Session C-3

Core – Electronics Materials(3)

Epitaxial Insulator Films on Si and a High Temperature-Operated SOI Pressure Sensors Applications (*Invited*)
Makoto ISHIDA, Hidekuni TAKAO, Kazuaki SAWADA ; Toyohashi University of Technology, Japan

Preparation and Characterization of (Bi,La)Ti_3O_{12} Thin Films for Nonvolatile Memory
Sun Hwan HWANG, Jun Seo RHO, Ho Jung CHANG ; Dankook University, Korea
Young Chul CHANG, Korea University of Technology and Education

Deposition of ZnO Films on Polyimide by Pulsed Laser Ablation
K. J. SUH, H. KINOSITA, H. OKADA, H. J. KIM, A. WAKAHANA, A. YOSHIDA, Toyohashi University of Technology, Japan

Characterization of Ultra Thin HfO_2 Gate Dielectrics Prepared by Atomic Layer Deposition
Taeho LEE, Jaemin OH, Jinho AHN, Hanyang University, Korea.
Youngbae KIM, Duckkyun CHOI, Jaehak JUNG, Evertek Corporation, Korea

Preparation and Characterization of $(Bi,La)Ti_3O_{12}$ Thin Films for Nonvolatile Memory

Sun Hwan Hwang, Jun Seo Rho, Young Chul Chang* and Ho Jung Chang
Department of Electronics Engineering, Dankook University,
Cheonanshi, Chungnam 330-714, Korea
* Department of Mechatronics, Korea University of Technology and Education,
Byungchun-myon 330-860, Korea

Abstract

$Bi_{3.7}La_{0.75}Ti_3O_{12}$(BLT) ferroelectric thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates by the sol-gel method. The as-coated films were crystallized by a post-annealing at the temperatures between 650℃ and 750℃ for 30min. The BLT thin films exhibited typical bismuth-layered perovskite structures and the crystalline quality was improved by the post-annealing in air ambient. The AES depth profiles indicated that there was no remarkable interfacial reaction layers between BLT film and lower electrode. The dielectric constant and the dissipation factor of BLT films post-annealed at 750℃ were about 402 and 0.04 at 5kHz, respectively. The leakage current density of the BLT films annealed at 650℃ was found to be $5\times10^{-7}A/cm^2$ at 3V. The BLT film annealed at 650℃ exhibited ferroelectric properties with a remanent polarization 2Pr ($Pr^+ - Pr^-$) of 32.5μ C/cm^2 and showed no degradation after 10^{10} polarization switching cycles under ±5V bipolar pulse, indication a good fatigue property.

Ⅰ. Introduction

As modern electronic devices such as mobile phones and notebook computers come to be popular, the demand for non-volatile memory devices has been increased. Therefore, ferroelectric thin films have been attracted much attention for the application of nonvolatile ferroelectric random access memories (NVFeRAM) from the view points of high speed operation, low power consumption and large scale integration.[1,2] There are two kinds of ferroelectric nonvolatile memory devices. One is a memory device with one transistor and one ferroelectric storage capacitor and another is the metal-ferroelectric-semiconductor field effect transistor (FET). Generally, the ferroelectric gate FET is recognized to be better memory devices due to the nondestructive read-out capability and large scale integration.

Until recently, some fabrication methods such as the sol-gel method, metalorganic decomposition (MOD), RF magnetron sputtering and pulsed laser deposition (PLD) have been prepared and demonstrated.[3-6] Among these various techniques, the sol-gel method provides a high quality films as well as the rapid and inexpensive processing on a large area substrate. This method is also compatible with many semiconductor fabrication technologies. Pb-free ferroelectric materials such as $SrBi_2Ta_2O_9$ (SBT), $(Bi,La)Ti_3O_{12}$ (BLT), $SrBi_4Ti_3O_{15}$ and $SrBi_2Nb_2O_9$(SBN) are known as promising materials [7,8] for the NVFeRAM application due to their good fatigue properties, low leakage current and high remanent polarization. [9-13] In particular, BLT is one of the most promising candidate for NVFeRAM.

In this study, BLT thin films were prepared on $Pt/Ti/SiO_2/Si$ substrate by the sol-gel method and investigated the dependence of crystallinity and electrical properties on the post-annealing temperatures.

Ⅱ. Experimental Procedure

BLT thin films were coated on $Pt/Ti/SiO_2/Si$ substrates by the sol-gel method. The BLT sol-gel solution was synthesized using the lanthanum acetate hydrate, bismuth 2-ethylhe xanoate and titanium isopropoxide with MEOH solution. The excessive Bi component with 20 mole% was added for the compensation of volatility during the post-annealing. The sol-gel solution was spin-coated onto substrate with two step rotational speeds at 2000rpm for 5s and then 4000rpm for 25s for obtaing the uniform coating on the film surface. After the spin coating, films were baked on a oven at 170℃ to remove residual solvent. The number of coating/drying cycle was repeated 3 times. The thicknesses of films are about 1000Å. The as-coated films were pre-annealed at 450℃ for 30s in O_2 atmosphere by the rapid thermal annealing (RTA) system (herein-after called as "as-coated film"). For the crystallization of BLT films, the post-annealing was conducted at the temperatures ranging from 650℃ to 750℃ for 30min under air ambient. For the electrical measurements, Al top electrode was deposited onto BLT film layer by the thermal evaporation through a metal shadow mask to form the ferroelectric capacitors. Annealing at 400℃ in N_2 ambient was carried out for 10 min in the furnace in order to obtain good ohmic contact between Al top electrode and BLT films. The crystalline structures of films were analyzed by X–ray diffractometer (XRD). The surfacial and cross-sectional morphologies were examined by the scanning electron microscopy (SEM) and atomic force microscopy (AFM). The chemical composition and impurity contents of the films were identified by auger electron spectroscopy (AES) and wave dispersive spectrometer (WDS). P-E hysteresis and fatigue properties were measured under the applied bias of ±5V by the RT66A measurement system. The electrical properties such as leakage current and dielectric constant (ε_r) were determined by using HP4145B and HP4192A.

Ⅲ. Results and Discussion

To investigate the atomic molar ratios of BLT films, the films were measured by WDS analysis. The atomic ratio of the as-coated film was found to be nonstoichiometry with the molar ratio of $Bi_{3.7}La_{0.75}Ti_3O_{12}$. The Bi component was decreased about 12 mole% with incresing the annealing temperature to 750°C, resulted in the volatile of Bi component during the post-annealing.

Figure 1 shows the XRD patterns of the (a) as-coated BLT films and annealed at (b) 650℃, and (c) 750℃, respectively. The films were exhibited typical bismuth layered perovskite structure. The peak intensities were increased and the full width at half maximum (FWHM) value of (006) peak was decreased from 0.31° to 0.27° with increasing the annealing temperature from 650℃ to 750℃, suggesting the improvement of the crystallinity.

Table 1. The atomic molar ratio dependences of BLT films on the annealing temperatures.

Annealing Temp.(℃)	Atomic molar ratio		
	Bi	La	Ti
As-coated	3.70	0.75	3.05
650	3.40	0.60	3.03
750	3.27	0.62	3.08

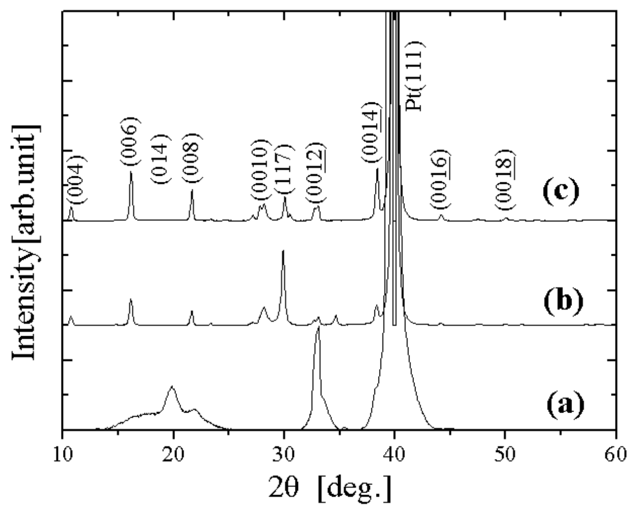

Fig. 1. XRD patterns of (a) the as-coated BLT films and the ones annealed at (b) 650℃ and (c) 750.

The depth profiles of the films were measured to confirm the interfacial reactions between film and lower electrode. Figure 2 represents the AES depth profiles of the (a) as-coated BLT film on $Pt/Ti/SiO_2/Si$ substrate and (b) the sample annealed at 750℃. AES results show that BLT/Pt interface is stable, and no remarkable interfacial reactions for both samples are found.

The SEM cross-sectional micrographs of the (a) as-coated BLT films and (b) the sample annealed at 750℃ are shown in Figure 3. From the cross-sectional views, we found that the thicknesses of BLT films are about 1000 Å.

Figure 4 shows the SEM surfacial morphologies of the (a) as-coated BLT films and annealed at (b) 650℃, and (c) 750℃. The surfacial morphology of the as-coated films was found to be smooth relatively. The grain size was increased with increasing of the annealing temperatures.

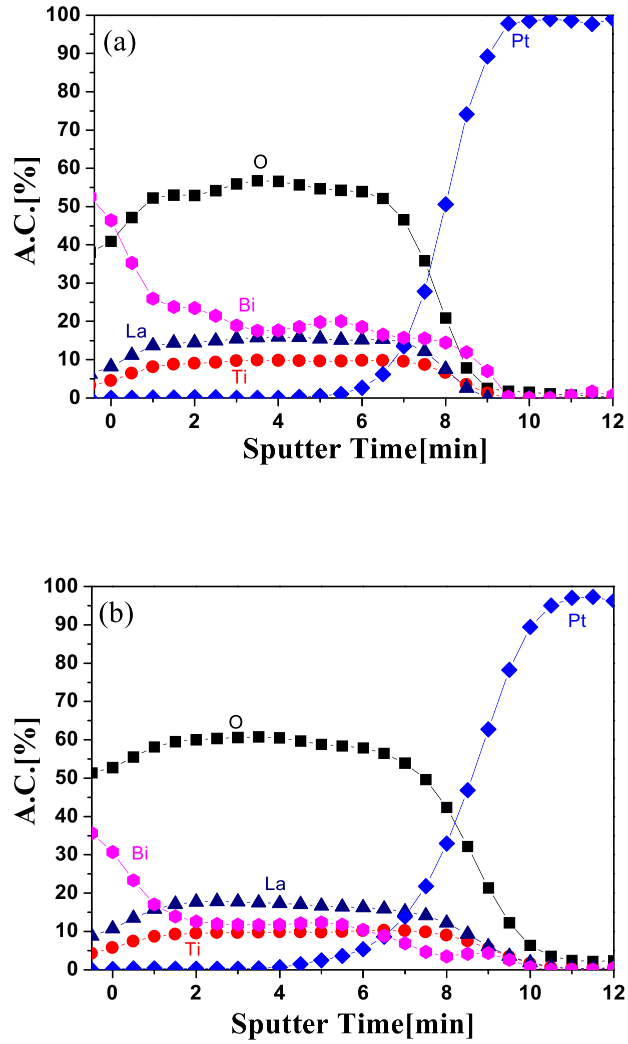

Fig. 2. AES depth profiles of the (a) as-coated BLT films and the film (b) annealed at 750℃.

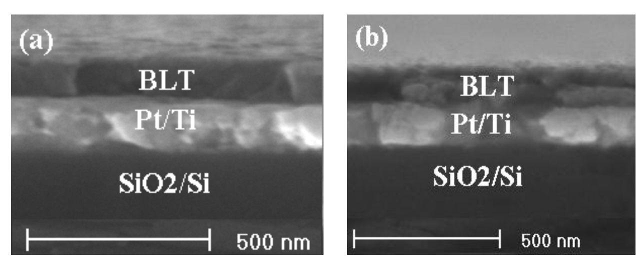

Fig. 3. SEM cross-sectional micrographs of the (a) the as-coated BLT films and (b) the film annealed at 750℃.

Figure 5 shows the AFM images of the (a) as-coated BLT films and the ones annealed at (b) 650℃ and (c) 750℃. AFM images indicate that the surface roughness was affected by the annealing temperatures. The R_{rms} value of the as-coated film was 3.82 Å with relatively smooth surface. Whereas, The R_{rms} value of BLT films annealed at 750℃ was increased to 12.9 Å showing the rough film surface. These results are corresponded with the SEM micrographs in Figure 4.

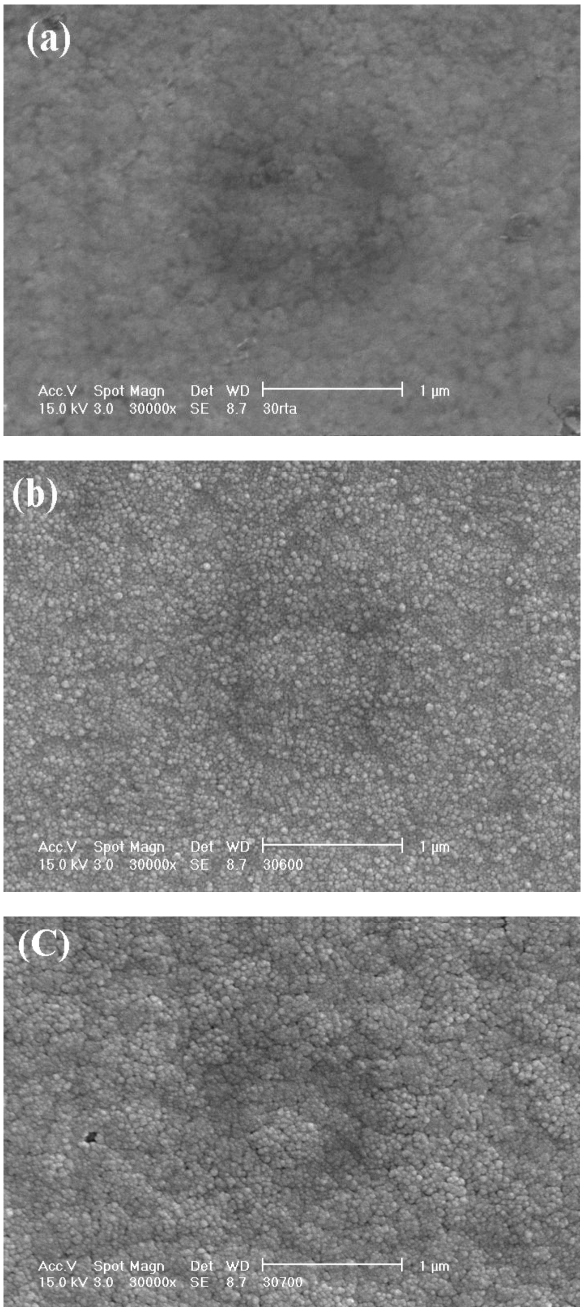

Fig. 4. SEM surfacial micrographs of (a) the as-coated BLT films and ones annealed at (b) 650℃ and (c) 750℃.

Figure 6 shows the P-E hysteresis loops of the as-coated BLT films and annealed samples at 650℃ and 750℃. The remanent polarization depended on the annealing temperatures. The hysteresis loop of the as-coated films showed paraelectric properties and changed to ferroelectric properties by the annealing temperatures at above 650℃. the remanent polarization ($2Pr=Pr^{+}-Pr^{-}$) of the film annealed at 650℃ was 32.5μ C/cm^2. To investigate the fatigue properties, the BLT films were exposed to ±5V bipolar switching pulses. We found that the BLT film showed no degradation in polarization after 10^{10} switching cycles indication a good fatigue property.

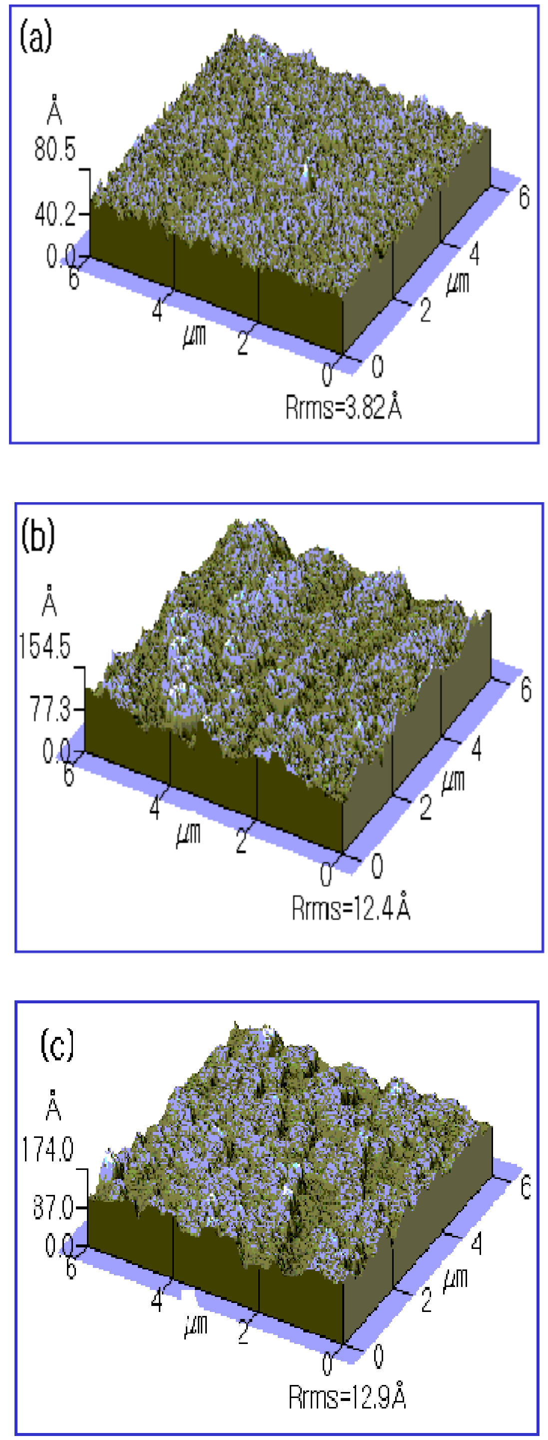

Fig. 5. AFM images of (a) the as-coated BLT films and the ones annealed at (b) 650℃ and (c) 750℃.

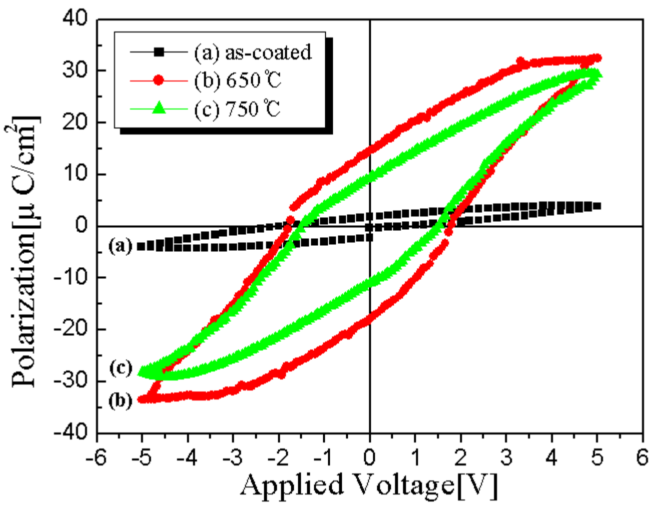

Fig. 6. P-E hysteresis loops of (a) the as-coated BLT films and the annealed at (b) 650℃, and (c) 750℃.

Figure 7 shows the dielectric constants (ε_r) and dissipation factor ($\tan\delta$) for BLT films annealed at various temperatures as a function of frequency. The dielectric constant of the as-coated film was about 305 and increased to 402 with increasing the annealing temperature to 750℃. This may be related to the increase of the grain size and the decrease of the grain boundary layers which have low dielectric constant.[14] The dissipation factor of the as-coated film was about 0.016 at 0.5kHz and decreased to 0.002 at 0.5MHz in the frequency for the film annealed at 750℃.

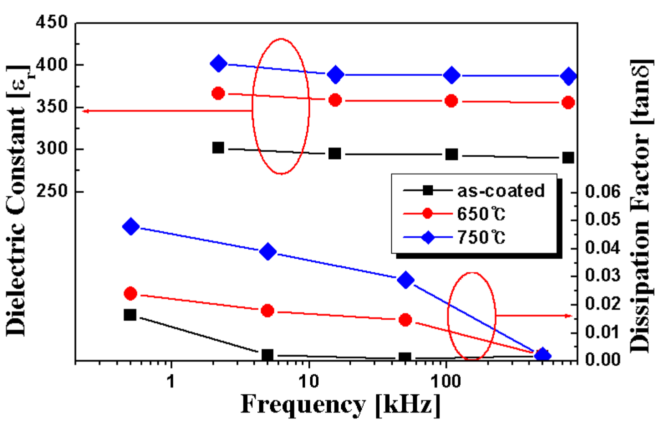

Fig. 7. Dielectric constants (ε_r) and dissipation factor ($\tan\delta$) of the various BLT films as a function of frequency.

The current density of the annealed BLT films at (a) 650℃ and (b) 750℃ as a function of applied voltages is shown in Figure 8. The current density of the BLT film annealed at 650℃was about $5\times10^{-7}A/cm^2$. It is also found that the film post-annealed at 750℃ has slightly larger leakage current than that post-annealed at 650℃. This reason can be explained that there occured grain growth due to the increase of the post-annealing temperature, which is found from the SEM morphologies in Fig. 4.

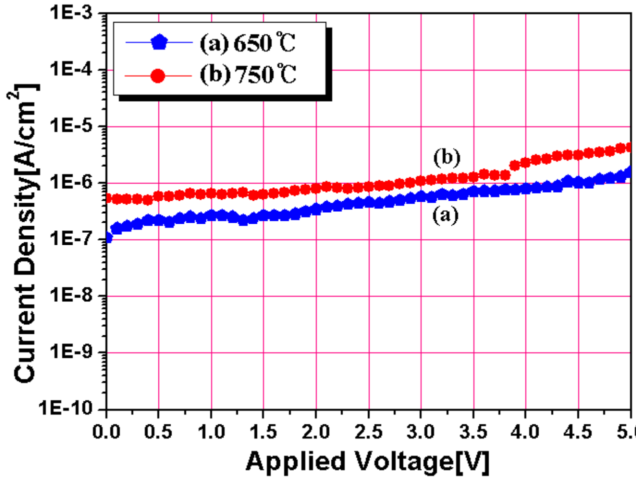

Fig. 8. Current-voltage curves of the BLT films annealed at (a) 650℃ and (b) 750℃ as a function of the applied voltage.

Ⅳ.Conclusions

$Bi_{3.7}La_{0.75}Ti_3O_{12}$ (BLT) ferroelectric thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates by the sol-gel method and followed by the crystallization at the temperatures between 650℃ and 750℃ under air ambient. The BLT thin films exhibited typical bismuth-layered perovskite structures and the crystalline quality was improved by the post-annealing. The AES depth profiles indicated that there was no remarkable interfacial reaction layers between BLT film and lower electrode. The dielectric constant and the dissipation factor of the films annealed at 750℃ were about 402 and 0.04 at 5kHz, respectively. The dielectric constant increased with increasing the post-annealing temperatures. The remanent polarization (2Pr=Pr+-Pr-) of the film annealed at 650℃ was 32.5μ C/cm^2. The BLT film annealed at 650℃ showed no degradation after 10^{10} polarization switching cycle.

Acknowledgments

This work was supported by a grant No. 2000-1-30100-017-3 from Korea Science & Engineering Foundation.

References

1. B. A. Tuttle, Mater. Res. Bull. Vol. 12 (1987), p.40.
2. J. F. Scott and C. A. Paz de Araujo, Science Vol. 246 (1989), pp.1400-1404.
3. D. Wu, A. Li, H. Ling, T. Yu, Z. Liu and N. Ming, J. Appl. Phys. Vol. 87 (2000), pp.1975-1981.
4. M. Noda, H. Sugiyama and M. Okuyama, Jpn. J. Appl. Phys. Vol. 38 (1999), pp.5432-5436.
5. N. Nukaga, K. Ishikawa and H. Funakubo, Jpn. J. Appl. Phys. Vol. 38 (1999), pp.5428-5432.

6. H. J. Chang, K. J. Suh, M. Y. Kim and G. K. chang, J. Korean Phys. Soc. Vol. 32 (1998), pp.S1679-S1681.
7. B. H. Park , B. S. Kang, S. D. Bu, T. W. Noh, J.Lee and W. Jo, Nature, Vol. 401 (1999), pp.682-685.
8. T. Nakamura, Y. Nakao, A. Kamisawa and H. Takasu, Jpn. J. Appl. Phys. Vol. 33 (1994), pp.5207-5210.
9. C. A. Paz de Araujo, J.D. Cuchiaro, L. D. McMillan and M. C. Scott, Nature, Vol. 374 (1995), pp.627-631.
10. Peir Y. Chu, Robert E. Jones, Jr, Peter Zurcher, Deborah J. Taylor, Bo Jiang, and Sherry J. Gillespie, J. Mater. Res. Vol. 11 (1996), pp.1065-1069.
11. M. Aoki, M. Mushiga, A. Itoh, T. Eshita, and Y. Arimoto, 1999 Sympo. VLSI Technol. Digest of Tech. Papers, (1999), pp.145-150.
12. M. Takashi, Y. Hiroyuki, W. Hitoshi and Carlos A. Paz de Araujo, Jpn. J. Appl. Phys. Vol. 34 (1998), pp.5233-5236.
13. K. Okamoto and E. Tokumitsu, Appl. Phys. Lett. Vol. 76, (2000), pp.2609-2613.
14. H. Wang and W. A. Schulze, J. Am. Ceram. Soc. Vol. 73, (1989), pp.825-830.