The Influence of Annealing Treatment on Physics and Electrical Characteristics of $Ba(Zr_{0.1}Ti_{0.9})O_3$ Ferroelectric Films on ITO/glass Substrate

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Abstract

Perovskite $Ba(Zr_{0.1}Ti_{0.9})O_3$ (BZ1T9) ferroelectric thin films well deposited on ITO/glass substrates for applications in system-on-panel (SOP) devices are produced and investigated. The sputtering parameters of as-deposited BZ1T9 thin films were rf power of 160 W, chamber pressure of 10 mTorr, substrate temperature of 550°C, and an oxygen concentration of 40%. From the SEM cross-sectional observation, the deposition rate of the as-deposited BZT thin films were about 2.5 nm/min. Additionally, the maximum dielectric constant and leakage current density of annealed BZT films under the rapid temperature annealing would be increased, as the temperature increased to 650⁰C. Further, the maximum remnant polarization and coercive field of BZT films were found and calculated from the p-E curves.

Introduction

Recently, electronic devices and systems on panel (SOP) technology had been widely discussed and researched. However, the indium–tin-oxide (ITO) glass substrate would be deformed and fused under high temperature process. The high temperature fabrication process for electronic devices is sometimes essential and indispensable technology, such as the conventional annealing, rapid thermal annealing and etc. [1]. Until now, the detailed structures and properties of Metal-Ferroelectric-Metal (MFM) structure, fabricated under various processes and technologies, on glass substrate for the potential applications of ferroelectric thin films on nonvolatile memory device have not been reported.

The high remanent polarization and low coercive field of many ferroelectric materials, such as $Pb(Zr,Ti)O_3$ (PZT), $Sr_2Bi_2Ta_2O_9$ (SBT), $SrTiO_3$ (ST), $Ba(Zr,Ti)O_3$ (BZT), and $(Ba,Sr)TiO_3$ (BST), have been widely utilized for applications in larger storage capacity FeRAM devices. However, BST and BZ1T9 ferroelectric materials are expected to replace the lead and bismuth elements in bismuth-layered ferroelectric structure (BLFS) materials because of the latter's environmentally damaging nature and high deposition temperature [2-9].

Several technologies such as the radio-frequency sputtering, activated reactive evaporation, ion beam sputtering, electron cyclotron resonance, plasma enhanced MOCVD, liquid source CVD, sol-gel, pulsed laser deposition method and MOD technique have been employed to deposit BST and BZT thin films.

The ferroelectric thin films by rapid temperature annealing (RTA) and conventional temperature annealing (CFA) processing have been reported extensively. Many studies had been reported that rapid temperature annealing method was successfully to increase the electrical and physical properties [7-9]. In addition, grain size, electrical properties and surface roughness are greatly affected by annealing temperature under conventional furnace annealing [7].

The subject of this work is to study the characteristics of thin films of perovskite oxide BZT, deposited on ITO glass substrate using the different RTA annealing temperatures. In which, the characteristics of the Al/BZT/ITO glass (MFM) structures, were reported and the relationship between the electrical properties and different annealing temperature of MFM structure was investigated. In addition, preferred orientation, crystal phase and dielectric properties of BZT thin films by different annealing temperatures will be also discussion and evaluated.

Experimental

The raw materials of $BaCO_3$, ZrO_2, and TiO_2 were weighed in accordance with the composition of $Ba(Zr_{0.1}Ti_{0.9})O_3$. After mixing and ball milling for 1 h, the mixture was dried and ground for 1 h. The calcining process was carried out at 1100^{o}C for 2 h and ground with an agate mortar for 1 h. The $Ba(Zr_{0.1}Ti_{0.9})O_3$ powder was pressed into pellets in a steel die, and the pressed target was sintered at 1450^{o}C in an air ambient for 2 h. The $Ba(Zr_{0.1}Ti_{0.9})O_3$ (BZ1T9) thin films were deposited on ITO/glass substrates by rf magnetron sputtering to form an MFM structure, as shown in Fig. 1.

The target of $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramic was placed about 5-8 cm away from the ITO/glass substrate. The BZ1T9 thin films were deposited for 1h by sputtering under the following conditions: rf power, 160 W; chamber pressure, 10 mTorr; substrate temperature, 550^{o}C; and different oxygen concentrations. In addition, as-deposited BZ1T9 films were treated by rapid thermal annealing (RTA) in oxygen atmosphere for 2 min. The crystalline structure of as-deposited BZ1T9 thin films was determined by X-ray diffraction using Cu Kα radiation, and the surface roughness of thin films was observed from the SEM images.

To complete the MFM structure, an array of Al circular top contacts with a diameter of 0.1 cm and a thickness of 500 nm was formed by thermal evaporation. The saturation polarization, remanent polarization, and coercive field properties of BZ1T9 thin films were measured using a Sawyer-Tower circuit. The dielectric constant and leakage current density of BZ1T9 thin films were measured using an impendence phase analyzer (HP 4194A) and a semiconductor parameter analyzer (HP 4156).

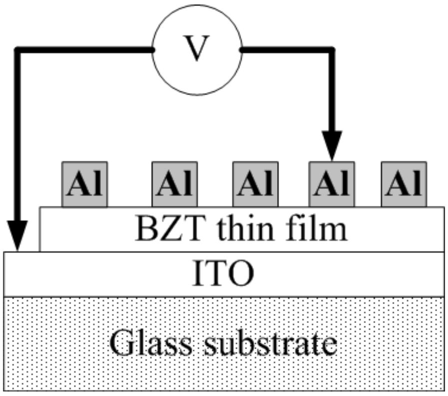


Figure 1. Sample configuration for electrical measurements.

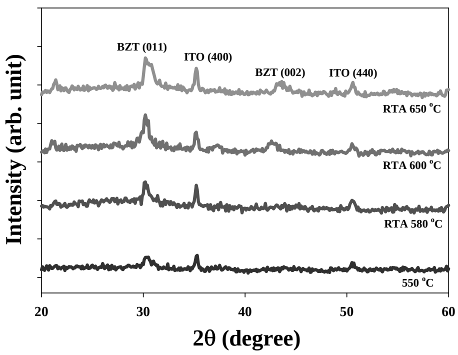
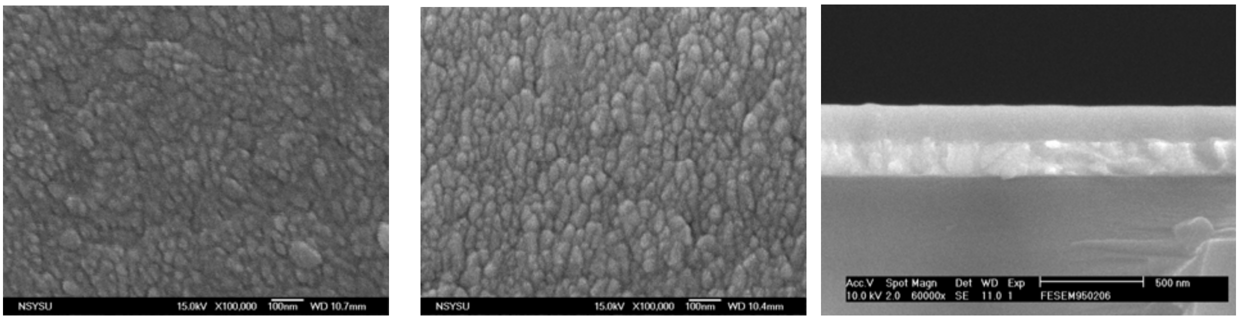


Figure. 2. XRD patterns of BZT films annealed at various temperature by RTA.

Discussion

The BZT films successfully deposited at ITO/glass under the optimal parameters, such as rf power of 160 W, substrate temperature of 550^{o}C chamber pressure of 10 mTorr and oxygen concentration 25 %. Moreover, the XRD patterns of as-deposited BZT thin films under 580~650^{o}C RTA process were shown in Fig. 2. From XRD patterns, the (011) and (002) peaks of BZT films would be found. The strongest and sharp peak along (011) crystal plane was observed, which means that BZT films grew epitaxially with ITO (400) bottom electrode. As shown in Fig. 2, the intensity of peaks increased with increasing the temperature of RTA. It may be assumed that those results are due to an increase of crystalline with resulted from the post-annealed process with increasing annealing temperature of 650^{o}C.

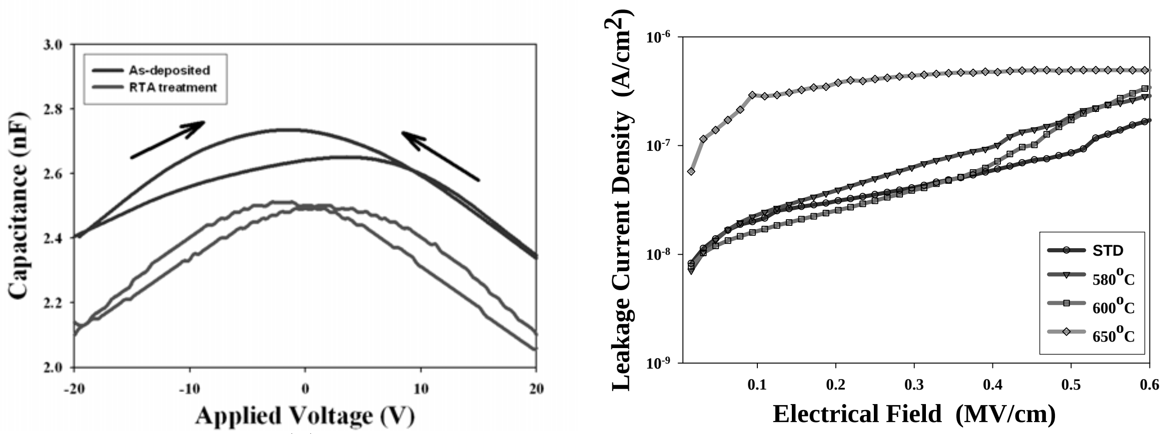
From the SEM morphology, the surface morphology and micro-structure of as-deposited BZT films under the RTA process were shown in fig. 3(a) and (b). The grain size and boundary of BZT thin films increased while the annealing temperature increased to 650^{o}C. However, the denser and tight surface structure of as-deposited and annealed BZT films would not be changed. In Fig. 3(c), the thickness of as-deposited BZT films would be calculated and found from the SEM cross-section images. Besides, the deposited rate of BZT films was about 20 nm/mim. From the SEM images obtained, the thickness of annealed BZT films under 650°C was similar to those of as-deposited films.



(a) (b) (c)

Figure. 3. Surface morphology of (a) as-deposited film, (b) RTA annealed films, and (c) cross-sectional images.

Figure 4(a) shows the capacitance versus applied voltage (C-V) curves of as-deposited and annealed BZT films when applied voltage of ±20V. From the experiments obtained, the capacitance of RTA annealed BZT films increased from 2.4 to 2.75 nF while the temperature increased to 650°C. Besides, the maximum dielectric constant of RTA annealed BZT films would be found, and these was about 120. In addition, the larger grain size of annealed BZT films could be attributed to this reason in fig. 3(b).



(a) (b)

Figure. 4. (a) Capacitance versus voltage (C-V) curves and (b) leakage current density versus electrical field (J-E) of RTA annealed BZT films.

The leakage current density versus applied electrical field (J-E) curves of as-deposited BZT films under 650°C RTA process were shown in Fig. 4(b). The leakage current densities of as-deposited BZT films using RTA process were about 2×10^{-6} A/cm^2 under the electrical field of 0.5 MV/cm. It showed that the leakage current density of annealed-BZT films was larger than those of as-deposited BZT. This can be verified by the grain size of BZT thin films from SEM morphology in fig 3(b). To investigate the difference between no annealing process treatment and annealed process treatment of as-deposited BZT films, the electrical properties of RTA-annealed films had been discussed.

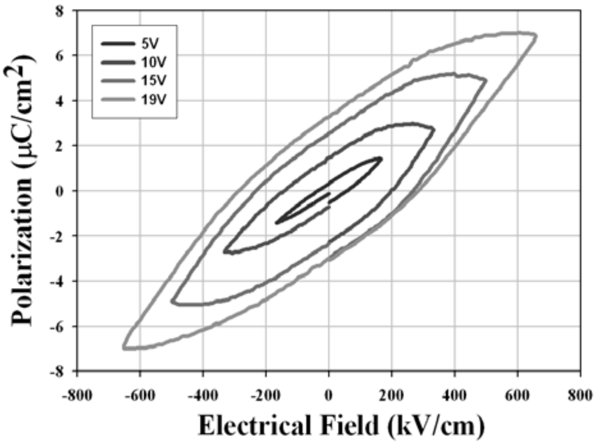


Figure. 5. Polarization versus electrical field (p-E) curves of RTA annealed BZT films.

The polarization versus applied electrical field (p-E) curves of as-deposited BZT thin films at a frequency of 100 kHz is shown in fig. 5. As the applied voltage increases, the remanent polarization of thin films increases from 1 to 3 $\mu C/cm^2$. In addition, the $2P_r$ and coercive field are also calculated and are about 6 $\mu C/cm^2$ and 250 kV/cm, respectively. According to our previous study, the BZT thin film deposited at a higher temperature exhibits a higher dielectric constant and a higher leakage current density because of its polycrystalline structure [10].

Conclusion

In summary, the optimal rf magnetron sputtering parameters for the deposition of BZT films on ITO/glass substrates were obtained. The capacitance and leakage current density of the as-deposited BSTZ films were about 2.4 nF and 10^{-7} A/cm^2, respectively. From the patterns of XRD, SEM, CV and IV curves measurements, we would be found that characteristics of BZT films improved by post annealing treatment process. Besides, the as-deposited and annealed BZT films exhibited the ferroelectric property, and the remnant polarization and coercive field would be found. Those were about 3 $\mu C/cm^2$ and 250 kV/cm at a frequency of 100 kHz. Finally, the as-deposited BZT thin films under the 650^{o}C RTA process will be an excellent candidate for the next generation of high density ferroelectric random access memories.

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