

## Enhanced electrical properties of BiFeO<sub>3</sub> films deposited on (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si substrates

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Metal-ferroelectric-insulator-semiconductor (MFIS) capacitor with a BiFeO<sub>3</sub> ferroelectric film and a Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> buffer layer on a silicon substrate was fabricated and characterized. BiFeO<sub>3</sub>/Si was studied for comparison. The Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub>/Si structure shows a negligible capacitance-voltage curve and a lower leakage current density of less than 10<sup>-7</sup> A/cm<sup>2</sup> at 10 V. The maximum memory window of BiFeO<sub>3</sub>/Si is only 0.38 V due to the severe charge injection. In contrast, a larger memory window of 1.93 V is found for BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si due to the reduced leakage current by using the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer. Compared with BiFeO<sub>3</sub>/Si, the BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si sample shows a smaller relative dielectric constant of 77.6 and a lower dissipation factor of 0.015 at a frequency of 100 kHz.

**Key words:** Ferroelectric, Thin films, BiFeO<sub>3</sub>.

### Introduction

Ferroelectric materials in thin film forms have been investigated widely for applications in ferroelectric random access memories (FeRAM) which is one of the promising nonvolatile memories [1, 2]. However, they have some drawbacks, such as a small data storage density, especially a destructive readout operation. In contrast, the ferroelectric field effect transistor (FeFET) with a single transistor (1T) memory cell has advantages of a nondestructive read-out operation, a higher density integration, a lower power consumption, and a higher speed operation [3, 4]. However, the interaction and interdiffusion between the ferroelectric films and Si substrates cause the property of the films to be deteriorated. Therefore, insertion of an insulating material is necessary to form a metal-ferroelectric-insulator-silicon (MFIS), which can lessen the interfacial problems [5]. Insulating materials such as Dy<sub>2</sub>O<sub>3</sub> [6], HfSiON [7], HfO<sub>2</sub> [4], ZrO<sub>2</sub> [8], SrTiO<sub>3</sub> [9], (Ba,Sr)TiO<sub>3</sub> [10], LaZrO<sub>x</sub> [11] have been selected. Among these materials, (Ba,Sr)TiO<sub>3</sub> has been paid more attention due to its unique combination of high dielectric constant, relatively low dielectric loss, and large electric field tenability [12].

In addition, BiFeO<sub>3</sub> with a rhombohedrally distorted perovskite structure, has a lower crystallization temperature, a larger remanent polarization, and a smaller dielectric

constant [13]. These characteristics are considered to be adequate for a FeFET operation. Based on these advantages, many studies have been focused on BiFeO<sub>3</sub>-based films for a MFIS structure [14, 15]. The maximum memory window of BiFeO<sub>3</sub> with a ZrO<sub>2</sub> insulating buffer by chemical solution deposition is only 0.78 V at ± 6 V [16]. However, the maximum memory window of Pt/BiFeO<sub>3</sub>/ZrO<sub>2</sub>/Si prepared by liquid delivery metal-organic chemical vapor deposition is increased to 2.26 V [17]. The drain current on/off ratio for an Al/BiFeO<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>/Si FeFET maintains more than 10<sup>3</sup> without deterioration after 10<sup>4</sup> s [18]. The effect of the annealing temperature and the buffer layer thickness on the memory of BiFeO<sub>3</sub>-based thin films were also investigated [19, 20].

In this study, the BiFeO<sub>3</sub> ferroelectric thin films were prepared by a metal organic decomposition (MOD) method deposited on (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si, and BiFeO<sub>3</sub> films without a (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer were also fabricated for comparison. We report on the effect of the insulating layer on the structure, insulating property, as well as the memory and dielectric properties.

### Experimental

Both BiFeO<sub>3</sub> and (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> thin films were fabricated on Si substrates using a MOD process. Firstly, the preparation of (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer was as follows. Barium acetate, strontium acetate and tetrabutyl titanate were selected as starting materials. Glacial acetic acid and ethylene glycol were used as solvents. Each wet layer of (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> was formed

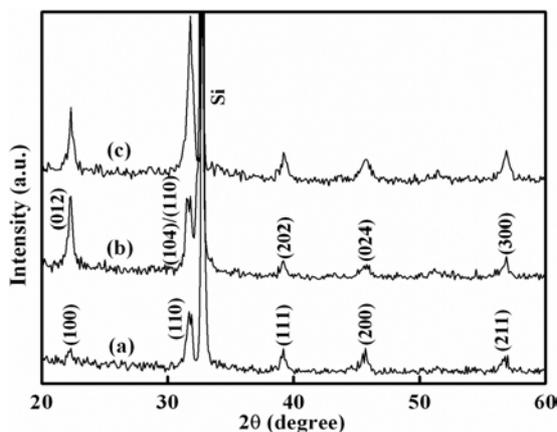
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on a p-Si substrate by spin coating and annealed at 650 °C for 2 minutes in an O<sub>2</sub> atmosphere by a rapid thermal processor (RTP). These steps were repeated three times to obtain a certain thickness. The preparation of a precursor solution for BiFeO<sub>3</sub> has been reported elsewhere [21]. Subsequently, the solution of BiFeO<sub>3</sub> was deposited on the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si and Si substrates. Both the BiFeO<sub>3</sub> films were annealed layer by layer in a RTP at 500 °C for 2 minutes in a N<sub>2</sub> atmosphere. For measurements of electrical properties, Au top electrodes were deposited on the films using a sputtering system through a shadow mask and an Au film was sputtered on the back of the silicon substrate as a bottom electrode. The crystallization was studied by X-ray diffraction using a Rigaku D/MAX-γA X-ray diffractometer. The insulating property was measured using a Keithley 4200 semiconductor characterization system. High-frequency capacitance-voltage (C-V) and dielectric characteristics were all measured using an impedance analyzer (HP4294A).

## Results and Discussion

Figure 1 shows the X-ray diffraction patterns of (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>, BiFeO<sub>3</sub> and BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> films prepared on p-Si substrates. The BiFeO<sub>3</sub> films on two different substrates are all polycrystalline without secondary phases. All detectable diffraction peaks match well to those of the distorted rhombohedral R3c structure. Note that the intensity of the XRD peaks of BiFeO<sub>3</sub> with the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer are stronger than that directly deposited on a Si substrate. This is due to the fact that the nucleation activation energy for BiFeO<sub>3</sub> decreases caused by the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer.

Before measuring the memory properties of the BiFeO<sub>3</sub> films, we first prepared the structure of Au/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si. As shown in Fig. 2(a), the C-V curve has a negligible hysteresis loop, which indicates there is no charge trapping or injection phenomena.



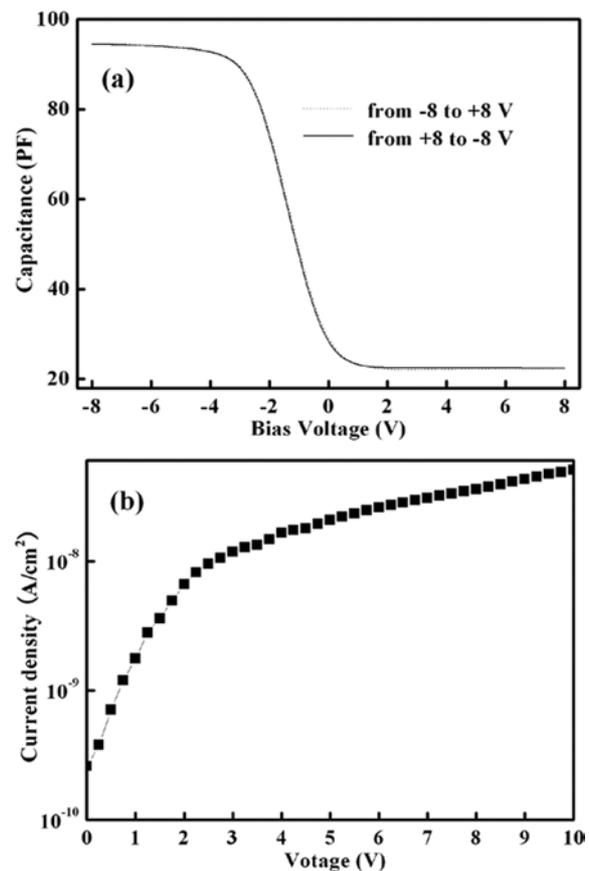
**Fig. 1.** XRD patterns of (a) (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>; (b) BiFeO<sub>3</sub>; (c) BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> films.

The relative dielectric constant of (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>  $\epsilon_r$  can be calculated from the following formula:

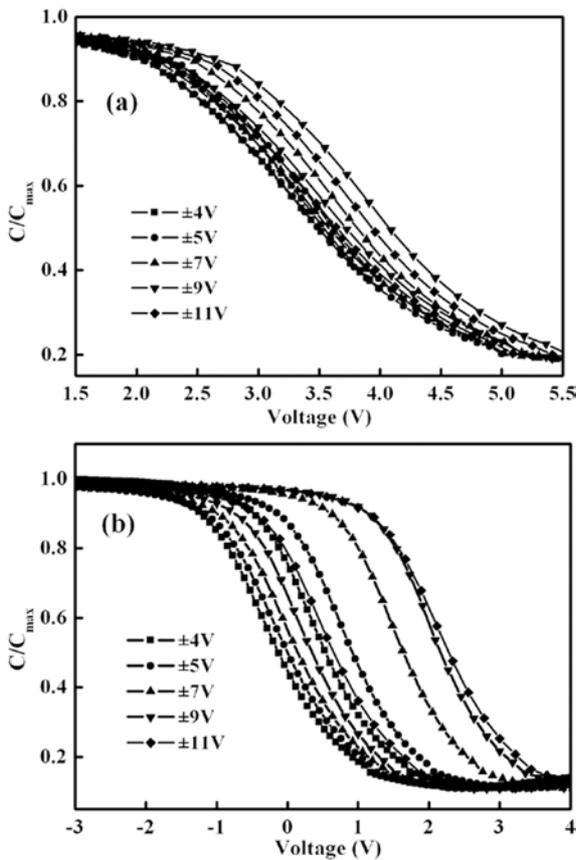
$$\epsilon_r = \frac{dC}{\epsilon_0 S} \quad (1)$$

Where d: is the thickness of (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>; C: is the accumulation capacitance of MFS;  $\epsilon_0$ : is the vacuum permittivity of  $8.85 \times 10^{-12}$  F/m; and S: is the electrode area. The value of the relative dielectric constant can be calculated to be about 17. Compared with TiO<sub>2</sub> ( $\epsilon_r = 12$ ) [22], SiO<sub>2</sub> ( $\epsilon_r = 3.9$ ) [5] HfO<sub>2</sub> ( $\epsilon_r = 15$ ) [23], the higher-*k* insulating layer of (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> is a benefit for guaranteeing a larger electric field across the ferroelectric layer [22]. Figure 2(b) shows the leakage current density is less than 10<sup>-7</sup> A/cm<sup>2</sup> when the applied voltage is not higher than 10 V. These results indicated that (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> can be used as a buffer layer.

Figure 3 exhibits the relationship between C-V curves and sweeping voltage for BiFeO<sub>3</sub> films with and without the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer. The gate voltage was swept from the accumulation to the inversion region and then swept back. The width of the memory window ( $V_m$ ) is defined as the difference of the flatband voltage ( $V_{fb}$ ) shift during the voltage sweeping [15]. The magnitude of the memory window

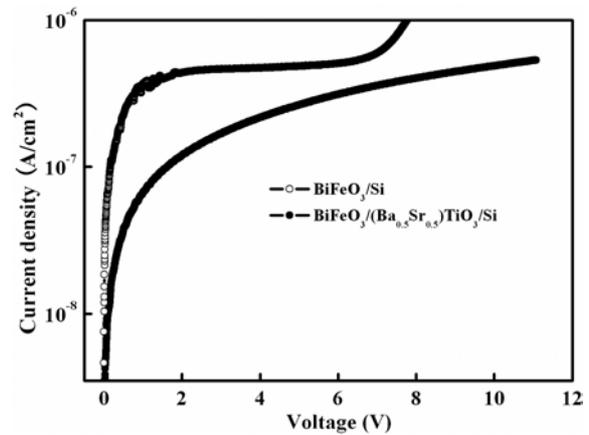


**Fig. 2.** (a) C-V and (b) I-V characteristics of the Au/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si structure measured at 1 MHz.

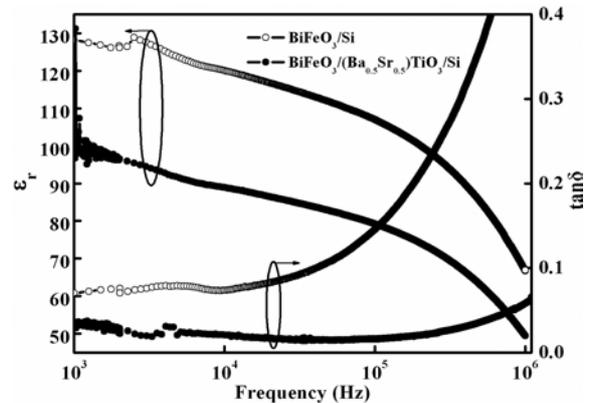


**Fig. 3.** The typical C-V curves of (a) BiFeO<sub>3</sub>/Si; (b) BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si.

is closely related to two factors: (1) the ferroelectric polarization effect of BiFeO<sub>3</sub> films, (2) the charge injection from the Si substrate or metal gate [16]. As shown in Fig. 3, a clockwise rotation in the C-V curve on p-type silicon can be observed for the BiFeO<sub>3</sub> deposited both on the Si and (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> substrates due to the ferroelectric polarization of BiFeO<sub>3</sub> films. We can see from Fig. 3(a) that the memory window for BiFeO<sub>3</sub>/Si is increased to be only 0.38 V when the applied voltage reaches  $\pm 9$  V. However, as seen from Fig. 2(b), at  $\pm 9$  V, the maximum memory window for Au/BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si is 1.93 V, which is comparative to those of La-substituted BiFeO<sub>3</sub>/CeO<sub>2</sub>/Si [24] and BiFeO<sub>3</sub>/HfLaO/Si [19]. Compared to BiFeO<sub>3</sub>/Si, this remarkable improvement of the memory window for BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si is attributed to the application of the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer. The (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> can suppress the charge injection from the Si substrate effectively when the voltage is not higher than  $\pm 9$  V. With the higher voltage further increasing, the memory window of BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> decreases rapidly. This phenomenon should be due to the fact that the ferroelectric polarization is overwhelmed by the injected charges [25]. The charges can be injected into the BiFeO<sub>3</sub> film at higher applied voltage even if the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer exists.



**Fig. 4.** The J-V characteristic of BiFeO<sub>3</sub> films with and without (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layers.



**Fig. 5.** The relative dielectric constant and dissipation factor ( $\epsilon_r$ ,  $\tan\delta$ ) of the BiFeO<sub>3</sub> films with and without (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layers as a function of frequency.

Figure 4 shows the leakage currents as a function of electric field measured at room temperature. For the case of the BiFeO<sub>3</sub> films deposited directly on Si, the leakage current increases dramatically when the voltage reaches 8 V. However, no breakdown can be observed in the range of the applied voltage adopted in the present study for the BiFeO<sub>3</sub> films with a (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer. The leakage current density is below  $5 \times 10^{-7}$  A/cm<sup>2</sup> when the voltage is not higher than 9 V. The leakage current of the BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> is obviously smaller than that of the BiFeO<sub>3</sub> films at the same voltage. This result provides supporting evidence for the above discussion on the memory properties of BiFeO<sub>3</sub> on a (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si substrate.

The relative dielectric constant and dissipation factor ( $\epsilon_r$ ,  $\tan\delta$ ) of the BiFeO<sub>3</sub> films were investigated as a function of frequency, as shown in Fig. 5. The AC driving voltage was 0.01 V. Both samples exhibit a slight dispersion as the frequency increases from 1 kHz to 100 kHz. The dielectric constant and dissipation factor of the BiFeO<sub>3</sub> films without the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer are 107.1 and 0.153, respectively at 100 kHz.

However, the dielectric constant and dissipation factor of the BiFeO<sub>3</sub> films with the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer are decreased to be 77.6 and 0.015. In the MFIS structure, the dielectric capacitor is connected in series with a ferroelectric capacitor. The capacitance of the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> buffer layer is much smaller than that of BiFeO<sub>3</sub> films. Therefore, the dielectric constant of the MFIS is smaller. Because the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> can serve as an insulating barrier to prevent charge injection, the dissipation factor of Au/BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si is smaller compared with Au/BiFeO<sub>3</sub>/Si.

### Conclusions

In conclusion, BiFeO<sub>3</sub> thin films have been successfully prepared on (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si and Si substrates using metal organic decomposition. The (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> bottom layer assists in the crystallization of the BiFeO<sub>3</sub> films. The maximum memory window of BiFeO<sub>3</sub> is effectively enhanced by inserting the (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> insulator layer due to the reduced leakage current. Compared with the Au/BiFeO<sub>3</sub>/Si, the Au/BiFeO<sub>3</sub>/(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub>/Si has a lower relative dielectric constant and dissipation factor.

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### References

1. S.J. Kim, D.H. Hwang, I.S. Lee, J.H. Ahn, and Y.G. Son, *J. Ceram. Process. Res.* 11 [4] (2010) 490-493.
2. I.S. Lee, J.E. Yoon, D.H. Hwang, S.J. Kim, J.H. Ahn, and Y.G. Son, *J. Ceram. Process. Res.* 10 [4] (2009) 541-543.
3. W.S. Kim, H.S. Lee, H.H. Park, and Y.T. Hwang, *Ferroelectrics.* 413 (2011) 1-10.
4. M.S. Bozgeyik, J.S. Cross, H. Ishiwara, and K. Shinozaki, *Microelectron. Eng.* 87 (2010) 2173-2177.
5. A.A. Saif, and P. Poopalan, *Solid State Electron.* 62 (2011) 25-30.
6. T.P. Juan, C.Y. Chang, and J.Y. Lee, *IEEE Electron Device Lett.* 27 (2006) 217-220.
7. X. Lu, H. Ishiwara, and K. Maruyama, *J. Mater. Res.* 23 [10] (2008) 2727-2732.
8. H.S. Choi, E.H. Kim, I.H. Choi, Y.T. Kim, J.H. Choi, and J.Y. Lee, *Thin Solid Films.* 388 (2001) 226-230.
9. E. Tokumitsu, R. Nakamura, and H. Ishiwara, *IEEE Electron Device Lett.* 18 (1997) 160-162.
10. C.H. Liu, J.M. Wu, and L.J. Wu, *Appl. Phys. Lett.* 88 (2006) 122901.
11. J.H. Im, H.S. Jeon, J.N. Kim, G.G. Lee, B.E. Park, and C.J. Kim, *J. Electroceram.* 23 (2009) 284-288.
12. P.C. Joshi, and M.W. Cole, *Appl. Phys. Lett.* 77 (2000) 289-291.
13. S.K. Singh, H. Ishiwara, K. Sato, and K. Maruyama, *J. Appl. Phys.* 102 (2007) 094109.
14. C.S. Yeh, and J.M. Wu, *Appl. Phys. Lett.* 93 (2008) 154101.
15. C.H. Yang, G.D. Hu, Z. Wen, and H.L. Yang, *Appl. Phys. Lett.* 93 (2008) 172906.
16. Y.W. Chiang, and J.M. Wu, *Appl. Phys. Lett.* 91 (2007) 142103.
17. X.G. Han, D. Xie, R. Li, T.L. Ren, and L.T. Liu, *Ferroelectric.* 405 (2010) 236-241.
18. C.M. Lin, W.C. Shih, I.Y. Chang, P.C. Juan, and J.Y. Lee, *Appl. Phys. Lett.* 94 (2009) 142905-1-3.
19. C.L. Sun, P.C. Juan, Y.W. Hsu, and Y.W. Liu, *Thin Solid Films.* 518 (2010) 7433-7436.
20. C.H. Yang, G.D. Hu, Z. W.B. Wu, J.C. Wang, and X. Wang, *Electrochem. Solid. St.* 13 [5] (2010) 43-46.
21. X.M. Chen, G.D. Hu, J. Yan, X. Wang, C.H. Yang, and W.B. Wu, *J. Phys. D : Appl. Phys.* 41 (2008) 225402.
22. D. Xie, X.G. Han, R. Li, T.L. Ren, L.T. Liu, and Y.G. Zhao, *Appl. Phys. Lett.* 97 (2010) 172901-1-3.
23. Trevor Pi-chun Juan, z Jong-hong Lu, and Ming-wei Lu, *J. Electrochem. Soc.* 155 [12] (2008) 991-994.
24. P.C. Juan, C.W. Hsu, C.H. Liu, M.T. Wang, and L.Y. Yeh, *Microelectron. Eng.* 88 (2011) 1217-1220.
25. H.Y. Chen, J.M. Wu, H.E. Huang, and H.Y. Bor, *Appl. Phys. Lett.* 90 (2007) 112907-1-3.