

METHODS FOR PREPARATION OF BaTiO₃ THIN FILMS

M. Cernea*

National Institute R&D of Materials Physics, PO BOX MG-7, Bucharest,
RO-77125, Romania

Chemical, physical and electrochemical general methods used for deposition of various materials were tested for preparation of BaTiO₃ films. Researchers are focusing on the influence of processing parameters on the stoichiometry and the properties of BaTiO₃ films for each deposition method. Dielectric properties of BaTiO₃ thin films prepared by different methods shown various values suggesting that the optimal parameters for deposition of BaTiO₃ be not well known. Great efforts are concentrated on the economical aspect of the deposition process. In the case of BaTiO₃ films, it is important to prepare crystallized films at low temperatures. The methods for deposition of BaTiO₃ look into and develop continuous due to increase of the domain to use of BaTiO₃ films.

(Received September 2, 2004; accepted November 29, 2004)

Keywords: Barium titanate, Thin film, Deposition methods

1. Introduction

Considerable amount of research has recently focused on the growth of ferroelectric thin films. The ferroelectric BaTiO₃ thin film is used in electronic [1-4] and electro-optic devices [5-7] due to its high permittivity phenomena, associated with the basic ferroelectric behaviour. For these applications it is important to have high-quality epitaxial thin films with smooth surfaces. Many chemical, electrochemical and physical methods were used to deposition and growth BaTiO₃ thin films. The primary objective of this review is to describe and discuss the features of the various techniques for preparation of BaTiO₃ thin films. The methods are classified on the basis of the main process, which contributes to obtain the film.

2. Physical methods for BaTiO₃ films

2.1. Radio frequency sputtering

Sputter deposition is performed by extracting ions (usually Ar) from a plasma at KeV energies that strike a target consisting of the material to be deposited [8]. The energetic Ar ions produce a continuous flux of sputtered atoms that deposit on a nearby substrate. A DC voltage, radio frequency (RF) power, or a magnetron operating at millitorr pressures sustains the plasma. The RF magnetron-sputtering technique is characterized by high reproducibility in the chemical composition, easy process control, and compositional change of the film can be achieved only by varying the composition of the target. Some results regarding the correlation between the deposition parameters and the properties of BaTiO₃ film are presented in literature. Kim et al. [9] and Ukino et al. [10] described the dependence of amorphous, cubic and tetragonal phase transitions of the substrate and annealing temperatures of BaTiO₃ thin films prepared by rf sputtering. They used

*Corresponding author: mcernea@infim.ro

magnesia, silicon and strontium titanate substrates, maintained in the temperature range 25-700°C. The sputtered BaTiO₃ films were annealed in air using temperatures from 800 to 1400 °C.

The films were amorphous when deposited on MgO if the substrate temperature was less than 450 °C, while for those grown on silicon the temperature had to be less than 500 °C.

Above these temperatures, the films were crystalline, with cubic symmetry. After annealing the thin films on magnesia, the crystal structure changed from cubic to tetragonal phase above 1100 °C. The thin films on SrTiO₃ were found to be c-axis oriented tetragonal films for a substrate temperature above 500 °C.

Mansingh et al. [11] studied the effect of the target on the structure of radio frequency sputtered barium titanate films. Films were sputtered from non-reduced hot-pressed ceramic, reduced hot-pressed ceramic, multiphase powder and single-phase powder. The substrates were fused quartz plates, kept at 200 °C. The X-ray diffraction (XRD) patterns of the different starting targets materials and films sputtered from these respective targets are shown in Figs. 1a to h.

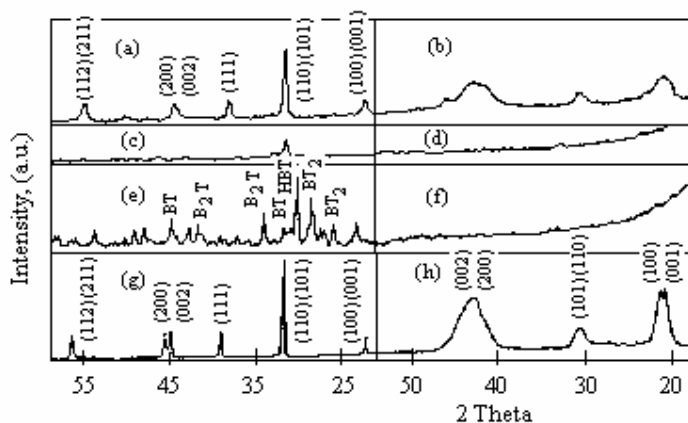


Fig. 1. X-ray diffractograms of BaTiO₃ films and the respective target materials. BaTiO₃ (BT), Ba₂TiO₄ (B₂T), BaTi₂O₅ (BT₂), hexagonal BaTiO₃ (HBT).

The hot-pressed ceramic has tetragonal structure (Fig.1a). Films sputtered from these targets were microcrystalline as evidenced from XRD patterns (Fig.1b). The structure of the hot-pressed ceramic is affected greatly by the reduction, as can be seen from the X-ray diffraction (Fig.1c) of reduced ceramic where only a small intensity peak corresponding to the (110) plane is observed. Films sputtered from this reduced target were amorphous (Fig.1d). However, annealing of this reduced target in an oxygen atmosphere helps the target to regain its original structure, and the films sputtered from this annealed target were microcrystalline, similar to that presented in Fig.1b. This suggests that the crystallinity of the films be greatly affected by the oxygen non-stoichiometry of the target. Fig. 1e shows the XRD patterns of the multiphase barium titanate powder, which contains a number of peaks. Films sputtered from the multiphase powder were amorphous (Fig.1f). Films sputtered from single-phase powder (tetragonal BaTiO₃, Fig.1g) were crystalline with tetragonal polymorph structure, as shown in Fig.1h. A split in pattern is observed in one peak (corresponding to the (001), (100) planes) in the XRD patterns as a consequence of the tetragonal structure of BaTiO₃.

Desu [12,13] studied the relationship between the film deposition process, stresses and the properties of ferroelectric BaTiO₃ thin films, deposited at 300-700°C and at pressures from 0.1 to 100 Pa, on both Si and sapphire single crystals. Film stress influences the properties of thin films and affects the reliability of thin film electronic device [14]. In ferroelectric thin films, film stresses can alter mechanical, dielectric and optical properties, domain structure, Curie point, and switching properties. The stresses generated by interaction of the film with the substrate can be classified into thermal, intrinsic, and extrinsic stresses. Thermal stresses arise due to differences between the mean coefficients of thermal expansion of the substrate and film and due to the differences in working temperature when compared to the deposition temperature. Intrinsic stress, which is often referred to as growth stress, is determined by the nature of both film and substrate, and is fundamentally related to the film deposition process, such as temperature, pressure, reactant concentration, and impurity

incorporation. Extrinsic stresses are caused by structural changes, which produce dimensional changes. Most of the films are subjected to increase in density due to structure evolution, such as crystallization of amorphous phase, or densification, which lead to film shrinkage and tensile stresses in the films. The variation of calculated intrinsic stress of BaTiO₃ thin films as a function of deposition pressure and deposition temperature respectively, is presented in Figs. 2 and 3.

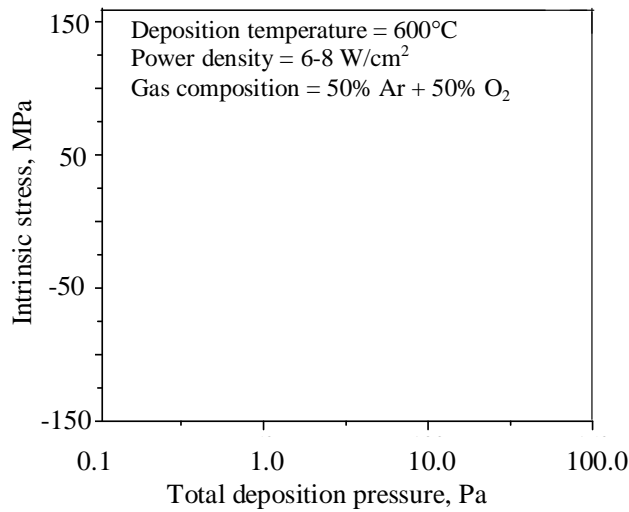


Fig. 2. Dependence of intrinsic stress on deposition pressure.

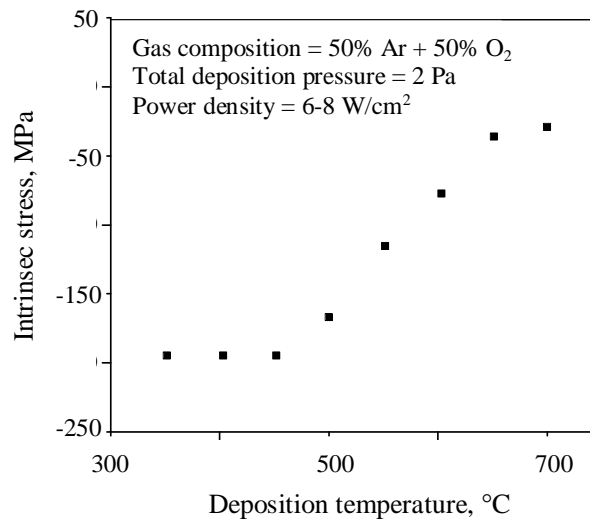


Fig. 3. Dependence of intrinsic stress on deposition temperature.

Fig. 2 indicates that increasing the deposition pressure from 0.5 to 40 Pa increased intrinsic stress from -80 MPa (compressive) to 140 MPa (tensile), the total change occurring between deposition pressures of 5 and 40 Pa. The intrinsic stress is more or less constant for deposition pressure between 0.5 and 5 Pa. At low deposition temperatures intrinsic stress is compressive in nature and is independent of temperature (Fig.3). For deposition temperatures above 500 °C, the intrinsic compressive stress linearly decreases with increasing deposition temperature. By a

judicious choice of deposition conditions, BaTiO₃ films having low intrinsic stresses and properties close to those of single crystals were obtained. For example, some of the properties of BaTiO₃ films deposited at 650°C and 2 Pa pressure on silicon substrate are: refractive index $n=2.37$ at 700 nm, coercive field $E_c=10.2$ Kv/cm, remanent polarization $P_r=15.9$ $\mu\text{C}/\text{cm}^2$, Curie point=129°C and intrinsic stress $\sigma_i=-47$ MPa. Based on these studies, many works were reported onto doped BaTiO₃ thin films produced by RF sputtering [15-18].

2.2. Pulsed laser deposition (PLD)

The pulsed laser deposition (PLD) named also, pulsed laser ablation (PLA) technique offers many advantages for film growth, including epitaxial or crystalline growth at low substrate temperatures, congruent deposition of materials with complex stoichiometries, facile deposition of materials with high melting points and ability to form metastable microstructures [19]. Conceptually and experimentally, PLD is extremely simple, probably the simplest among all thin film growth techniques [20]. It consists of a target holder and a substrate holder housed in a vacuum chamber. A high-power laser is used to vaporize materials and to deposit thin films.

Norton et al. [19,21,22] demonstrated that epitaxial BaTiO₃ thin films could be grown on (001)-oriented single-crystal MgO by pulsed laser ablation. The films produced were oriented with their c-axis perpendicular to the film-substrate interface plane (c-axis oriented). It has been shown that the microstructure of the films can be varied by changes in the deposition parameters. Optimizing these variations permits the formation of thin films with controlled microstructures and properties [23]. They obtained thin films of BaTiO₃ with a Curie temperature of 110 °C by PLD at 670 °C temperature of the substrate and 53 Pa ambient oxygen pressure.

Nakata et al. [24-27] make interesting studies onto the plume dynamics and the relationship between the deposition conditions and film characteristics. They obtained BaTiO₃ thin films on MgO substrate by PLD at an oxygen pressure of 0-500 mTorr and at a heater temperatures of 800 and 850 °C. The lattice parameter of the film BaTiO₃ was decreased as the oxygen pressure was increased. The similar behavior has been reported by T. -F. Tseng et al. [28] for (1-x)SrTiO₃-xBaTiO₃ films deposited on Si by PLD. The oxygen pressure also greatly influences the surface morphology of these films. The size of the grain observed on the film surface is larger as the pressure increase. At 10 mTorr, BaTiO₃ thin film with smooth surface could be obtained. Fig. 4 shows an AFM image of Ce-doped BaTiO₃ surface film with a mean surface roughness of 48 nm deposited by PLD in a small ambient oxygen pressure (30 Pa) [29].

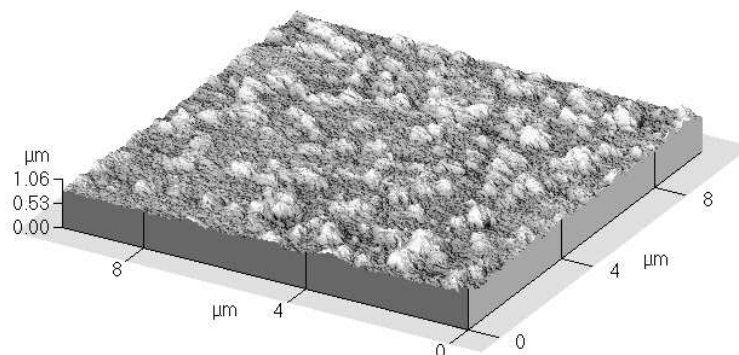


Fig. 4. AFM image of BaTiO₃ doped with 5.5 mol%Ce film.

Tsukada et al. [30] found close correlation between the dielectric constant and the degree of preferential (111) orientation for Ba(Ti_{0.85}Sn_{0.15})O₃ solid-solution thin films deposited on a Pt/Ti/SiO₂/Si(100) substrate by pulsed laser deposition. They shown that substrate temperature is the principal factor which determines orientation and crystalline quality of the films. The studies on the

relationship between the characteristics of the laser-plasma deposited films and the film properties must be continued.

2.3. Laser molecular beam epitaxy (MBE) technique

Computer-controlled laser molecular beam epitaxy (laser MBE) is a promising method which use the both merits of PLA and conventional MBE for depositing films from high melting point ceramics and multicomponent solids, and for the control of the growth layer in atomic scale [31]. Molecular beam epitaxy (MBE) uses continuous molecular beams generated by Knudson sources [32]. There is very little information available in the literature on the preparation of BaTiO₃ thin films by laser MBE. Da-Fu Cui et al. [31], reported the growth of BaTiO₃ thin films by laser MBE on SrTiO₃ (001) substrates. Single-crystal tetragonal BaTiO₃ thin films with fully c-axis orientation were obtained by laser MBE at 750 °C in vacuum ($\sim 10^{-6}$ Torr). AFM and TEM observations demonstrated that the BaTiO₃ thin film surface is very smooth (atomically smooth surface) and the BaTiO₃/SrTiO₃ interface is flat and sharp. The root mean square (rms) surface roughness value is 0.29 nm. Epitaxial BaTiO₃ film with a smooth surface is suitable for optical waveguide devices.

2.4. Flash evaporation technique

Slack et al. [33] and then Beltran et al. [34] deposited BaTiO₃ thin films using the flash evaporation technique. Barium titanate thin films were deposited on top of Si substrates. Samples were put in a sample holder into the chamber, 30 cm above the filament. This technique uses a vacuum system which it was adapted a pressure controlled feeder that allows the barium titanate evaporation on a grain basis. The samples inside the chamber were brought to a base pressure of 2×10^{-4} Pa, which rose to 1.4×10^{-3} Pa when barium titanate grains were evaporated. Some samples received a thermal treatment in oxygen ambient for times between 15 seconds and 2 minutes at 850°C. Auger spectrum for an as-deposited sample shows the in-depth uniform distribution of Ba, Ti and O. Samples which received the thermal treatment showed Ba migration towards the interface and Ti diffusion towards the layer surface. Thin flash-evaporated barium titanate films have shown promising features to be used as dielectric layer in MIS (metal-insulator-semiconductor) sensors for relative humidity detection [34]. Some problems related to inhomogeneities of the deposited layers remain to be solved.

3. Chemical methods for BaTiO₃ films

3.1. Chemical vapor deposition (CVD) technique

The deposition flux in chemical vapor deposition (CVD) is derived from the reaction of two or more gaseous chemicals on or above a heated substrate [35,36]. Heaters above the substrate provide the energy necessary to sustain the reaction. Metal-organic chemical vapor deposition (MOCVD) is similar to CVD, but in MOCVD the reacting gases are metal-organic compounds that widen the range of materials [37] that can be deposited by CVD.

Metal-organic chemical vapor deposition [38-40] and metal-organic deposition (MOD) [41] were used to obtain BaTiO₃ thin films. Kim et al. [42] prepared epitaxial BaTiO₃ thin film on Nb-doped SrTiO₃, on SrTiO₃ [43] and MgO substrates [44] by coating-pyrolysis process. In brief, the mixed solution of barium and titanium naphthenates was used as a precursor solution. The precursor solution was diluted in toluene to adjust the concentration (~ 0.2 mmol/g) and viscosity for spin coating. The precursor solution was spin spin-coated on Nb-doped SrTiO₃ substrate at 2000 rpm for 5s. The amorphous film pyrolyzed at 470 °C was crystallized with high orientation after heat-treatment at 850 °C under low oxygen partial pressure. X-ray diffraction (Fig. 5) indicated that the BaTiO₃ film was epitaxial relationship with Nb-doped SrTiO₃ substrate.

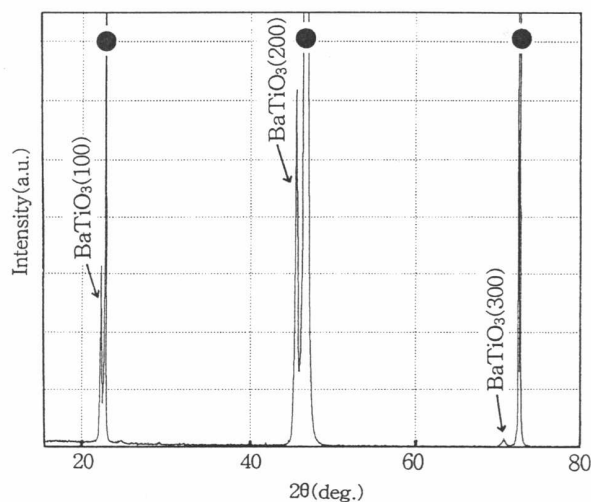


Fig. 5. XRD pattern of BaTiO₃ thin film. (* indicates the XRD pattern of Nb-doped SrTiO₃ substrate).

The dielectric constant was approximately 230 at 1 KHz.

3.2. Sol-gel techniques

Among the various techniques, sol-gel is gaining interest for the fabrication of ferroelectric films due to low equipment cost and ease of integration with the already existing semiconductor technology. The sol-gel techniques can be classified in function of precursors used. Sharma et al. [45] prepared BaTiO₃ thin film from barium acetate and titanium (IV) isopropoxide precursors. The films were found to be amorphous, which crystallized to tetragonal phase after annealing at 700°C in air for one hour. The value of the dielectric constant of the thin film at 1 KHz was 370 at the Curie temperature of 125°C. All the sol-gel routes used for preparation of BaTiO₃ powders can lead to BaTiO₃ thin films.

3.3. Hydrothermal method

The hydrothermal method is an attractive technique for formation of perovskite type ceramic. The ABO₃ thin film can be synthesized on substrates of the B-site metal being reacted in an alkaline aqueous solution containing the A-site elements, through the autoclave at sealed conditions. Pilleux et al. [46] have prepared BaTiO₃ films by treating the substrate (titanium deposited on silicon wafer by sputtering) in a 0.25 M Ba(OH)₂ solution at 250 °C for 8 h. The BaTiO₃ film thickness was about 50 nm. The effects of the preparatory conditions, such as reacting species, reactant concentration, reaction temperature and time, on the properties of the titanate film formed, grain size and reaction rate, have not been studied [47].

4. Electrochemical technique for BaTiO₃ films

4.1. Electrophoretic deposition method

There are few reports on the electrophoresis deposition of BaTiO₃ thick films [48,49]. This method utilizes the phenomenon of the movement of colloidal particles suspended in a medium in a dc electric field. It is therefore important to select a suitable suspension medium for the powders.

Diethylene glycol dimethyleter; 1-nitropropane; pyridine, and a mixed ethanol-acetylacetone have been used as suspension media for BaTiO₃ powders. Nagai et al. [50] obtained barium titanate thick films 10-70 μm thick using a electrophoretic deposition technique, which utilizes a mixed ethanol-acetylacetone suspension as dispersive medium. The capacitance of the BaTiO₃ films was measured as 25-75 nF, at temperature of up to 200 °C giving a dielectric constant of 4000-12000 and dielectric loss (tanδ) of 0.13-0.51. In the sintered (2 h at 1400 °C) films thus deposited on the Pt cathode, (111) orientation was observed, and the degree of orientation was found to increase with decrease of the thickness of the films. In so-oriented films, the Curie point was near 120 °C.

5. Conclusions

There are numerous methods for preparation BaTiO₃ thin films. The classification that is presented here is not rigorously delimited because appeared mixed methods as sol-electrodeposition method [51], laser molecular beam epitaxy (LMBE) technique (PLA-MBE) and hydrothermal-electrochemical technique [52]. The properties of obtained BaTiO₃ thin films are influenced by the processing conditions, which are specifically to each deposition technique. Academic and industrial researchers must develop these methods to produce high-quality thin films economically.

References

- [1] P. J. Harrop, D. S. Campbell, *Thin Solid Films* **2**, 273 (1968).
- [2] F. T. Wooten, *Proc. IEEE* **55**, 564 (1967).
- [3] R. S. Muller, J. Conrigan, *IEEE Trans. Electron. Devices* ED-12, 590 (1965).
- [4] J. R. Fiebigler, R. S. Muller, *J. Appl. Phys.* **38**, 1948 (1967).
- [5] A. B. Kaufman, *IEEE Trans. Electron. Devices* ED-16, 562 (1969).
- [6] N. F. Borelli, M. M. Layton, *IEEE Trans. Electron. Devices* ED-16, 511 (1969).
- [7] G. W. Taylor, *IEEE Trans. Electron. Devices* ED-16, 565 (1969).
- [8] R. F. Bunshah, (Ed.), *Deposition Technologies for Films and Coatings*, Noyes Pub. Park Ridge, New Jersey, USA (1982).
- [9] J. H. Kim, S. Hishita, *Journal of Materials Science* **30**, 4645-4650 (1995).
- [10] K. Uchino, N. Lee, T. Toba, N. Usuki, H. Aburatani, Y. Ito, *J. Ceram. Soc. Jpn.* **100** 1091 (1992).
- [11] A. Mansingh, C. V. R. Vasanta Kumar, *Journal of Materials Science Letters* **7**, 1104-1106 (1988).
- [12] S. B. Desu, *J. Electrochem. Soc.*, **140**(10), 2981-2986 (1993).
- [13] S. B. Desu, *Mat. Res. Soc. Symp. Proc.* **20**, 199 (1990).
- [14] M. F. Doerner, W. D. Nix, *CRC Crit. Rev. Solid State Mater. Sci.*, **14**, 225 (1988).
- [15] C. B. Samantaray, Anushree Roym M. Roy, M. L. Mukherjee, S. K. Ray, *Journal of Physics and Chemistry of Solids* **63**, 65 (2002).
- [16] Wen-Chou Tsai, Tseung-Yuen Tseng, *J. Am. Ceram. Soc.* **81**(3), 768 (1998).
- [17] F. Fujimoto, Y. Kobayashi, K. Kubota, *Thin Solid Films* **109**, 249 (1989).
- [18] M. Cernea, I. Matei, A. Iuga, C. Logofatu, *Journal of Materials Science* **36**(20), 5027 (2001).
- [19] M. G. Norton, K. P. B. Cracknell, C. B. Carter, *J. Am. Ceram. Soc.* **75**(7), 1999 (1992).
- [20] Douglas B. Chrisey, Graham K. Hubler, *Pulsed Laser Deposition of Thin Films*, John Wiley and Sons, Inc., New York, (1994).
- [21] M. G. Norton, C. B. Carter, *J. Mater. Res.* **5**, 2762 (1990).
- [22] M. G. Norton, C. Scarfone, J. Li, C. B. Carter, J. W. Mayer, *J. Mater. Res.* **6**, 2022 (1991).
- [23] C. Scarfone, M. G. Norton, C. B. Carter, J. Li, J. W. Mayer, in *Surface Chemistry and Beam-Solid Interactions*, Mataterials Research Society Symposium Proceedings, Vol. 201. Edited by H. Atwater, F. A. Houle and D. Lowndes, Materials Reaearch Society, Pittsburg, PA, 1990, p.183-88

- [24] Y. Nakata, W. K. A. Kumuduni, T. Okada, M. Maeda, *Appl. Phys. Lett.* **64**, 2599 (1994).
- [25] T. Okada, Y. Nakata, H. Kaibara, M. Maeda, *Jpn. J. Appl. Phys.* **11B**, 1536 (1995).
- [26] Y. Nakata, H. Kaibara, T. Okada, M. Maeda, *J. Appl. Phys.* **80**, 2458 (1996).
- [27] Y. Nakata, G. Soumagne, T. Okada, M. Maeda, *Appl. Sur. Sci.* **127-129**, 650 (1998).
- [28] T. -F. Tseng, M. -H. Yeh, K. -S. Liu and I. -N. Lin, *J. Appl. Phys.* **80**, 4984 (1996).
- [29] M. Cernea, A. Ianculescu, O. Monnereau, L. Argème, V. Bley, B. Bastide, C. Logofatu, *J. Materials Science* **39** (8), 2755 (2004).
- [30] M. Tsukada, M. Mukaida, S. Miyazawa, *Jpn. J. Appl. Phys.* **35**, 4908 (1996).
- [31] Da-Fu Cui, Hui-Sheng Wang, Zheng-Hao Chen, Yue-Liang Zhou, Hui-Bin Lu, Guo-Zhen Yang, Kun Ma, Hong Chen, Lin Li, Wei Liu, Yun Zhang, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **15**(2), 275-278 (1997).
- [32] E. H. C. Parker, *The Technology and Physics of molecular Beam Epitaxy*, Plenum, New York (1986).
- [33] J. R. Slack, J. C. Burfoot, *Thin Solid Films* **6**, 233 (1970).
- [34] N. Beltran, V. Fuenzalida, C. Grahmann, Thin films of barium titanate for sensor devices, in "Euroceramics II, Electroceramics and ceramics for special applications, G. Ziegler and H. Husner, eds., Deutsche Keramische Gesellschaft, p.2475-79, (1991).
- [35] D. P. Stinton, T. M. Besmann, R. A. Lowden, *Ceram. Bull.* **67**, 350 (1988).
- [36] R. Meissner, ed. (1988), *MRS Bull.* **13**, 11 (10).
- [37] G. B. Stringfellow, *J. Elec. Mater.* **17**, 327 (1988).
- [38] C. S. Chern, J. Zhao, L. Luo, P. Lu, Y. Q. Li, P. Norris, B. Kear, F. Cosandey, C. J. Maggiore, B. Gallois, B. J. Wilkens, *Appl. Phys. Lett.* **60**, 1144 (1992).
- [39] D. L. Kaiser, M. D. Vaudin, L. D. Rotter, Z. L. Wang, J. P. Cline, C. S. Hwang, P. B. Marinenko, J. G. Gillen, *ibid.* **66**, 2801 (1995).
- [40] Y. S. Yoon, M. N. Kang, H. S. Shin, S. S. Yom, T. W. Kim, J. Y. Lee, D. J. Choi, S-S. Baek, *J. Appl. Phys.* **73**, 1547 (1993).
- [41] W. O. Benomar, S. S. Xue, R. A. Lessard, A. Singh, *J. Mater. Res.* **9**, 970 (1994).
- [42] S. Kim, O. -Y. Kwon, *Journal of Materials Science* **34**, 707 (1999).
- [43] S. Kim, T. Manabe, I. Yamaguchi, T. Kumagai, S. Mizuta, *ibid.* **12**, 1141 (1997).
- [44] S. Kim, T. Manabe, I. Yamaguchi, T. Kumagai, S. Mizuta, *Thin Solid Films* **310**, 199 (1997).
- [45] H. Basantakumar Sharma, H. N. K. Sarma, A. Mansingh, *J. Mater. Sci.* **34**, 1385-1390 (1999).
- [46] Pilleux M. E., Fuenzalida V. M., *J. Appl. Phys.* **74**, 4664 (1993).
- [47] C. -F. Kao, C. -L. Yang, *J. Europ. Ceram. Soc.* **19**, 1356 (1999).
- [48] S. Senderoff, W. E. Reid, Jr., U. S. Pat. No. 2 843 541, (1958).
- [49] V. A. Lamb, H. I. Salmon, *Am. Ceram. Soc. Bull.* **41**, 781-82 (1962).
- [50] M. Nagai, K. Yamashita, T. Umegaki, Y. Takuma, *J. Am. Ceram. Soc.* **76** (1), 253 (1993).
- [51] T. Hosokura, S. Shindo, M. Kuwabara, *Key Engineering Materials*, **248**, 69 (2003). Trans. Tech. Publications, Switzerland.
- [52] M. Yoshimura, W. L. Suchanek, T. Watanabe, *J. Eur. Ceram. Soc.* **19**, 1353 (1999).