The Korean Journal of Ceramics, **6**[3] 219-223 (2000)

Ferroelectric $SrBi_2Ta_2O_9$ Thin Films by Liquid-Delivery Metalorganic Chemical Vapor Deposition using $Sr[Ta(OEt)_5(dmae)]_2$ and $Bi(C_6H_5)_3$

Woong-Chul Shin, Kyu-Jeong Choi, Chong-Man Park and Soon-Gil Yoon

Department of Materials Engineering, Chungnam National University, Daeduk Science Town, Taejon, 305-764, Korea

(Received March 31, 2000)

The ferroelectric SBT films were deposited on $Pt/Ti/SiO_2/Si$ substrates by liquid injection metalorganic chemical vapor deposition (MOCVD) with single-mixture solution of $Sr[Ta(OEt)_5(dmae)]_2$ and $Bi(C_6H_5)_3$. The Sr/Ta and Bi/Ta ratio in SBT films depended on deposition temperature and mol ratio of precursor in the single-mixture solution. At the substrate temperature of 400°C, Sr/Ta and Bi/Ta ratio were close to 0.4 and 1 at precursor mol ratio of 0.5~1.0, respectively. As-deposited film was amorphous. However, after annealing at 750°C for 30 min in oxygen atmosphere, the diffraction patterns indicated polycrystalline SBT phase. The remanent polarization (Pr) and coercive field (Ec) of SBT film annealed at 750°C were 4.7 $\mu C/cm^2$ and 115.7 kV/cm at an applied voltage of 5 V, respectively. The SBT films annealed at 750°C showed practically no polarization fatigue up to 10^{10} switching cycles.

Key words: Ferroelectric, Liquid injection MOCVD, Single-mixture solution

I. Introduction

Ferroelectric Bi-layered $SrBi_2Ta_2O_9$ (SBT) thin films have a large potential application as capacitor materials in nonvolatile random access memories (NVRAM) because it has good ferroelectric properties such as fatigue-free characteristics.[1,2] SBT films have been fabricated by various deposition methods such as metalorganic-decomposition (MOD),[3,4], pulsed laser deposition (PLD),[5] rf magnetron sputtering,[6,7] and metalorganic chemical vapor deposition (MOCVD)[8~12] Among these preparation methods of SBT thin films, a metalorganic chemical vapor deposition (MOCVD) method has attracted great attention. For increase of integration levels, a demand for thin films fabrication methods with precise composition control, conformal step coverage, good uniformity and high throughput are increasing. Chemical vapor deposition technique is acknowledged as the best approach to fulfill those requirements. However, CVD processes of complex oxides with conventional gas delivery methods with bubbling of low volatile sources exhibit poor composition controllability and low growth rate arising from the use of solid sources. Recently, liquid source delivery metalorganic chemical vapor deposition (MOCVD) has been developed to solve these problems. Compared to solid source, the advantages of using liquid source for MOCVD are well known and include achieving homogeneity at atomic level in the solution, which results in good control over the stoichiometry of the deposited films. A major advantage of using a single mixture liquid source is that the stoichiometry can be controlled in the deposited film by precisely adjusting the ratio of the individual components in the liquid source. However, it is not easy to handle this source, since its vapor pressure is rather low.

The MOCVD of SBT has thus far been severely restricted by a lack of suitable metal-organic precursors. Conventional precursors include $Sr(thd)_2$ or $Sr(thd)_2$-tetraglyme and $Ta(OEt)_5$ or $Ta(O\text{-}iC_3H_7)_4(thd)$, which are generally incompatible, having very different physical properties and decomposition characteristics. A potential solution to this problem is the use of single-source precursors such as $Sr[Ta(OC_2H_5)_6]_2$ and $Sr[Ta(OEt)_5(dmae)]_2$ which contain the elements required in the oxide film in a single stoichiometric compound.[13-15] A potential advantage of single-source precursors is that the metal/metal ratio in the precursor matches that in the deposited oxide film.

In this study, we present the use of $Sr[Ta(OEt)_5(dmae)]_2$ for the deposition of SBT thin films, and discuss characteristics of SBT thin films by liquid injection MOCVD.

II. Experiment

The SBT films were deposited on $Pt/Ti/SiO_2/Si$ substrates of 3×3 cm^2 size by liquid injection Metalorganic Chemical Vapor Deposition. Fig. 1 shows a schematic diagram of liquid injection MOCVD apparatus. The liquid injection MOCVD apparatus consists of two main parts; a CVD reactor with a vacuum system and liquid source delivery system with micro-syringe pump (KD Scientific Inc., KDS100) and vaporizer. The vaporizer is composed of a stainless steel chamber, a stainless steel mesh filter, diaphragm vacuum

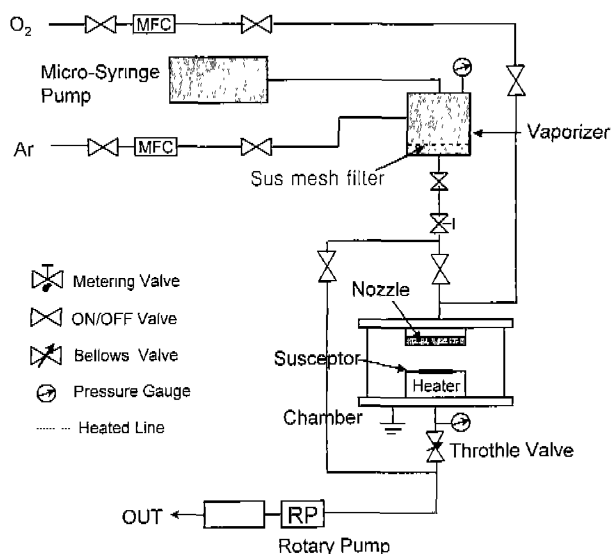

Fig. 1. Schematic diagram of liquid injection MOCVD system.

Table 1. Deposition Condition of $SrBi_2Ta_2O_9$ thin Films

Deposition temperature	350-550°C
Deposition pressure	10 Torr
Vaporizer temperature	210°C
N_2 flow rate	200 sccm
O_2 flow rate	500 sccm
Precursor flow rate	0.1 ml/min
Deposition time	20 min.
Substrate	$Pt/Ti/SiO_2/Si$
Annealing condition	650-750°C, Oxygen, 30 min

gauge and heating system. Carrier gas containing metal-organic source and oxidants were uniformly supplied onto a substrate through a showerhead type nozzle with a lot of holes. The $Pt/Ti/SiO_2/Si$ substrates were mounted on the susceptor and heated with a resistance heater. The typical SBT deposition conditions were summarized in Table 1. For the SBT growth, $Sr[Ta(OEt)_5(dmae)]_2$ (Inorgtech Chemicals) and $Bi(C_6H_5)_3$ (Strem Chemicals) were used as starting materials for Sr, Bi, and Ta, respectively. Triphenyl bismuth $[Bi(C_6H_5)_3]$ was used because of its thermally good stability.

The organic precursors were dissolved in a solvent (tetrahydrofran, C_4H_8O, Sigma-Aldrich Chemicals) to form a source solution of 0.1 M concentration of $Sr[Ta(OEt)_5(dmae)]_2$ and $Bi(C_6H_5)_3$. A solution of each precursor was mixed together and the single-mixture solutions with various concentrations were used for preparation of SBT thin films. The temperature of the vaporizer was maintained at 210°C during the deposition. When the single-mixture sources were pumped into the vaporizer at a flow rate of 0.1 ml/min by micro-syringe pump, they evaporated immediately and were carried into the reactor by 200 sccm flow of N_2 carrier gas. All the gas lines were uniformly heated by ribbon heaters at 210°C. The reactor pressure was maintained at 10 torr during the deposition. Substrate temperature was varied from 350-550°C. After deposition, the films were cooled down to room temperature in an oxygen atmosphere. The thickness of SBT films was about 120 nm. Annealing treatments were typically carried out in a tube furnace at temperatures ranging from 650-750°C for 0.5 h in oxygen atmosphere. The increase and decrease rates of temperature were about 50°C/min and 10°C/min, respectively.

The microstructure of SBT films was determined by using the scanning electron microscope (SEM, TOPCON DS-130C). X-ray diffraction (XRD, Rigaku D/MAX-RC) using Cu K_α radiation and an Ni filter was carried out to determine the crystal structure and preferred orientation of the films. The composition of films was determined by electron probe X-ray microanalysis (EPMA, CAMECA SX-51). The surface roughness of films was measured by atomic force microscopy (AFM, AUTOPROBE CP). The ferroelectric properties were measured using RT66A ferroelectric tester (Radient Technology) operating in the virtual ground mode. The dielectric properties were measured as a function of frequency with a Hewlett-Packard (4194A) impedance-gain phase analyzer. The current-voltage (I-V) measurements were performed with a Keithley 617 programmable electrometer. The measurements were carried out using a metal-insulator-metallic (MIM) configuration. Pt top electrode was prepared at room temperature by dc sputtering using a 0.1 mm diameter shadow mask.

Results and Discussion

Fig. 2 shows the deposition temperature dependence on film composition. The mole ratio, $Sr[Ta(OEt)_5(dmae)]_2/Bi(C_6H_5)_3$ in the single-mixture solution, was maintained at 0.5. The film composition was primarily controlled by varying the deposition temperature and the concentration of the single-mixture solution. As shown in Fig. 2, the Bi/Ta mol ratio is increased with increasing the deposition tempera-

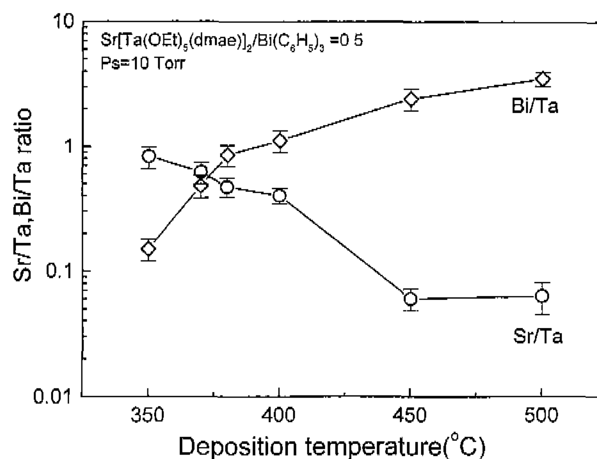

Fig. 2. Variation of composition of SBT thin films with deposition temperatures.

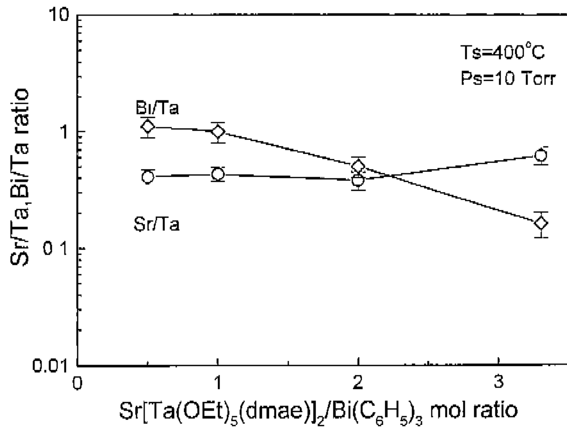

Fig. 3. Variation of composition of SBT thin films deposited at 400°C with precursor mol ratio in single-mixture solution.

ture, and it is considered to be due to the fact that the deposition rate of $Bi(C_6H_5)_3$ is much faster than that of $Sr[Ta(OEt)_5(dmae)]_2$. However, the Bi/Ta ratio is very low below 400°C and is about 1.1 at 400°C. It has been reported that the Bi content in SBT thin films using the triphenyl bismuth is very low below 500°C because the decomposition temperature of triphenyl bismuth is very high.[12] On the other hand, the Sr/Ta ratio is decreased with increasing the deposition temperature, and approaches the stoichiometric value at 380°C. However, the Sr content in SBT thin films is very low at temperature above 400°C. This may be due to decomposition of the $Sr[Ta(OEt)_5(dmae)]_2$ at high temperatures, leading to partial separation of the Sr and Ta components, and the deposition rate of $Sr(OC_2H_5)_2$ is lower than that of $Ta(OC_2H_5)_2$.

Fig. 3 shows the composition variation with mole ratio of precursors in the single-mixture solution. The deposition temperate and system pressure are 400°C and 10 torr, respectively. As shown in Fig. 3, the Bi/Ta mol ratio decreases with increasing the mol ratio of precursor in the single-mixture solution. The mol ratio of precursor to obtain the optimum Bi/Ta ratio in SBT thin films is about 0.5~1.0 at 400°C. However, the Sr/Ta ratio increases slightly as the precursor mol ratio increases. The optimum Sr/Ta ratio in SBT thin films is obtained irrespective of the mol ratio of precursor in the single-mixture solution at 400°C. At the optimum substrate temperature of 400°C, and at precursor

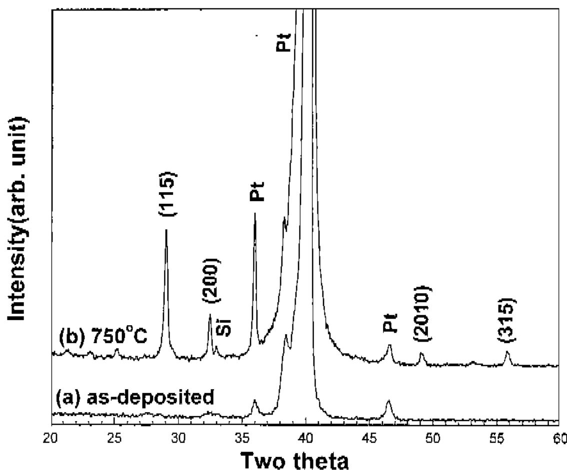

Fig. 4. XRD patterns of SBT thin films (a) as-deposited and (b) annealed at 750°C.

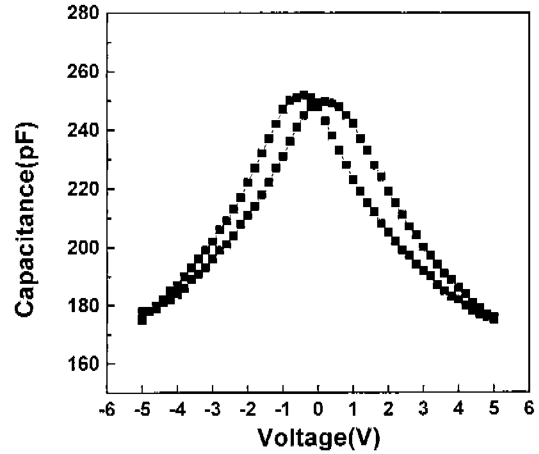

Fig. 5. C-V curve of SBT thin films annealed at 750°C.

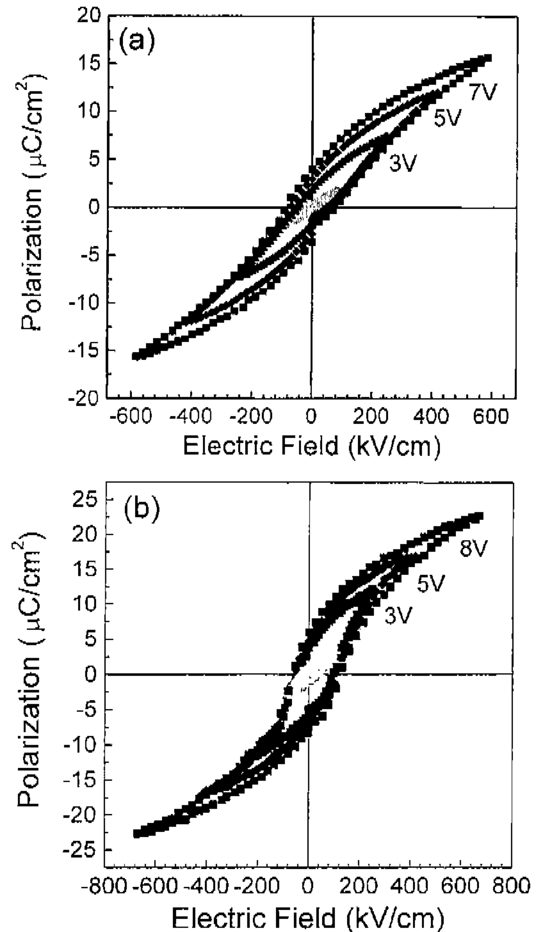

Fig. 6. P-E curves of SBT thin films annealed at (a) 700°C and (b) 750°C.

mol ratio of 0.5~1, Sr/Ta and Bi/Ta ratio is close to 0.4 and 1, and also matches the required Sr/Ta and Bi/Ta ratio in $SrBi_2Ta_2O_9$ thin films.

The XRD patterns of as-deposited SBT film and annealed at 750°C for 30 min in oxygen atmosphere are shown in Fig. 4. These SBT films were deposited at 400°C, and the Sr/Ta and Bi/Ta ratio of SBT thin films were about 0.4 and 1.1, respectively. As shown in Fig. 4(a), as-deposited film shows amorphous. However, after annealing at 750°C in oxygen atmosphere, the diffraction patterns indicate polycrystalline SBT phase.

Fig. 5 shows capacitance versus voltage (C-V) characteristic of SBT thin film of Fig. 4(b). The thickness of films is 120 nm, and the small signal capacitance was measured at 100 kHz, 5 V when the electric voltage was swept from a positive bias to a negative bias and back again. The C-V curve shows typically hysteresis behavior and this result indicates that the dielectric film has a ferroelectric property.

Fig. 6(a) and 6(b) show P-E hysteresis loops of a capacitor composed of a 120-nm-thick SBT thin film in Fig. 4(b). As shown in Fig. 6, the SBT film annealed at 700°C indicates poorer saturation and lower remanent polarization than that annealed at 750°C. The remanent polarization (Pr) and coercive field(Ec) of SBT film annealed at 750°C are 4.7 $\mu C/cm^2$ and 115.7 kV/cm at an applied voltage of 5 V, respectively.

Fig. 7 shows the effect of applied voltage on the remanent polarization (2Pr) and coercive field (Ec). For applied voltages from 1 to 8V, the SBT film annealed at 750°C shows the higher 2Pr value than that of SBT film annealed at 700°C. For the SBT film annealed at 750°C, the 2Pr value increases with increasing applied voltage and then tends to saturate above 6V. On other hand, the 2Pr value of sample annealed at 700°C increases monotonically with increasing applied voltage.

Fatigue characteristics of SBT films annealed at 750°C are shown in Fig. 8(a) and 8(b). Fatigue tests were performed using a 5 V bipolar square pulses at 1 MHz input through a function generator. As shown in Fig. 8(a), the SBT films show practically no polarization fatigue up to 10^{10} switching cycles. The P-E hysteresis loops of the SBT films before and after the fatigue test are shown in Fig. 8(b). The hysteresis loops obtained after the fatigue tests were nearly identical to those observed before the fatigue test.

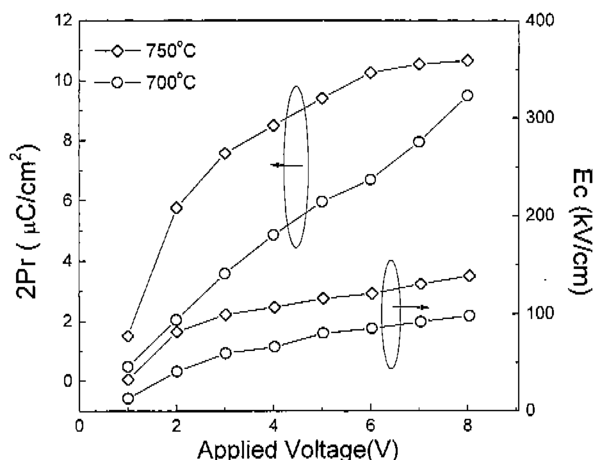

Fig. 7. Effect of applied voltage on the remanent polarization (2Pr) and coercive field (Ec) of SBT films.

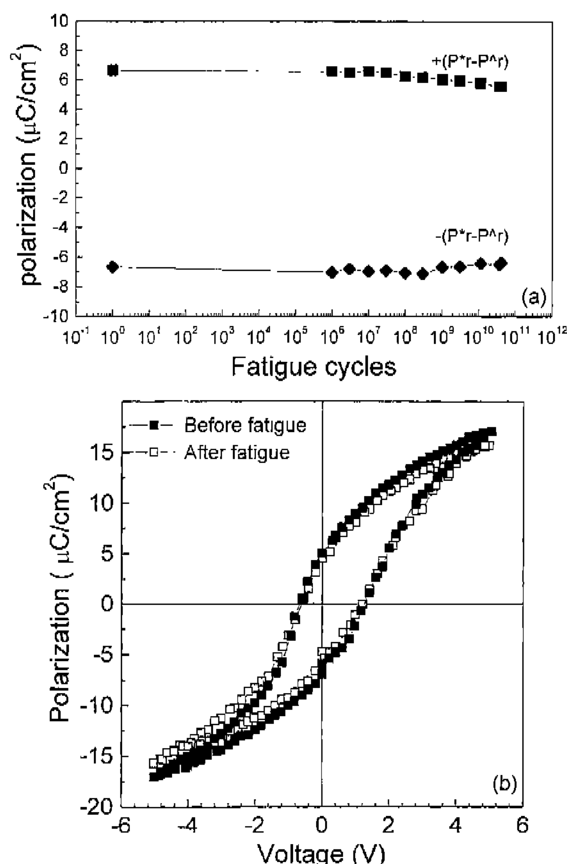

Fig. 8. Fatigue characteristics of SBT films annealed at 750°C.

III. Conclusions

The SBT films were successfully deposited on $Pt/Ti/SiO_2/Si$ substrates by liquid injection metalorganic chemical vapor deposition (MOCVD) with single-mixture solution of $Sr[Ta(OEt)_5(dmae)]_2$ and $Bi(C_6H_5)_3$. The film composition was primarily controlled by varying the deposition temperature and the concentration of the single-mixture solution. The Bi/Ta mol ratio is increased with increasing the deposition temperature. The Bi/Ta ratio is very low below 400°C at precursor mol ratio of 0.5. On the other hand, the Sr/Ta ratio is decreased with increasing the deposition temperature, and approaches the stoichiometric value at 380°C. At the substrate temperature of 400°C, Sr/Ta and Bi/Ta ratio were close to 0.4 and 1 at precursor mol ratio of 0.5~1.0. The remanent polarization (Pr) and coercive field (Ec) of SBT film annealed at 750°C were 4.7 $\mu C/cm^2$ and 115.7 kV/cm at an applied voltage of 5 V, respectively. The SBT films annealed at 750°C showed practically no polarization

fatigue up to 10^{10} switching cycles. Thus, we conclude that the liquid injection metalorganic chemical vapor deposition (MOCVD) with single-mixture solution of $Sr[Ta(OEt)_5(dmae)]_2$ and $Bi(C_6H_5)_3$ is a promising method for the preparation of $SrBi_2Ta_2O_9$ and $Sr[Ta(OEt)_5(dmae)]_2$ has good potential for the MOCVD of SBT at low substrate temperature.

Acknowledgments

This work was financially supported by Grant No. KOSEF 1999-301-001-2 from the Korea Science and Engineering Foundation. The authors would like to thank Dr. Seok-Hoon Lee of Korea Basic Science Institute for carrying out Electron Probe X-ray Micro Analysis.

References

1. C. A. Paz de Araujo, L. D. McMillan, J. D. Cuchiaro and M. C. Scott, International Patent Publication No. WO 93/12542 (1993).
2. J. F. Scott, F. M. Ross, C. A. Paz de Araujo, M. C. Scott and Huffman, *Mater. Res. Bull.*, **20**, 33 (1996).
3. K. Amanuma, T. Hase and Y. Miyasaka, *Appl. Phys. Lett.*, **66**, 221 (1995).
4. M. Klee, Paper Presented at 7th International Symposium on Integrated Ferroelectrics held in Colorado Springs, CO, March, 20-22, (1995).
5. R. Dat, J. K. Lee, O. Auciello and A. I. Kingon, *Appl. Phys. Lett.*, **67**, 572 (1995).
6. S. S. Park, C. H. Yang, J. H. Ahn, H. G. Kim and S. G. Yoon, *J. Electrochem. Soc.*, **144**, 2855 (1997).
7. J. K. Lee, T. K. Song and H. J. Jung, *Integrated Ferroelectrics*, **15**, 115 (1997).
8. T. Li, Y. Zhu, S. B. Desu, C. H. Peng and M. Nagata, *Appl. Phys. Lett.*, **68**, 616 (1996).
9. P. C. Van Buskirk, S. M. Bilodeau, J. F. Roeder and P. S. Kirlin, *Jpn. J. Appl. Phys.*, **35**, 2520 (1996).
10. Y. Zhu, S. B. Desu, T. Li, S. Ramanathan and M. Nagata, *J. Mater. Res.*, **12**, 783 (1997).
11. C. Isobe, T. Ami, K. Hironaka, K. Watanabe, M. Sugiyama, N. nagel, K. Katori, Y. Ikeda, C. D.Gutleben, M. Tanaka, H. Yamoto and H. Yagi, *Integrated Ferroelectrics*, **14**, 95 (1997).
12. B. C. Hendrix, F. Hintermaier, D. A. Desrochers, J. F. Roeder, G. Bhandari, M. Chappuis, T. H. Baum, P. C. Van Buskirk, C. Dehm, E. Fritsch, N. Nagel, W. Honlein and C. Mazure, *Mater. Res. Soc. Symp. Proc.*, **493**, 225 (1998).
13. Y. Kojima, H. Kadokura, Y. Okuhara, M. Matsumoto and T. Mogi, *Integrat. Ferroelectr.*, **18**, 183 (1997).
14. T. Jimbo, H. Sano, Y. Takahashi, H. Funakubo, E. Tokumitsu and H. Ishiwara, *Jpn. J. Appl. Phys.*, **38**, 6456 (1999).
15. M. J. Crosbie, P. J. Wright, H. O. Davies, A. C. Jones, T. J. Leedham, P. Obrien and G. W. Crichlow, *Chem. Vap. Deposition*, **5**, 9 (1999).