

Fabrication and Characterization of Pulsed Laser Deposited Lead Free Thin Film Capacitors

Deepshikha Kushwaha, Ravikant, Kirandeep Singh, Monika Aggarwal

Abstract-The current study explores the dielectric and ferroelectric properties of pulsed laser deposited $(Ba_{1-x}Sr_x)TiO_3$, $Ba(Zr_xTi_{1-x})O_3$ and $[(Ba_{1-x}Sr_x), (Zr_yTi_{1-y})] O_3$ thin films deposited on $LaNiO_3$ bottom electrode. The crystallographic study of these films done using XRD reveals that these films were crystalline in nature having (110) preferred orientation. An improved crystallite structure with intense (110) reflection was observed for BSZT/LNO/Si thin film. The atomic force micrographs indicate that BST, BZT and BSZT thin films have different grain distributions and grain sizes and is in consistence with XRD results. The high value of remnant polarization (P_r) and low value of coercive field (E_c) of BSZT thin film shows that it can be used in memory devices. In addition, excellent dielectric properties with high dielectric constant were observed for the BSZT capacitor. A highest tunability of 68% was measured at a frequency of 1 MHz could be achieved for BZST thin film, showing that BSZT would be suitable candidate for tunable devices.

Keywords- Dielectric properties, Pulsed laser deposition, Tunability X-ray diffraction

I. INTRODUCTION

The continuing drive towards greater miniaturization of electronic components has led to the development of thin film materials for a wide variety of applications, and among these are the thin film ferroelectrics. Barium titanate ($BaTiO_3$ or BT)-based materials have been widely studied because of their fascinating properties like high dielectric, piezo-electric and pyro-electric coefficients. Due to these properties, BT is used in a number of applications such as ceramic capacitors, microwave tunable devices dynamic random access memory (DRAM) devices, and infrared detectors, etc [1-3].

In order to improve the working of these BT based devices, suitable impurities are added modify the properties of pure BT. Usually, for ABO_3 perovskite, substituting A and/or B sites by other ions can modify the dielectric behaviour of the material. The addition of Sr ion into Ba site of barium titanate [BST] can shift the Curie transition (T_c) of BT to a lower temperature [4]. Lowering of T_c increases the room temperature dielectric constant of the material. BST has a nonlinear response to the electric field thus make it much suitable for switching purpose and for infrared sensors [5-6].

Recently, great attention has been focused on a B-site doped $BaTiO_3$ perovskite, $Ba(Zr_xTi_{1-x})O_3$, where the substitution of Zr of larger ionic radius into Ti-sites of smaller ionic radius takes place. It is a solid solution of barium titanate ($BaTiO_3$) and barium zirconate ($BaZrO_3$) and shows a lot of analogies to BST solid solution. The Zr^{4+} ion is chemically more stable than the Ti^{4+} therefore, the substitution of Ti with Zr would depress the conduction by electronic hopping between Ti^{4+} and Ti^{3+} thus maintains a low leakage current [7-9]. It is reported that an increase in the Zr content induces a reduction in the average grain size [10], this is possible because, Zr^{4+} ion has larger ionic size (0.087 nm) than Ti^{4+} (0.068 nm). Zr /Ti ratio is very important in BZT system and a 0.20/0.80 mole fraction is known to show very good bulk properties [11]. It is interesting to note that the BZT system exhibits a pinched phase transition at $x= 0.20$; i.e., all the three phase transitions corresponding to pure $BaTiO_3$ are merged or pinched into one broad peak, and further increase in Zr concentration would result in a typical ferroelectric relaxor behaviour [12]. BSZT is a solid solution of $BaTiO_3$ and $SrZrO_3$, therefore, it is expected that the additives of Sr and Zr to $BaTiO_3$ have the effect of both materials. The bottom electrode plays an important role in deciding the quality of thin films & also in determining the performance of thin film capacitors. $LaNiO_3$ has been chosen as a bottom electrode as it has same crystal structure and similar lattice parameter as that of most of the perovskite type ferroelectric materials like BST, BZT & BSZT, thus reduces the atomic dislocation and the lattice stain between the interface and improves electrical performances [13-17], also a good quality thin film is expected to grow on the top of bottom electrode

Table 1: Temperatures at which sintering and calcination were done for BST, BZT and BSZT targets

Sample	Sintering Temperature (degree Celsius)	Sintering time (Hrs)	Calcination Temperature (Degree Celsius)	Calcination time (Hrs)
LNO	1250	4	1300	5
BST	1300	4	1450	5
BZT	1300	4	1450	5
BSZT	1300	4	1450	5

Manuscript published on 30 December 2012.

* Correspondence Author (s)

Deepshikha Kushwaha- ECE, B.G.I.E.T, Sangrur, India

Ravikant- ECE, B.G.I.E.T, Sangrur, India,

Kirandeep Singh- Physics Department, I.I.T. Roorkee, Roorkee, India.

Monika Aggarwal- ECE, B.G.I.E.T, Sangrur, India.

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an open access article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Table 2: Different PLD processing parameters at which BZT, BST and BSZT thin films were grown i.e LNO.

Sample	T-S distance (cm)	No of shots	Laser energy (mJ)	oxygen partial pressure (m Torr)	Substrate temp (degree celcius)
LNO	3.5	10,000	300	200	700
BST	3.5	10,000	300	200	700
BZT	3.5	10,000	300	200	700
BSZT	3.5	10,000	300	200	700

Moreover LNO is conductive metal oxide having low value of resistivity, excellent diffusion properties and have good thermal stability [18].

II. EXPERIMENTAL DETAILS

The dense ceramic targets of $(Ba_{0.5}Sr_{0.5})TiO_3$ [BST], $Ba(Zr_{0.2}Ti_{0.8})O_3$ [BZT], $(Ba_{0.5},Sr_{0.5})(Zr_{0.2}Ti_{0.8})O_3$ [BSZT] & $LaNiO_3$ [LNO] was prepared by conventional solid state reaction method using $BaCO_3(99.99\%)$, $SrCO_3(99.9\%)$, $ZrO_2(99.9\%)$, $TiO_2(99.9\%)$, $La_2O_3(99.9\%)$ and $Ni_2O_3(99.9\%)$ powders. The sintering and calcination of these targets were done at different temperatures which are shown in table 1. The thin films were deposited using PLD at a laser repetition rate of 10 Hz substrate frequency of 5 Hz and at a laser energy of 250mJ. The vacuum chamber was first pumped down to a background pressure of 2×10^{-5} Torr. Oxygen was then introduced as an active gas for the deposition of BZT & LNO oxide thin films. The target to substrate distance was kept fixed at 3.5 cm. LNO which serves as a bottom electrode for our thin film capacitors was deposited at 700°C substrate temperature and 100mTorr oxygen partial pressure. The LNO thin film shows (110) preferred orientation and a resistance of 50 ohm at these conditions. After the deposition of LNO stoichiometric thin films BST, BZT & BSZT were subsequently deposited at a 700°C substrate temperature and 200mTorr oxygen partial pressure. The PLD parameters at which thin films of LNO, BST, BZT and BSZT were grown is shown in table 2.

Crystallographic structure of dielectric films were studied using XRD (burker D8 discover) equipped with $CuK\alpha$ radiation. The surface morphology of these films were analyzed by field emission scanning electron microscope (FE-SEM). For measuring the dielectric & ferroelectric properties, silver (Ag) top electrode were sputter deposited onto the ferroelectric films through a shadow mask of 0.5mm diameter. The 4394A precision impedance analyzer was used to measure the frequency dispersion relation of dielectric constant in the range of 1 kHz to 1MHz & also for measuring the DC response of dielectric constant for these films. The ferroelectric loops were studied using radiant precision work station at an electric field range of +300kV/cm to -300kV/cm.

III. RESULTS AND DISCUSSION

A. Structural properties

Fig (1) shows the XRD pattern of BST, BZT and BSZT thin films grown over LNO coated Si substrate. It is evident that films are crystalline in nature having (110) preferred

orientation. The inset of figure shows the slight shift of (110) plane. The angle shifts towards higher side in case of BST

Table 3: Different parameters calculated using XRD and FE-SEM

Sample	FWHM (degree)	Crystallite Size (\AA)	Grain Size	Lattice parameter a (\AA)
BZT	0.11802	69	66	3.3812
BST	0.1094	74	85	3.808
BSZT	0.1042	78	100	3.809

on addition of Sr ion. The constriction of perovskite lattice is related to the fact that the ionic radii of Sr^{2+} is smaller than Ba^{2+} ion.

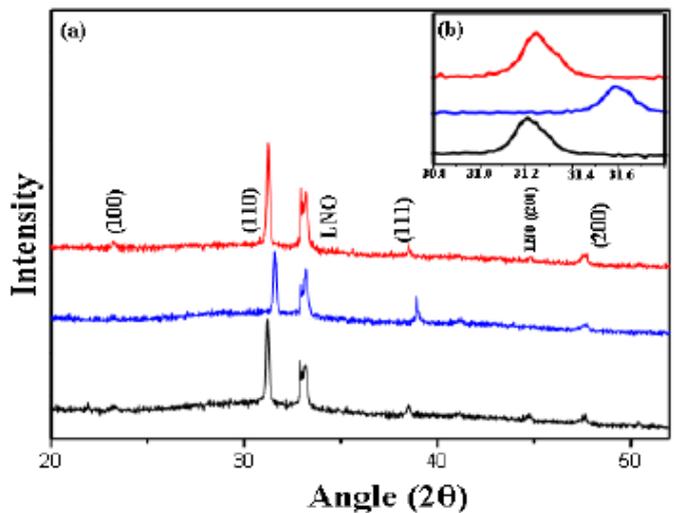


Figure 1: XRD Pattern of BZT, BST and BSZT

Substitution of Ti by Zr leads to the expansion of perovskite lattice in $BaTiO_3$ thin film which is related to the fact the ionic radius of Zr^{4+} is greater than that of Ti^{4+} . Table 3 shows the lattice parameters, crystallite size and FWHM calculated from X-ray diffraction data.

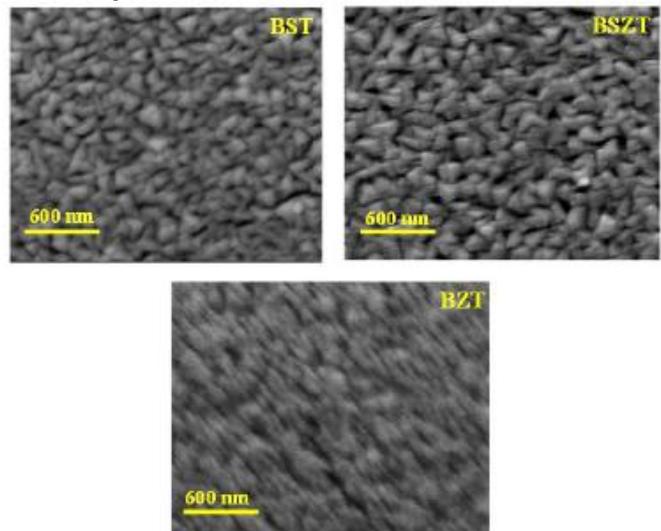


Figure 2: Surface morphology of lead free ferroelectric thin films studied using FE-SEM

The lattice parameters of BST, BZT and BSZT shown in table 3 are in agreement with the facts that addition of Sr ion shrinks the original BaTiO₃ lattice and addition of Zr ion expands the BT lattice. The (110) peak of BSZT lies in between the (110) peak of BST & BZT which is due to the fact that BSZT is a mixture of both BZT & BST. Surface morphology of these films have been studied using FE-SEM (fig 2).

FE-SEM images are in agreement with our XRD data and shows that grain size of BSZT thin film is larger than BST and BZT thin films. The grain size of BaTiO₃ lattice decreases with the addition of Zr ion which is due to slow diffusion of the Zr⁴⁺ ion, which has bigger ionic radii than Ti⁴⁺. The addition of Sr²⁺ ion increases the grain size. The larger grain size is attributed to more rapidly diffused Sr²⁺ ion which has smaller ionic radii than Ba²⁺. The increase in Sr²⁺ concentration above some value leads to the problem of densification which further degrades the grain growth.

B. Ferroelectric properties

The ferroelectric nature of BST, BZT and BSZT thin films deposited on LNO has been confirmed from the polarization hysteresis measurements done at room temperature for an electric field of ± 300 kV/cm as shown in fig (3).

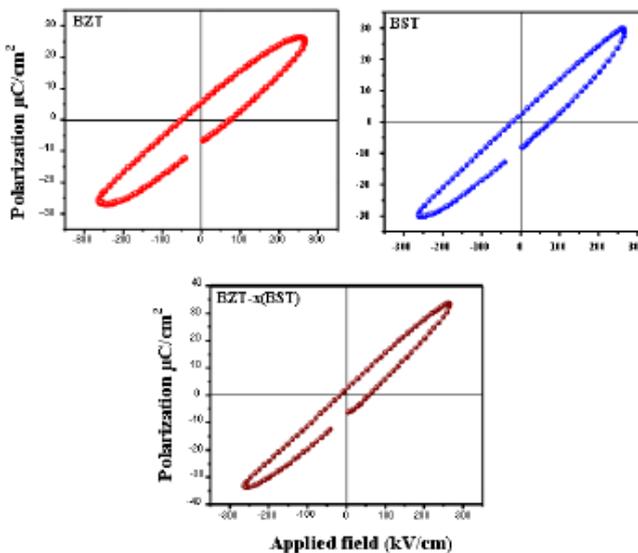


Figure 3: P-E loops of BZT,BST,BZST thin film

Table 4: Different parameters calculated from dielectric properties and P-E loops

Sample	Max. Polarization (μC/cm ²)	Retentivity (μC/cm ²)	Coercive field (kV/Cm)	Dielectric constant at 1 kHz	Tunability (%) at 1 MHz
BZT	22.07	2.50	41.95	302	48
BST	29.85	2.91	16.89	346	65
BSZT	33.51	4.4	11.4	1050	68

The measured values of saturation and remanent polarization of different thin films has been listed in table (3). BSZT is found to have best ferroelectric properties, it is due to the dependence of ferroelectric properties on the grain size. It is well known that ferroelectric properties are determined mainly by the ferroelectric domain structure,

domain nucleation and domain mobility and the domain structure and domain mobility are related to grain sizes [19].

The films with small grain sizes experience more suppression of ferroelectric character under an applied external field by grain boundary effects which produce hindrance of polarization switching. So reversal polarization process of a ferroelectric domain is much easier inside a large grain than in a small grain. The non-saturation behavior in hysteresis characteristics may arise from several sources, including residual stress in the films, presence of depolarizing fields and the domination of conduction over polarization switching currents [20]. The asymmetric behaviour in the films can be induced by various factors such as defect, charges present in the ferroelectric material or due to different work functions of the top and bottom electrodes [21].

C. Dielectric properties

Fig. (4) shows the frequency dispersion relation of dielectric constant in the range from 1 kHz to 1 MHz for BST, BZT and BSZT thin films capacitor deposited on LNO bottom electrode. It is noted that for all samples, there is a decrease in the dielectric constant with increasing frequency, which is a typical characteristic of normal dielectric. The fall in dielectric constant arises from the fact that the polarization does not occur instantaneously with the application of the electric field as charges possess inertia.

The delay in the response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant. A lowest dielectric constant was obtained for the BST thin film this can be attributed to the increased number of grain boundaries due to smaller grain sizes. The greater amount of grain boundaries lead to the lower polarization intensity and therefore contribute to the lower dielectric constant [22]. The electric field dependence of relative permittivity of the BST, BZT and BSZT thin films were characterized at room temperature.

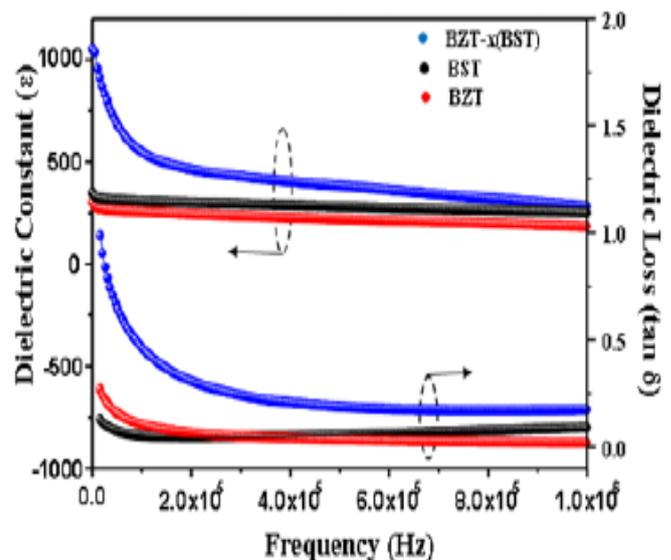


Figure 4: Dielectric constant and dielectric loss variation of BZT,BST,BSZT thin films with frequency



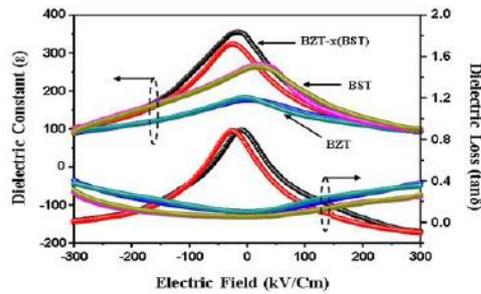


Figure 5: Electric Field dependence of dielectric constant and dielectric loss

Fig. (5) shows the typical relative permittivity-surface electric field (ϵ -E) characteristics of the BST, BZT and BSZT thin films. The ϵ -E curves were measured at a frequency of 1 MHz. The mechanism of the relationship between relative permittivity and external dc bias field is not clear yet. The ϵ -E dependence of the ferroelectric materials (when in the paraelectric state) is generally found to follow Johnson's formula as expressed [22].

$$\epsilon_r(T, E) = \frac{\epsilon_r(T, 0)}{\{1 + [\epsilon_0 \epsilon_r(T, 0)]^2 B(T) E^2\}^{1/3}} \quad (1)$$

where $\epsilon_r(T, 0)$ and ϵ_0 are the relative permittivity and vacuum permittivity, respectively, and $B(T)$ is a phenomenological constant, which provides information on the degree of an harmonic contributions of the polarization to the Helmholtz free energy. However, for thin films in ferroelectric state, in addition to a background contribution coming from the intrinsic behavior, it was found that a polar cluster contribution (Langevin-type polar cluster contribution) term should be taken into account. Thus, the dc bias dependence of relative permittivity should be described with a modified Devonshire relation including a term of local polar clusters or regions [23], the so-called multipolarization mechanism model proposed by Chen et al [24].

$$\epsilon_r(T, E) = \frac{\epsilon_r(T, 0)}{\{1 + [\epsilon_0 \epsilon_r(T, 0)]^2 B(T) E^2\}^{1/3}} + \left(\frac{P_r \chi}{\epsilon_0}\right) [\cosh(E\chi)]^{-2} \quad (2)$$

Where $\chi = \frac{P_r L^3}{2k_b T}$ with the cluster polarization P_r and size L , k_b is the Boltzmann's constant. The first term on the right hand side of Eq. (2) is in fact the Johnson's relationship, describing the ϵ -E relation in the paraelectric regime. The second term on the right hand side of Eq. (2) corresponds to the contributions from the possible polar clusters. The tunability K defined as $1 - \frac{\epsilon_r(E)}{\epsilon_r(0)}$ has been calculated from fig (5) for BST, BZT thin films.

IV. CONCLUSION

The BST, BZT and BSZT thin films were deposited via Pulsed laser deposition technique on LaNiO_3 -coated silicon substrates. The films were crystalline in nature. The addition of Zr to the BaTiO_3 lattice decreased the particle size while the addition of strontium increases the grain size of BaTiO_3 . Relative permittivity of BSZT, BST and BZT was measured in the frequency range of 1 kHz to 1 MHz, showing that ϵ of the BSZT thin film is the highest it is due to fact that BSZT has larger grain size than BST and BZST. Tunability of 68% at $E_{\max} = \pm 300$ kV/cm was achieved in BSZT thin film. The high dielectric constant, low loss tangent and high tunability of BSZT thin films at room temperature, indicates that these are promising for tunable capacitor application

REFERENCES

- [1] H. Basantakumar Sharma, H. N. K. Sarma, A. Mansingh. Fatigue in sol-gel derived barium titanate films. *J. Appl. Phys.* **85**(1). (1999). pp. 341-346
- [2] S. Kim, T. Fujimoto, T. Manabe, I. Yamaguchi, T. Kumagai, S. Mizuta. Dense and Smooth Epitaxial BaTiO_3 Thin Films by the Dipping-Pyrolysis Process. *J. Mater. Res.* **14**(2). (1999). pp. 592.
- [3] B. H. Hoerman, G. M. Ford, L. D. Kaufmann, B. W. Wessels. Dielectric properties of epitaxial BaTiO_3 thin films. *Appl. Phys. Lett.* **73**(16). (1998). pp. 2248.
- [4] Manoj Kumar, Ashish Garg, Ravi Kumar, M.C. Bhatnagar. Structural, dielectric and ferroelectric study of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Zr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics prepared by the sol-gel method. *Physica B.* **403** (2008). pp. 1819.
- [5] T. Ueda, A. Noma, D. Ueda, GaAs MMIC Chip-sets for mobile communication systems with on-chip ferroelectric capacitors. *Integr. Ferroelec.* **7** (1995). pp. 45-60
- [6] V.N. Keis, A.B. Kozyrev, M. L. Khazov, J. Sok, J. S. Lee, *Electron. Lett.*, **34** (1998) 1107
- [7] T.B. Wu, C.M. Wu, M.L. Chen, Highly insulative barium zirconate-titanate thin films prepared by rf magnetron sputtering for dynamic random access memory applications. *Appl. Phys. Lett.* **69** (18). (1996). pp. 2659-2662
- [8] S. Hoffmann, R. Waser, Dielectric properties, leakage behaviour, and resistance degradation of thin films of the solid solution series $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$. *Integrated Ferroelectrics.* **17** (1997). pp. 141-152
- [9] D. Hennings, A. Schnell, G. Simon, *J. Am. Ceram. Soc.* **65** (11) (1982) 539.
- [10] J. Zhai, Xi Yao, H. Chen. Structural and dielectric properties of $\text{Ba}_{0.85}\text{Sr}_{0.15}(\text{Zr}_{0.18}\text{Ti}_{0.85})\text{O}_3$ thin films grown by a sol-gel process. *Ceramics International.* **30** (2004). pp. 1237-1240
- [11] C. Fu, F. Pan, W. Cai, X. Deng, X. Liu. Microstructures and dielectric properties of $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$. *Ceramics. Journal of Physics.* **152** (2009). pp. 1-6
- [12] N.Y. Chan, G.Y. Gao, Y. Wang, H.L.W. Chan. Preparation and characterizations of $\text{Ba}(\text{Zr,Ti})\text{O}_3/(\text{Ba,Sr})\text{TiO}_3$ heterostructures grown on $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.35}$ single crystal substrates by pulsed laser deposition. *Thin Solid Films.* **518** (2010). pp. e82-e84
- [13] Y.H.Gao, J.L.Sun, J.H.Ma, X.J.Meng, J.H.Chu. *Applied Physics A* **91** (2008) 541.
- [14] J.W. Zhai, X.Yao, Z.K.Xu, H.Chen. Enhancement of ferroelectricity in the compositionally graded $(\text{Pb,Sr})\text{TiO}_3$ thin films derived by a sol-gel process. *Journal of Crystal Growth.* **286** (2006). pp. 37-41
- [15] J.W.Zhai, X.Yao, Z.Xu, H.Chen. Effect of Orientation on the Ferroelectric Behavior of $(\text{Pb,Sr})\text{TiO}_3$ Thin Films. *Journal of the American Ceramic Society.* **89** (2006). pp. 354-357
- [16] K.T.Kim, C.I.Kim. Dielectric properties of highly (1 0 0) oriented $(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films grown on LaNiO_3 electrodes. *Thin Solid Films.* **447-448** (2004). pp. 651-655
- [17] C.M.Wu, T.B.Wu. Low temperature deposition of $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ thin films on LaNiO_3 -buffered electrode by rf magnetron sputtering. *Materials Letters.* **33** (1997). pp. 97-100
- [18] Sang Sub Kima, Tae Soo Kang, Jung Ho Je. Microstructures of LaNiO_3 films grown on Si(001) by pulsed laser deposition. *Thin Solid Films.* **405** (2002). pp. 117-121
- [19] C.C. Leu, C.Y. Chen, C.H. Chien. Domain structure study of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ferroelectric thin films by scanning capacitance microscopy. *Appl. Phys. Lett.* **82** (2003). pp. 3493-3495
- [20] L. J. Sinnamon, M. M. Saad, R.M. Bowman, J.M.Gregg. Exploring grain size as a cause for "dead-layer" effects in thin film capacitors. *Appl. Phys. Lett.* **81** (2002). pp.703-705
- [21] C.C. Choi, J.Lee, B.H. Park, T.W. Noh, *Integr. Ferroelectr.* **3** (1997) 39
- [22] K.M. Johnson. Variation of Dielectric Constant with Voltage in Ferroelectrics and Its Application to Parametric Devices. *J. Appl. Phys.* **33** (1962). pp. 2826-2831
- [23] J. Yang, J.H. Chu, M.R. Shen. Analysis of diffuse phase transition and relaxorlike behaviors in $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films through dc electric-field dependence of dielectric response. *Appl. Phys. Lett.* **90** (2007). pp. 242908-242910
- [24] A. Chen, A.S. Bhalla, R.Y. Guo, L.E. Cross. Dielectric loss of SrTiO_3 single crystals under direct current bias. *Appl. Phys. Lett.* **76** (2000). pp. 1929-1931.