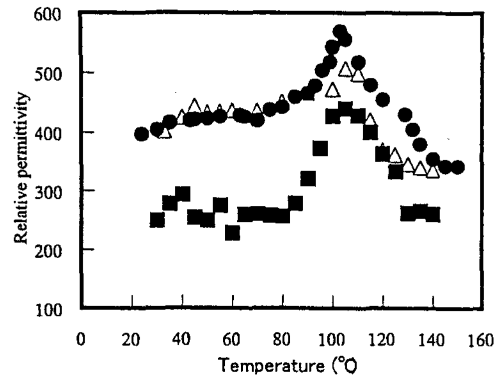

Fig.4. Change in relative permittivity of $BaTiO_3$ films annealed at 700°C with tempwrature.
BT films were deposited by BT05 sol-gel casting(■), hybrid method of BT05 and BT01 sol-gel casting(△), and hybrid method of BT05 sol-gel-casting and sol-gel method(●). (Solid content of the slurry was 72wt.%)

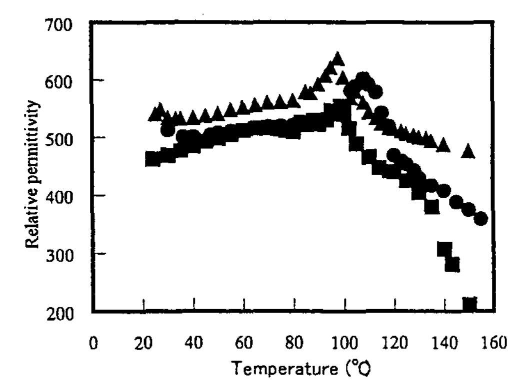

Fig.5. Change in relative permittivity of $BaTiO_3$ films annealed at 800°C with tempwrature.
BT films were deposited by BT05 sol-gel casting(■), hybrid method of BT05 and BT01 sol-gel casting(▲), and hybrid method of BT05 sol-gel-casting and sol-gel method(●).(Solid content of the slurry was 72wt.%)

From these results, preparation of well dispersed slurry with high solid content is considered to be essential to improve the sol-gel-casting. Effect of solid content on the electrical properties of the resultant films are obvious. Figure6 shows the temperature dependence of the relative permittivity of hybrid BT films from slurry with solid content of 46 wt.% and annealed at 800 ºC. In this case, relative permittivity of the resultant film was not so high and the curie temperature did not observed. In addition, hybrid films from slurry with low solid content showed large leakage current and the capacitance of these films could not be measured. This confirmed the above discussion.

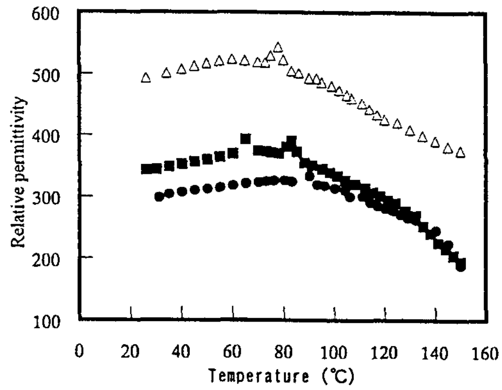

Fig.6. Change in relative permittivity of $BaTiO_3$ films annealed at 800°C with tempwrature. BT films were deposited by BT05 sol-gel casting(■), hybrid method of BT05 and BT01 sol-gel casting(△), and hybrid method of BT05 sol-gel-casting and sol-gel method(●). (Solid content of the slurry was 46wt.%)

(3) Ferroelectricity

Figure7 exhibits the P-E hysteresis loops for the BT thin films prepared by the sol-gel-casting, showing the relatively good ferroelectricity. Among them, BT thin films deposited from slurry of BT05 powder exhibited better results. This result is good agreement with the temperature dependence of relative permittivity for the sol-gel-casted BT thin films (Figs. 3,4). If compared with the relative permittivity, BT films deposited by the hybrid method showed higher values, because of the improved microstructure of the film. However, the ferroelectricity of resultant BT thin film was mainly affected by the amount of tetragonal BT particles derived from BT05 powders in the slurry. Therefore, preparation of good slurry with higher solid content of tetragonal BT powder to deposit ferroelectric BT thin film on Si wafer at relatively low temperatures.

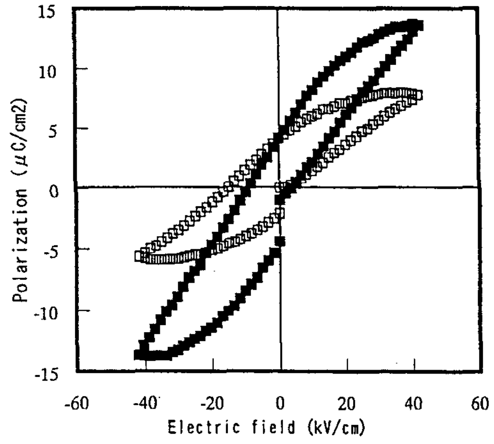

Fig.7. P-E hysteresis loop of $BaTiO_3$ films annealed at 800℃. BT films were deposited by BT05 sol-gel casting (■), and hybrid method of BT05 and BT01 sol-gel casting (□). (Solid content of the slurry was 72wt.%)

IV. Summary

In this paper, a new class of processing for low-temperature deposition of barium titanate thin films with ferroelectricity was demonstrated. This process included dispersion of barium titanate fine particles in the alkoxide-derived precursor sol followed by the casting on a substrate and annealing at relatively low-temperatures. Sol-gel derived ultrafine particles infiltrated in the pores of the densely packed crystalline particles to form relatively dense films with ferroelectricity by annealing above 700 ºC. The key to deposit the ferroelectric thin film at relatively low temperatures by the sol-gel-casting is to prepare a well dispersed slurry with high solid content. Sol-gel-casting is very promising for a new class of processing to prepare ceramic thin films above 1 μm thick at relatively low temperatures. Further investigation is essential for the dispersant and precursor sol, which crystallizes at low temperatures, to deposit high performance ceramic thin films by the sol-gel-casting. This paper exhibited the possibility and important factors of the sol-gel-casting for the case of barium titanate thin films.

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