Journal of the European Ceramic Society **19** (1999) 1477–1480

PII: S0955-2219(98)00457-9
0955-2219/99/$ - see front matter

Specific Heat in Ferroelectric $BaTiO_3$ Epitaxial Thin Films

A. Onodera,[a]* Y. Kawamura,[a] T. Okabe[b] and H. Terauchi[b]

[a]Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan
[b]Department of Physics, Kwansei-Gakuin University, Nishinomiya 662, Japan

Abstract

The specific heat (C_p) *of thin epitaxial films of* $BaTiO_3$ *(thickness of 2000 and 60 Å) on* $SrTiO_3$ *substrates was studied by a.c. calorimetry. A broad anomaly in* $BaTiO_3$ *films was found, which is quite different from a sharp anomaly observed at 403 K* (T_c) *in bulk* $BaTiO_3$ *crystal. The anomalies in* C_p *were observed at about 443 K for the film with 2000 Å thickness, and at 690 K for the film with 60 Å thickness. No other anomaly in* C_p *was observed in the low-temperature region down to 80 K. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: films, ferroelectric properties, thermal properties, $BaTiO_3$ and titanates, perovskites.

1 Introduction

Oxide perovskites show a variety of interesting properties, such as ferroelectricity, piezoelectricity, electrooptic effects and high-T_c superconductivity.[1] Barium titanate, $BaTiO_3$, is a typical ferroelectric material used in many practical applications in the forms of ceramic and single crystals. It undergoes successive phase transitions to three phases as the temperature is lowered: first from the prototype cubic perovskite to tetragonal at 403 K (T_c), then to orthorhombic at 278 K, and finally to a trigonal phase below about 183 K. The ferroelectricity has been observed in the three low-temperature phases.

Recently extensive attention has been paid on ferroelectric thin films, because they are promising materials for functional thin film devices such as surface acoustic wave devices, pyroelectric sensor, electrooptic modulators, ferroelectric memory devices and ferroelectric integrated devices. Many attempts have been done to prepare $BaTiO_3$ films by electron-beam evaporation and r.f. sputtering methods.[2] These as-grown films were usually polycrystalline and did not show any dielectric anomaly in the neighbourhood near 403 K (T_c). Thick films of about 1 μm shows an anomaly at T_c. This suggested the ferroelectric phase was unstable for thin films below about 0·1 μm. However, Slack and Burfoot showed that the thin films of about 0·004 μm thick showed ferroelectric switching behavior in flash-evaporated $BaTiO_3$ films.[3] Tomashpolski *et al.*[4] found that vacuum-deposited films showed sharp dielectric anomaly near 403 K even in the film with 0·023 μm thickness: this anomaly disappeared for films with 0·01 mm. There are still many discrepancies in experimental results and detailed fundamental properties have not been studied yet.

Several advanced techniques and their modifications have been incorporated to obtain good quality of films. Recently, Iijima *et al.*[5–10] prepared high-quality thin epitaxial films of $BaTiO_3$ (4000 Å thick) on $SrTiO_3$ substrates and found a ferroelectric hysteresis loop and dielectric anomaly at 388 K. In this paper, the thermal properties of $BaTiO_3$ thin films was studied by a.c. calorimetry. No detailed specific heat measurements of thin films have been performed because of its difficulties in preparing enough amount of thin films. Recent development of a.c. calorimetry has approved to be possible to measure the specific heat of thin films.[11–13]

2 Experimental

Epitaxial $BaTiO_3$ films were grown on $SrTiO_3$ substrates by the activated reactive evaporation method. Details of the deposition technique are described in papers.[4,5,14] The films were characterized

---

*To whom correspondence should be addressed. Fax: +81-11-746-5444; e-mail: onodera@pop.high. hokudai.ac.jp by X-ray diffraction with CuK_α monochromatized by a pyrolytic graphite (50 kV, 240 mA). The lattice parameter of the film is found to be $c = 4.01$ Å, while the lattice parameter of $SrTiO_3$ substrate is 3.91 Å. Two films with thickness of 2000 and 60 Å were prepared for the present specific heat measurements. The heat capacity was measured using an a.c. calorimeter (Shinku-Riko ACC-1 M/L). The sample was heated periodically by chopped light from a halogen lamp at the frequency of 2–5 Hz. The thermal response of the sample was monitored by a digital lock-in amplifier (Shinku-Riko LAD-1A) with a chromel-constantan thermocouple (diameter of 25 μm), which was attached by a small amount of varnish (GE7031). The bath temperature was monitored using a Pt resistance thermometer and controlled within a stability of 1 mK.

3 X-ray Diffraction Profile of $BaTiO_3$ Film

X-ray diffraction profiles scanned along the [0 0 1] direction was shown in Fig. 1 for the (0 0 1) $BaTiO_3$ film with 60 Å thickness at room temperature. Only the (0 0 *l*) reflections were observed. The sub-maximum peaks of the Laue function were observed around the fundamental peaks of the (0 0 1), (0 0 2), (0 0 3) and (0 0 4). The strong peaks denoted as 'sub' in this figure mean the (0 0 *l*) reflections from the $SrTiO_3$ substrate. This evidence indicates that this film is an epitaxial crystal with a perovskite structure.[6–10]

4 Specific Heat of $BaTiO_3$ Film

The a.c. calorimetric method is a suitable technique for measurements of the specific heat (C_p) in thin specimens and small crystals. However, the total amount of C_p from the $BaTiO_3$ film and the $SrTiO_3$ substrate was measured in the present case, since it is rather complicated to separate two thermal components. We can understand relative changes in thermal behaviour in $BaTiO_3$ films from the measurements in the neighbourhood of the paraelectric–ferroelectric transition temperature. In $SrTiO_3$ bulk crystal, there is only one phase transition at about 106·5 K. The temperature dependence of C_p is shown in Fig. 2 for the $BaTiO_3$ film with thickness of 2000 Å. The thermal behavior was found to show very weak temperature dependence even in the neighbourhood of T_c. No usual λ-type anomaly in C_p was observed in the temperature range from room temperature to 550 K, while a sharp jump was observed in bulk $BaTiO_3$ single crystal at 408·33 K.[13,15] In the film of 2000 Å thickness, two small kink-like anomalies were found at about 356 and 530 K. The specific heat shows a relatively large thermal hysteresis between these two temperatures. Similarly, the dielectric constant of the film with 4000 Å shows a broad and non-Curie–Weiss-type anomaly in the neighbourhood of T_c, of which maximum is at 388 K.

The X-ray intensity of the (0 0 4) reflection of the film with 4000 Å thick shows an anomaly at about 453 K. Although these temperatures observed in dielectric constant and X-ray intensity are slightly different, they might be related to the paraelectric–ferroelectric phase transition temperature, T_c, but the behaviour of this anomaly is very diffusive.[10] As the anomaly in C_p is also quite broad, it is not so clear to determine the exact T_c. The average temperature of two temperatures observed in the present 2000 Å film, T_{av}, is 443 K, which is in good agreement with that obtained by X-ray diffraction.[10]

Figure 3 shows thermal behaviour of C_p of thin film with 60 Å, which showed two anomalies at 620 and 760 K on cooling run, while rather smooth behaviour on heating run. The average temperature

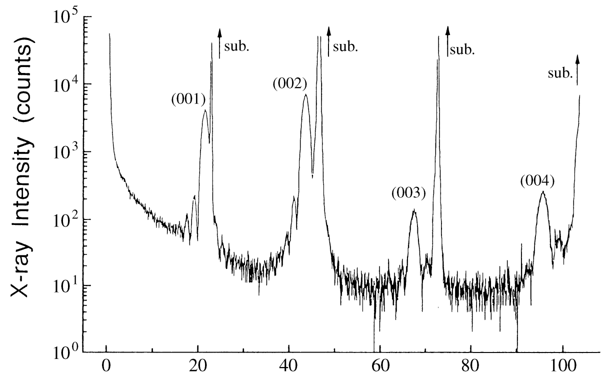

Fig. 1. X-ray diffraction patterns of $BaTiO_3$ thin film with 60 Å thick on the (0 0 1) $SrTiO_3$ substrate, scanned along the [0 0 1] direction (CuK_α monochromatized by a pyrolytic graphite, 50 kV, 240 mA).

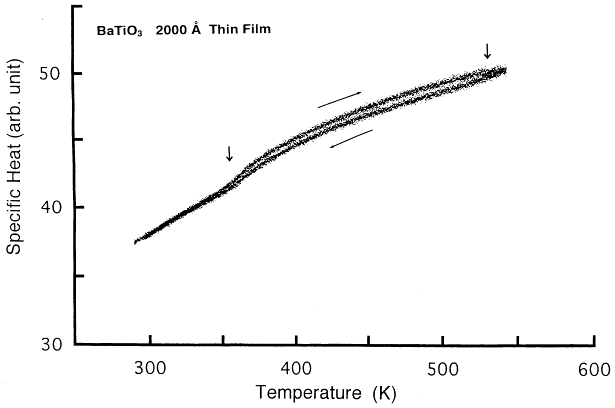

Fig. 2. Temperature dependence of specific heat of $BaTiO_3$ film (2000 Å thick) on $SrTiO_3$ substrate measured by an a.c. calorimeter. The arrows show the direction of heating and cooling.

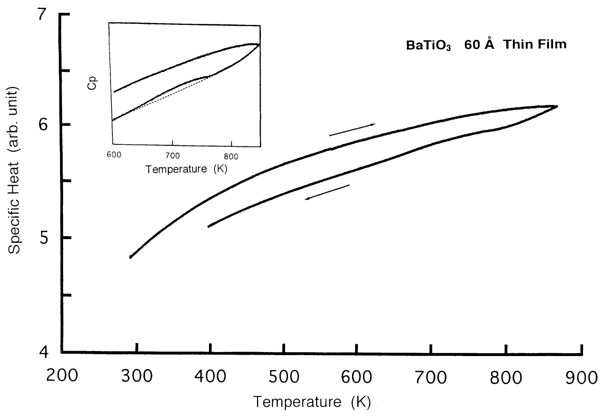

Fig. 3. Temperature dependence of specific heat of BaTiO$_3$ film (60 Å thick) on SrTiO$_3$ substrate measured by an a.c. calorimeter. The thermal behavior around 600 K is shown in the inset.

$T_{\rm av}$ is 690 K. Furthermore, large hysteresis behaviour in $C_{\rm p}$ between on heating and cooling was found in as-grown films, which became small after several sequences of measure-ments from r.t. to 850 K. The thermal behaviour of this as-grown film is shown in Fig. 4.

The thermal behaviour of these two films in the low-temperature region is almost the same, which is shown in Fig. 5. The structural phase transition in SrTiO$_3$ occurs at 106·5 K for a stressed monodomain bulk crystal and at 102·5 K for a stress-free polydomain crystal.[13] The small cusp at $T_{\rm o} = 107{\cdot}2$ K corresponds to the structural phase transition of SrTiO$_3$ substrate. Other phase transitions observed in bulk BaTiO$_3$ suppressed in thin films.

5 Discussion

The shape of anomaly in $C_{\rm p}$ in the neighbourhood of the paraelectric-ferroelectric phase transition of bulk BaTiO$_3$ is very different. Peculiar broad anomalies were found in both films with 2000 and 60 Å, while a sharp anomaly was observed at 403 K in bulk crystal. This new behaviour may be due to the two-dimensional clamping of the films. A phenomenological theory of single-domain BaTiO$_3$ epitaxial films has been recently studied.[16] The two-dimensional clamping of the films results in a shift of the $T_{\rm c}$. The misfit strain $u_{\rm m}$ defined as $(b-a_{\rm o})/b$ where $a_{\rm o}$ and b are the lattice constants of the film and the substrate, respectively, is about $-0{\cdot}025$ in the present sample. The shift of the average temperature $T_{\rm av}$ in the film of 60 Å thickness from the $T_{\rm c}$ in bulk BaTiO$_3$ is about 302 K, which shows a similar tendency with the calculated $T_{\rm c}$ versus $u_{\rm m}$ phase diagram after Takantsev *et al.*[16]

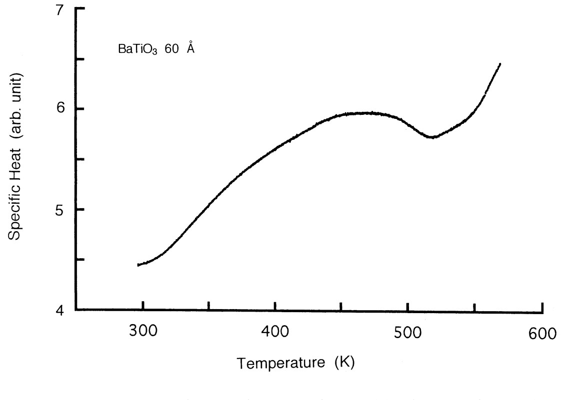

Fig. 4. Temperature dependence of specific heat of BaTiO$_3$ as-grown film (60 Å thick) on SrTiO$_3$ substrate.

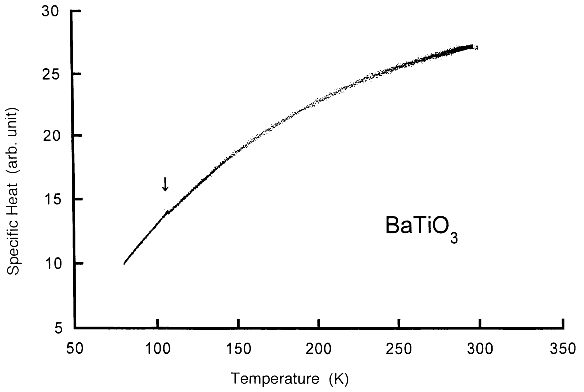

Fig. 5. Specific heat of BaTiO$_3$ film (60 Å thick) on SrTiO$_3$ substrate in the low-temperature region. One anomaly found at 107·2 K is that due to the structural phase transition of SrTiO$_3$ substrate.

The existence of surface tetragonal layers in bulk BaTiO$_3$ crystals has been reported by several authors. Kanzig suggested a fine particle of ferroelectric BaTiO$_3$ exhibits a surface layer of 100 Å thickness.[17] In BaTiO$_3$ thin films, the tetragonal lattice constants a and c do not coincide even at about 800 K, which show that the crystal structure of BaTiO$_3$ films still remains tetragonal above $T_{\rm av}$.[7–10] Furthermore, if the anomaly of the films in $C_{\rm p}$ results from the same mechanism of phase transition in bulk BaTiO$_3$, the dielectric anomaly in films must be large and shows the Curie–Weiss behaviour, following the soft mode theory after Cochran.[18,19] This suggests that the thermal behaviour and the mechanism of phase transition in thin films are different from those in bulk crystals. Further studies should be important to clarify the interesting nature of thin ferroelectric films.

6 Conclusion

The specific heat of thin films of BaTiO$_3$ was successfully measured. A broad anomaly in $C_{\rm p}$ was found in BaTiO$_3$ film, of which behaviour is quite different from that expected from the theory of ferroelectric phase transition for bulk crystals. The anomalies were found at 443 K for the film with

2000 Å, and at 690 K for the film with 60 Å. In low temperatures below room temperature, no clear anomaly in C_p was observed. It was found that the technique of a.c. calorimetry is suitable to evaluate thermal properties in thin films.

References

1. Lines, M. E. and Glass, A. M., *Principles and Applications of Ferroelectric and Related Materials*, Oxford University Press, London and New York, 1977, Chapter 8, pp. 241–292.
2. Feuersanger, A. E., In *Thin Film Dielectrics*, ed. F. Vratny. Electrochemical, New York, 1969, p. 209.
3. Slack, J. R. and Burfoot, J. C., *J. Phys.*, 1971, **C4**, 898.
4. Tomashpolski, Y. Y., Sevostianov, M. A., Pentagova, M. V., Sorokina, L. A. and Venevstsev, Y. N., *Ferroelectrics*, 1974, **7**, 257.
5. Iijima, K., Terashima, T., Yamamoto, K., Hirata, K. and Bando, Y., *Appl. Phys. Lett.*, 1990, **56**, 527.
6. Iijima, K., Terashima, T., Bando, Y., Kamigaki, K. and Terauchi, H., *J. Appl. Phys.*, 1992, **72**, 2840.
7. Terauchi, H., Watanabe, Y., Kasatani, H., Kamigaki, K., Yano, Y., Terashima, T. and Bando, Y., *J. Phys. Soc. Jpn.*, 1992, **61**, 2194.
8. Terauchi, H., Watanabe, Y., Kasatani, H., Kamigaki, K., Terashima, T. and Bando, Y., *Ferroelectrics*, 1992, **137**, 33.
9. Terauchi, H., Yoneda, Y., Watanabe, Y., Kasatani, H., Sakaue, K., Kamigaki, K., Iijima, K., Yano, Y., Terashima, T. and Bando, Y., *Ferroelectrics*, 1994, **151**, 21.
10. Yoneda, Y., Kasatani, H., Terauchi, H., Yano, Y., Terashima, T. and Bando, Y., *J. Phys. Soc. Jpn.*, 1993, **62**, 1840.
11. Kraftmakher, Y. A., *Zh. Prikl. Mekh. and Tech. Fiz.*, 1962, **5**, 176.
12. Sullivan, P. and Seidel, G., *Phys. Rev.*, 1968, **173**, 679.
13. Hatta, I. and Ikushima, A. J., *Jpn. J. Appl. Phys.*, 1981, **20**, 1995.
14. Terashima, T., Bando, Y., Iijima, K., Yamamoto, K., Hirata, K., Hayashi, K., Kamigaki, K. and Terauchi, H., *Phys. Rev. Lett.*, 1990, **65**, 2684.
15. Hatta, I. and Ikushima, A. J., *J. Phys. Soc. Jpn.*, 1976, **41**, 558.
16. Tagantsev, A. K., Pertsev, N. A. and Zembilgotov, A. G., *J. Kor. Phys. Soc.*, 1998, **32**, S. 1457.
17. Kanzig, W., *Phys. Rev.*, 1955, **98**, 549.
18. Chochran, W., *Adv. in Phys.*, 1960, **9**, 387.
19. Chochran, W., *Adv. in Phys.*, 1961, **10**, 401.