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## Study of Internal Friction on Size Effect in BaTiO<sub>3</sub> Thin Films

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**Abstract.** The size effect on the phase transition was studied by a flexible resonance method in BaTiO<sub>3</sub> thin films. The different transitional behaviors were observed in the measurements of internal friction in the films with different thickness. The stress in the films plays an important role in size effect of thin film. It was also confirmed by the measurement of Raman spectrum.

### 1. INTRODUCTION

Ferroelectric thin film has excellent optical, piezoelectric and pyroelectric properties[1][2][3]. BaTiO<sub>3</sub> is a typical ferroelectric material with the useful properties of high dielectric constant and spontaneous polarization. So, it has received much attentions in recent years. The size effects in ferroelectric materials have been found and studied since Kanzig et al [4][5] studied the dielectric properties of ferroelectric ultrafine particles. The interest in size effects has been increased with the development of fabrication and investigation of ferroelectric thin films recently. Kanata et al [6] pointed out that T<sub>c</sub> of BaTiO<sub>3</sub> ceramics decreased with grain size and the dielectric constant  $\epsilon$  had a maximum at 10  $\mu$ m grain size. Kanzig [5] and Surowiak [7] studied the dependence of T<sub>c</sub> or  $\epsilon$  on the grain size in BaTiO<sub>3</sub> fine particles and thin films respectively. However, different researchers had different conclusions about the changes of  $\epsilon$ , P<sub>s</sub> (spontaneous polarization), T<sub>c</sub> and the order of phase transformation with the grain size and thickness. Each worker gave an explanation which emphasized either stress or surface layer corresponding to his experimental results. But a strong theory which can explain all these different experimental phenomena is still needed. BaTiO<sub>3</sub> is a typical perovskite materials. Its simple structure makes it easier for us to grasp the physical essence of a problem. In this paper, we report the measurements of the internal friction and Raman spectrum in BaTiO<sub>3</sub> thin films with different thickness and the size effects in this films are also discussed.

### 2. EXPERIMENTAL

BaTiO<sub>3</sub> thin films were deposited on the Si substrates using RF-magnetic sputtering technique from a ceramic target[8]. The films with different thickness were got by different deposited time and then they were annealed at

800 ° C for half an hour. The average dimension of the grains is about 50 nm. The measurement of internal friction(IF) was formed by a flexible resonance method.

3. RESULTS AND DISCUSSION

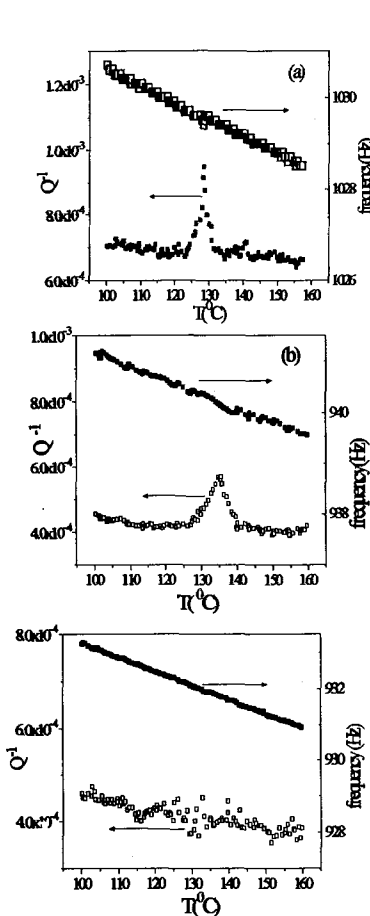


Fig1 (a) 3μm film (b) 5μm film (c) Si substrate

BaTiO<sub>3</sub> undergoes three transitions when it is cooled from high temperature : Cubic - tetragonal - orthorhombic phase at about 120 ° C , 0 ° C and - 80 ° C respectively. B.L.Cheng et al [9] observed three peaks of internal friction and variation of modulus at near the transition temperatures in bulk ceramic BaTiO<sub>3</sub> materials. In order to clarify the size effect on the phase transition in thin films, the internal friction and modulus were measured by a flexible resonance technique in BaTiO<sub>3</sub> thin films with different thickness. A Si plate of 0.18 mm on which BaTiO<sub>3</sub> thin film was deposited with thickness 1μm , 3μm , 5μm , 8μm and 10μm respectively was used. Fig 1 shows the internal friction and modulus of Si substrates with the thickness of 3μm (a), 5μm (b) BaTiO<sub>3</sub> thin film and Si substrate (c) only as a function of temperature. The IF peak appeared at near 120 ° C is associated with the transition from cubic to tetragonal phase . This IF peak showed thermal hysteresis similar to the bulk materials , which indicated that the phase transition in the film has still the characteristic of first order phase transition . The hysteresis temperature is 14°C, 20°C and 22°C respectively in the films with the thickness 1.5 μm, 3μm and 5μm. i.e the film thicker was, the obvious characteristic of first order phase transition had. Usually, a few degrees

difference of IF peak temperature was observed in different measuring cycle . It showed the temperature of phase transformation of the films was less stable. The pumping and heating process during measurements has changed the distribution of the oxygen and the stress in the films. The stability of T<sub>c</sub> for the 5 μm thick was better than that of 3 μm film, which indicated the properties of thicker films were more stable since the ratio of the surface layers was smaller in thicker films. The Curie temperatures of 1.5μm, 3μm and 5μm thick film were 110°C, 127°C and 133 ° C during heating respectively. i.e T<sub>c</sub> decreased with the decreasing of the film thickness. Desu [10] pointed out that

the compressive stress raised the Curie temperature of their films, correspondingly, we presumed that the tensile stress lowered  $T_c$  of our films. The thinner the films was, the larger effects the tensile stress had. To clarify

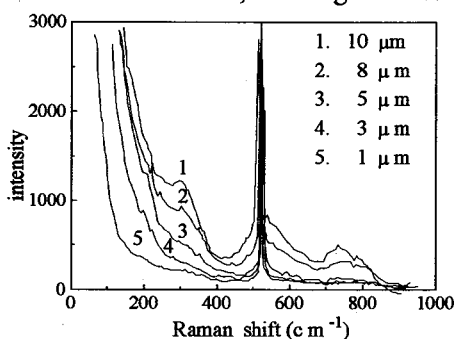


Fig2 Raman spectrum of different thickness  $\text{BaTiO}_3$  thin film on Si substrate

the effect of stress in  $\text{BaTiO}_3$  thin films, Raman spectrum was measured with 488nm radiation on SPEX 1403 spectrometer in  $\text{BaTiO}_3$  thin films. Fig 2 shows the Raman spectra of the films with the thickness of  $1\mu\text{m}$ ,  $3\mu\text{m}$ ,  $5\mu\text{m}$ ,  $8\mu\text{m}$ ,  $10\mu\text{m}$  and similar grain size on Si substrates. Three peaks, around  $300\text{ cm}^{-1}$ ,  $550\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$ , displaying the

characteristic of perovskite  $\text{BaTiO}_3$  film appear for the film thicker than  $5\mu\text{m}$ . The modes around  $300\text{ cm}^{-1}$ ,  $550\text{ cm}^{-1}$ ,  $750\text{ cm}^{-1}$  correspond to the bulk materials  $270\text{ cm}^{-1}$ ,  $520\text{ cm}^{-1}$ ,  $720\text{ cm}^{-1}$  mode respectively. The former two were thought to belong to higher order Raman scattering [11]. The peak around  $720\text{ cm}^{-1}$  might be attributed to A1 and E modes. The frequencies of the peak are  $310\text{ cm}^{-1}$ ,  $300\text{ cm}^{-1}$ ,  $295\text{ cm}^{-1}$  and  $770\text{ cm}^{-1}$ ,  $760\text{ cm}^{-1}$ ,  $745\text{ cm}^{-1}$  for the film thickness of  $5\mu\text{m}$ ,  $8\mu\text{m}$  and  $10\mu\text{m}$ . i.e The shift of frequency was observed with the variation of the film thick. According to the experiments of Taguchi et al[12] and Fujimoto et al[11] on  $\text{PbTiO}_3$  single crystal and  $\text{BaTiO}_3$  thin films, when a hydrostatic press was applied, the peak frequency of Raman spectrum shifted to the lower frequency. we attributed the observed shifts of Raman peaks of the films to higher frequencies compared with bulk materials to tensile stress in the films. The thinner the film is, the more the Raman peaks shift to higher frequencies. Which indicated that tensile stress has more effects in thinner films. The measurements of internal friction and Raman spectrum in  $\text{BaTiO}_3$  thin film indicated that the size effect on phase transition, such as shift of  $T_c$  et al, is attributed to the tensile stress in  $\text{BaTiO}_3$  thin film i.e the stress in film is play an important role in size effect. Fig 3 shows the internal friction and modulus at lower temperature in  $\text{BaTiO}_3$  film with the thickness of  $3\mu\text{m}$  and  $5\mu\text{m}$ . An internal friction peak was found at about 260 K. It was due to the transition from tetragonal to the orthorhombic phase.

#### 4. Conclusion:

Internal friction and modulus associated with the phase transition were measured in  $\text{BaTiO}_3$  thin film with different thickness. Observed different transition behaviors were attributed to the different tensile stress in the films.

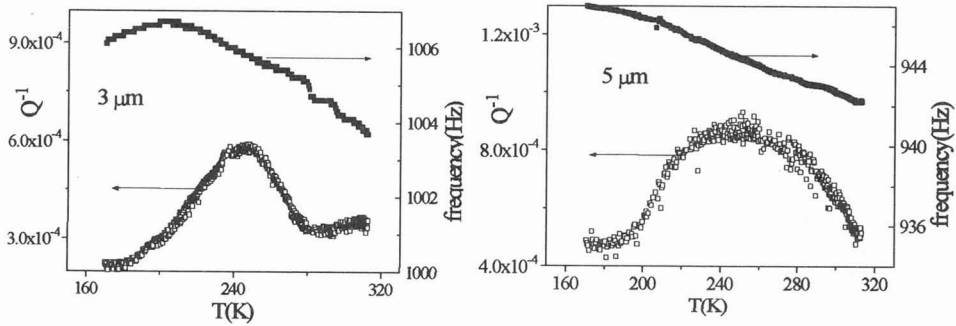


Fig 3. Low temperature  $Q^{-1}$  and modulus of  $BaTiO_3$  films of different thickness

#### Acknowledgments

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