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Preparation and Properties of Ferroelectric BaTiO3 Thin Films on Pt Substrate by Sol-Gel Method.

Takashi Hayashi, Hiroshi Takahashi and Takaaki Sakai.

Department of Materials Science and Ceramic Technology, Shonan Institute of Technology, 1-1-25 Tsujido-Nishikaigan, Fujisawa, Kanagawa 251, JAPAN

ABSTRACT

The preparation of ferroelectric $BaTiO_3$ thin films on Pt substrate by sol-gel method was carried out by two methods ; method A involves heating at 950℃ for 1h in O_2 after repeating the process of dip-coating/preheating at 400℃ for 5 min, and method B involves repeating the process of dip-coating/heating at 850℃ for 1h in O_2. $BaTiO_3$ thin films prepared by method A exhibited poor ferroelectric properties because of relatively porous grain structure with grain sizes of 70-150 nm.

On the other hand, $BaTiO_3$ thin films with a thickness of 450 nm prepared by method B showed dense grain structure with grain sizes of average 50 nm and exhibited ε_r of 830, tan δ of 0.04, Pr of 3.8 $\mu C/cm^2$, Ec of 20 kV/cm at room temperature. And , the dielectric constant -temperature characteristic curve of BaTiO3 thin films gave a broad cuire peak at around 70℃.

1. Introduction

$BaTiO_3$ thin films have been expected for application to multilayer hybrid capacitors, pyroelectric detectors, thermistors and capacitor of dynamic random access memories and nonvolatile random access memories(NvRAM's). Many studies on the preparation of $BaTiO_3$ thin films by vacuum evaporation , rf sputtering, chemical vapor deposition, activated reactive evaporation and sol-gel method have been carried out. And , the ferroelectricity of $BaTiO_3$ thin films prepared on $Pt/SiO_2/Si$ substrates at 650℃ by sol-gel method was observed. But, the dielectric properties of the thin films were inferior to ceramics and a single crystal of $BaTiO_3$. Moreover, in the dielectric constant - temperature characteristic curves of sol-gel derived $BaTiO_3$ thin films, no anomaly related to curie peak was seen at about 120℃. It was considered to be attributable to the stress from the substrates , low crystallinty and domain pinning due to fine grains

In this work , in order to promote further grain growth of $BaTiO_3$ grains, thin films were prepared on Pt substrates at a higher temperature of 850℃ by sol-gel method . Their crystallinity , surface morphology and electrical properties were invetigated.

2. Experimental

$BaTiO_3$ thin films were prepared on Pt substrate by two methods using metal alkoxides ; method A involves heating at 950℃ for 1h in O_2 after repeating the process of dip-coating/preheating at 400℃ for 5 min, and method B involves repeating the process of dip-coating / preheating at 120℃ for 1h in a flow of O_2/water vaper mixed gas, followed by heating at 850℃ for 1h in O_2(Fig.1). The final concentration of $BaTiO_3$ precursor solutions was about 0.13mol/L. Film thickness was controlled by repeating the cycles of coating/heating process. The speed of dip-coating was 1.5mm/s.

The crystalline phases of thin films were identified by X-ray diffraction (XRD). The microstructure of the thin films was observed with a field-emission scanning electron microscope (FE-SEM). Gold electrodes of 0.2mm diameter

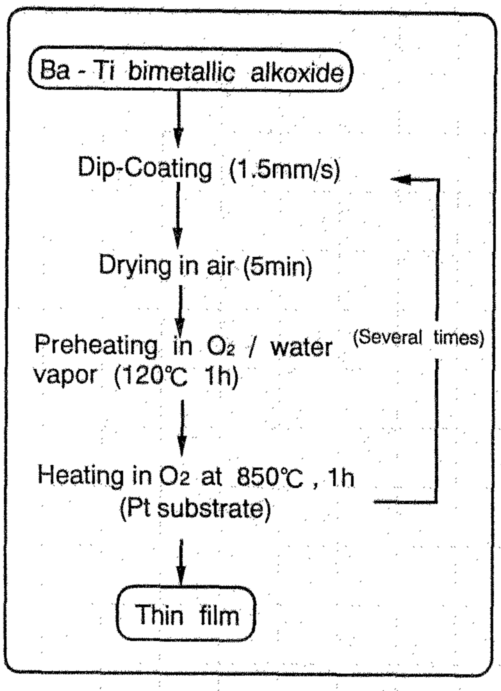

Fig.1 Flow diagram for the sol- gel processing of $BaTiO_3$ thin fims.

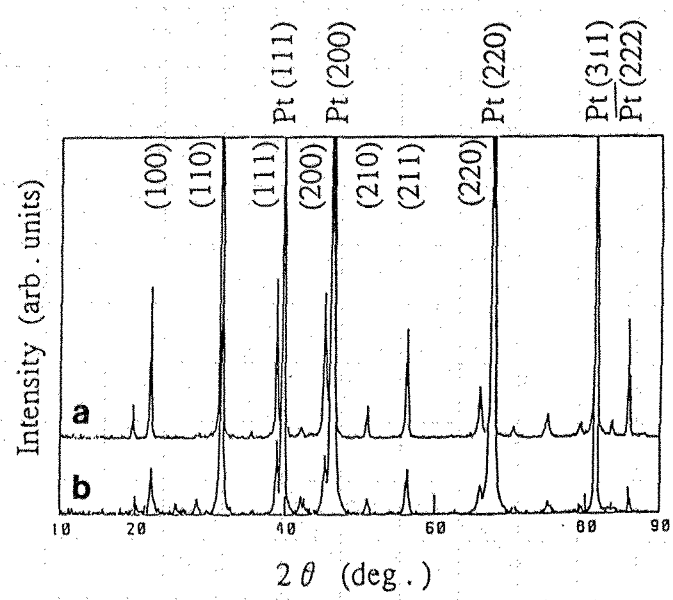

Fig.2 XRD patterns of $BaTiO_3$ thin films prepared by method A:a and method B:b.

were vacuum- deposited through a mask onto the surface of $BaTiO_3$ thin films. Values of the dielectric constant (ε_r) were mesured in the range from room temperature to 200℃ with an impedance analyzer (YHP - 4192A) at 1 kHz using a micromanipulator. P-E hysteresis loops were also obtained for $BaTiO_3$ thin films using a RT-66A (RADIANT TECHNOLOGIES, Inc.) at 1 kHz. Applied voltage was 10V.

3. Results and Discussion

3.1 Microstructure and Crystal Structure

Figure 2 shows XRD patterns of $BaTiO_3$ thin films prepared by methods A and B. $BaTiO_3$ thin films prepared by these methods exhibited no preferred orientation. The $BaTiO_3$ thin films with a thickness of 290 nm prepared by method A showed a higher crystallinity than those of method B with a thickness of 450nm. Figure 3 shows FE-SEM micrographs of surfaces of $BaTiO_3$ thin films prepared on Pt substrate. $BaTiO_3$ thin films prepared by method A exhibited

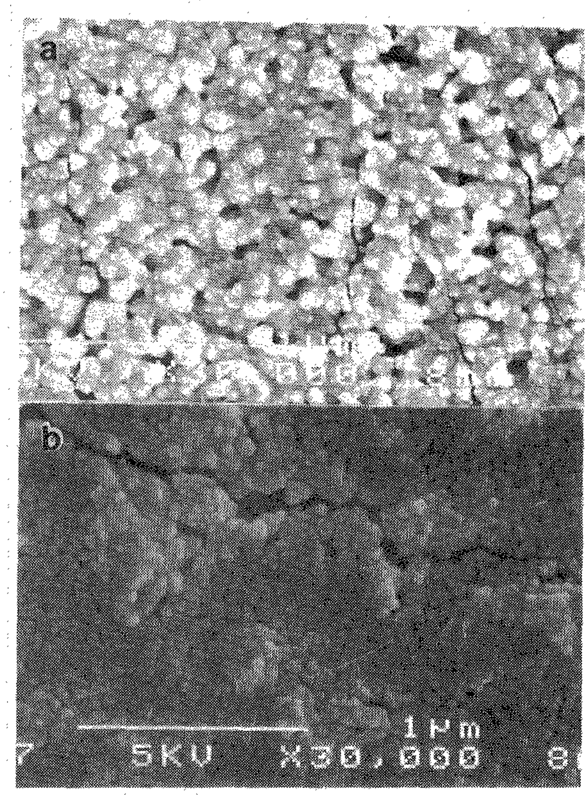

Fig.3 SEM micrographs of $BaTiO_3$ thin films prepared by method A:a and method B:b.

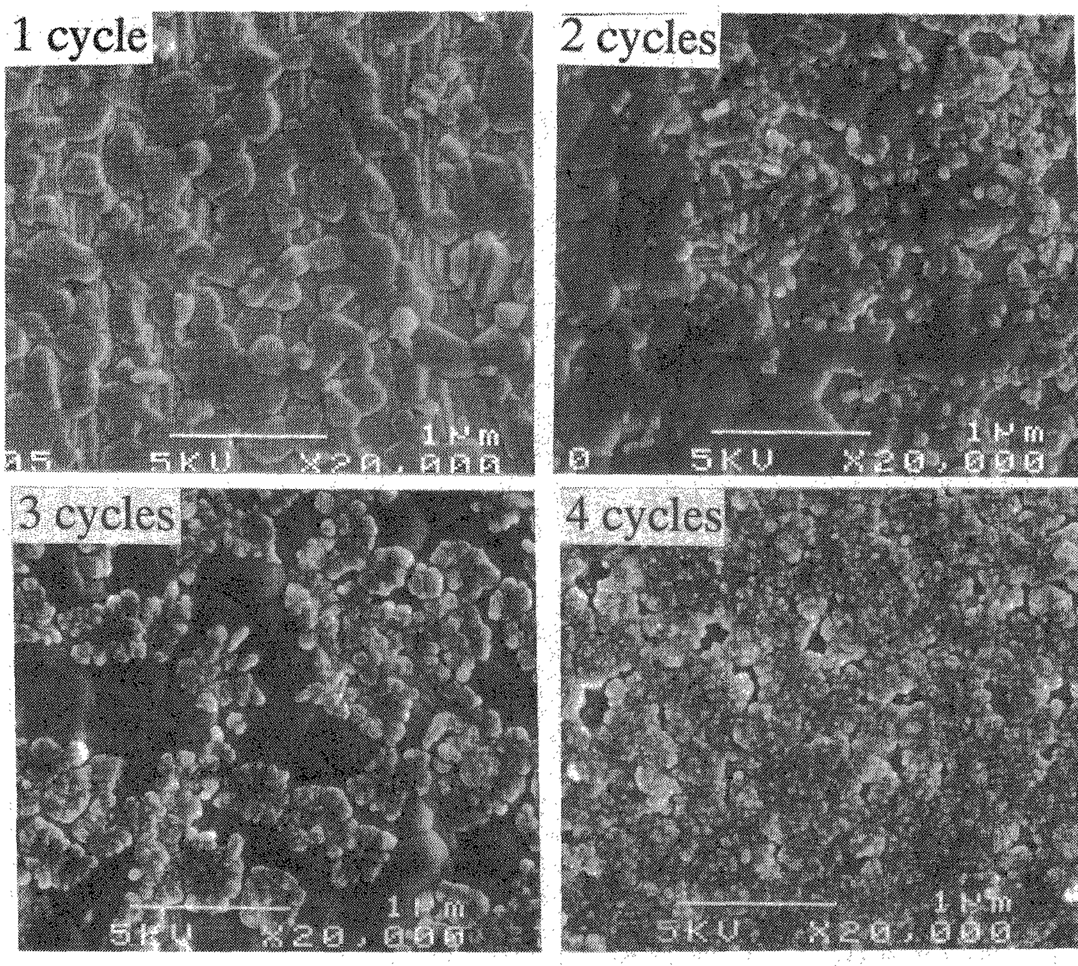

Fig.4 SEM micrographs of $BaTiO_3$ thin films with various cycles of coating/heating process prepared by method B.

somewhat porous grain structure with grain sizes of about 70-150 nm , while those prepared by method B showed dense grain structure with grain sizes of average 50 nm. Figure 4 shows FE-SEM micrographs of surfaces of $BaTiO_3$ thin films with various cycles of coating/heating process. The microstructure of single-layer films showed inhomogeneous texture with large grains of about 400 nm. Increasing with the cycles of coating/heating process, fine grains as small as about 100 nm formed among large $BaTiO_3$ grains and, finally, thin films prepared by multiple coating / heating processes were strongly textured with fine grains. That is, the grain sizes of the top layer of the thin films were always much finer than those of the first coating. Such grain refinement may be due to seeding effect of large grains formed in first layer.

3.2 Dielectric Properties of $BaTiO_3$ Thin Films

$BaTiO_3$ thin films with a thickness of 300 nm prepared by method A exhibited poor ferroelectric properties because of porous grain structure. Figure 5 shows P-E hysteresis loop of the 450 nm thick $BaTiO_3$ films prepared on Pt substrate at 850℃ for 1h by method B. The thin film indicated well-saturated hysteresis loop. The values of remanent polarization , Pr , and coercive field, Ec , were 3.8 $\mu C/cm^2$ and 20kV/cm , respectively. Figure 6 shows the dielectric constant- temperature characteristic curve of

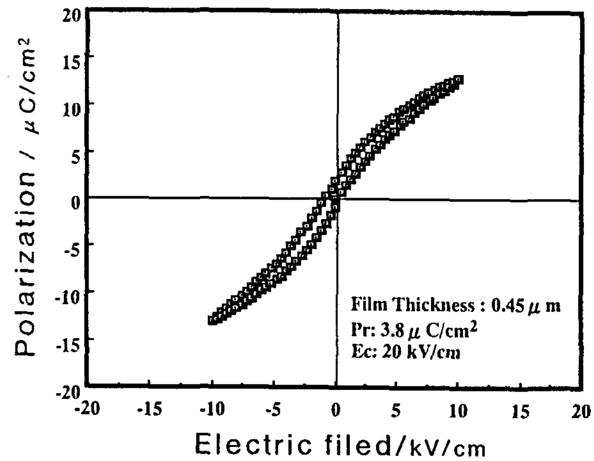

Fig. 5 Ferroelectric hysteresis loop of $BaTiO_3$ thin film prepared at 850℃ for 1h on Pt substrate.

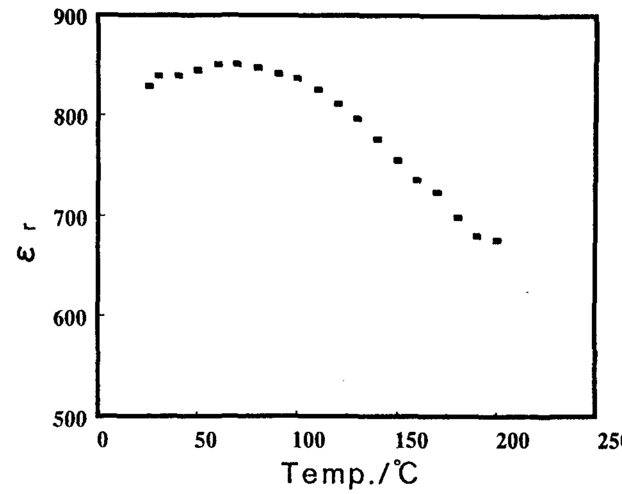

Fig.6 Temperature dependence of dielectric constant of $BaTiO_3$ thin film

$BaTiO_3$ thin films prepared by method B. $BaTiO_3$ thin films exhibited ε_r of about 830 and tan δ of 0.04 at room temperature. And , in this films , the curie point was not seen at around 120 ℃ , however, a broad curie peak was observed at around 70℃.

4. Conclusions

$BaTiO_3$ thin films were prepared on Pt substrates at 850℃ by sol-gel method using metal alkoxide. $BaTiO_3$ thin films consisted of fine grains of about 50 nm and exhibited good crystallinity. The grain sizes of the top layer of the thin films were always much finer than those of the first coating. The 450 nm thick $BaTiO_3$ films exhibited ε_r of 830 , Pr of 3.8 $\mu C/cm^2$ and Ec of 20kV/cm. A broad curie peak was seen at around 70℃ on the dielectric constant - temperature characteristic curve of $BaTiO_3$ thin films.

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