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Deposition and properties of highly (100)-oriented barium titanate thin films on $LaNiO_3$ electrode

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Abstract

Highly crystallized and (100)-oriented barium titanate thin films having a composition of $Ba(Zr_{0.12}Ti_{0.88})O_3$ (BZT) were deposited on (100)-textured $LaNiO_3$ electrode by rf magnetron sputtering at temperature from 300 to 550°C. The films had a very flat interface which was epitaxially bonded to the $LaNiO_3$ electrode. However, the film deposited on Pt electrode was only weakly crystallized and had a rugged film/electrode interface. Satisfactory dielectric constant of value around 220~270 was achieved for the films of 50 nm thick when deposited on $LaNiO_3$ electrode at temperatures of 400~550°C, while a much lower dielectric constant was obtained for that deposited on Pt electrode. More importantly, the films showed a very good insulating characteristic against biasing voltage, i.e. a low leakage current density, $\leqslant 10^{-9}$ A/cm^2, was maintained before reaching an onset voltage as high as ~5 V, as compared to the film deposited on Pt electrode. It was also found that the current emission of the BZT thin films deposited on $LaNiO_3$ followed the relation of Schottky emission, and a high Schottky barrier of 0.73 eV was evaluated from the temperature dependance of current emission.

Keywords: Properties; A. Films

1. Introduction

Barium titanate thin films, such as $(Ba_{1-x}Sr_x)TiO_3$ (BST) [1–3], $Ba(Zr_xTi_{1-x})O_3$ (BZT) [4,5], $Ba(Sn_xTi_{1-x})O_3$ [6], etc. are promising materials of high dielectric constant for applications in fabricating cell capacitors of giga-bit density dynamic random access memories (DRAMs). A high processing temperature, e.g. ~600°C, is generally required for the fabrication of thin film capacitors of barium titanate, in which the normal metal, Pt, is usually used as the bottom electrodes, due to the low crystallization ability of barium titanates. However, a high processing temperature is detrimental to the integrated CMOS circuits of the DRAM devices.

One way to enhance the crystallization ability of barium titanate thin films is through the reduction of activation energy of crystallite nucleation by deposition on electrodes having a structure crystallographically matching that of barium titanates. Among many electrode materials, $LaNiO_3$ (LNO) is one of the metallic oxide having a perovskite structure similar to that of barium titanates [7]. Moreover, highly smooth and (100)-textured thin films of $LaNiO_3$ can be easily prepared by sputtering deposition at a moderate temperature [8] and it has been successfully used as a bottom electrode for the deposition of ferroelectric thin films [8–10]. Therefore, the effect of $LaNiO_3$ electrode on the crystallization and characteristics of sputter-deposited thin films of barium titanate was studied in this work. The BZT was chosen for this study because it not only has a high dielectric constant as that of BST but also possesses a superior leakage current characteristic to that of BST [4,5].

2. Experimental procedure

The $LaNiO_3$ electrode of 250 nm was deposited on platinized substrates of Si ($Pt/Ti/SiO_2/Si$) by rf magnetron sputtering at 350°C. Stoichiometric BZT thin films having a composition of $Ba(Zr_{0.12}Ti_{0.88})O_3$ were then deposited on the $LaNiO_3$ electrode at temperatures in the range of 300 to 550°C, by sputtering in which an Ar/O_2 mixture gas of ratio equal to 50/50 with a pressure of 5×10^{-3} Torr was used. For electrical characterization,

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Pt top electrodes of 100 μm in diameter were coated on the BZT films by sputtering at room temperature.

The crystallization and the interfacial structure of the BZT films were examined, respectively, by X-ray diffraction (XRD, Cu K_α radiation) and transmission electron microscopy (TEM). The composition depth profile of the BZT films deposited on $LaNiO_3$ was also analyzed by secondary ion mass spectroscopy (SIMS). An HP4192 Impedance Analyzer was used to measure the dielectric properties of the BZT films, and an HP4140B pA meter was employed for the measurement of the current–voltage characteristics of the films with positive bias applied on the top electrode.

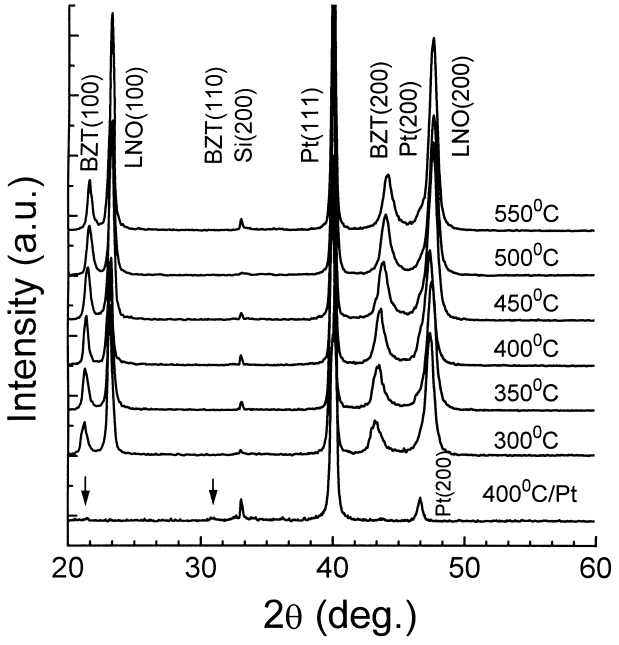

Fig. 1. The XRD patterns of the BZT thin films deposited on $LaNiO_3$ at temperatures from 300 to 550°C, as well as that deposited on Pt at 400°C.

3. Results and discussion

The XRD patterns of 50 nm thick BZT films deposited on the $LaNiO_3$ electrode at different temperatures, as well as one directly deposited on the platinized Si substrate at 400°C, are shown in Fig. 1. Highly (100)-oriented BZT films were formed on the (100)-textured electrode of $LaNiO_3$. However, a weakly crystallized BZT film was obtained for deposition on the Pt electrode. The result clearly reveals that the crystallization of the BZT films was significantly enhanced by deposition on the $LaNiO_3$ electrode.

The cross-sectional transmission electron micrograph and lattice image of the BZT films on $LaNiO_3$ and Pt electrodes are shown in Figs. 2 and 3, respectively. A very flat and epitaxially bonded interface was formed between the BZT and $LaNiO_3$, but not for the film deposited on Pt. The result clearly indicated that the crystallization of BZT film was indeed enhanced by a lattice-matched nucleation on the $LaNiO_3$ electrode.

Fig. 4(a) and (b) shows the SIMS depth profiles of the BZT films deposited on $LaNiO_3$ at 300 and 550°C, respectively. It was found that the composition gradient at the interface between the BZT and $LaNiO_3$ was sharp and insensitive to the deposition temperature, indicating

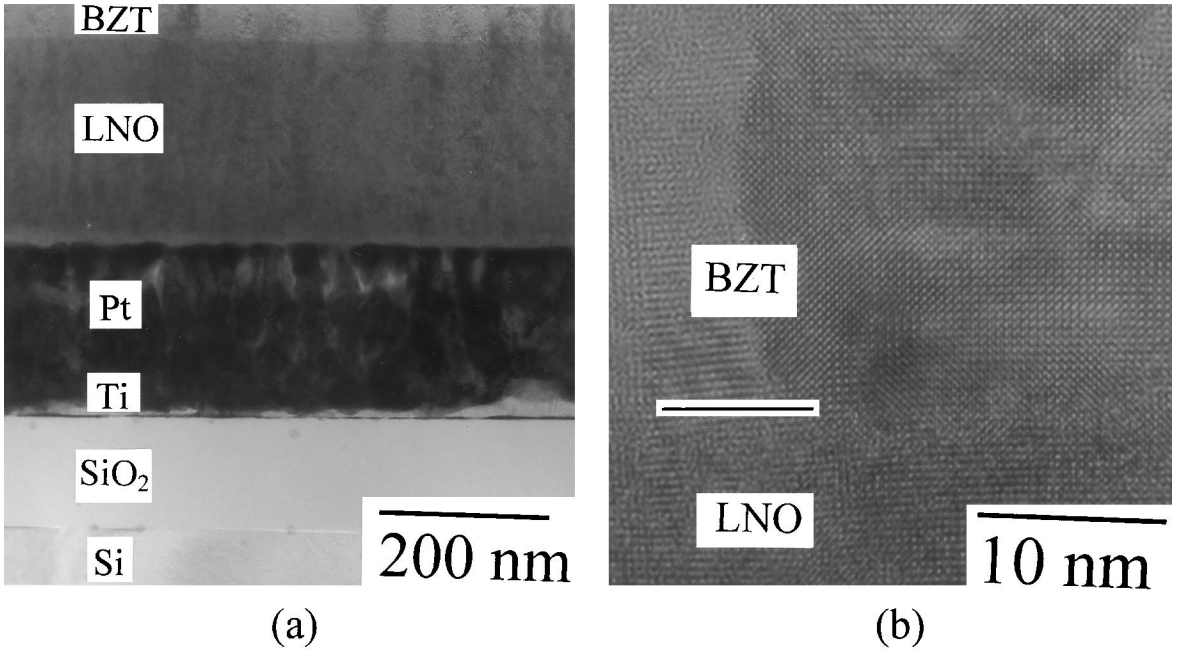

Fig. 2. Transmission electron micrographs of BZT thin film deposited on $LaNiO_3$: (a) cross-sectional micrograph, and (b) lattice image.

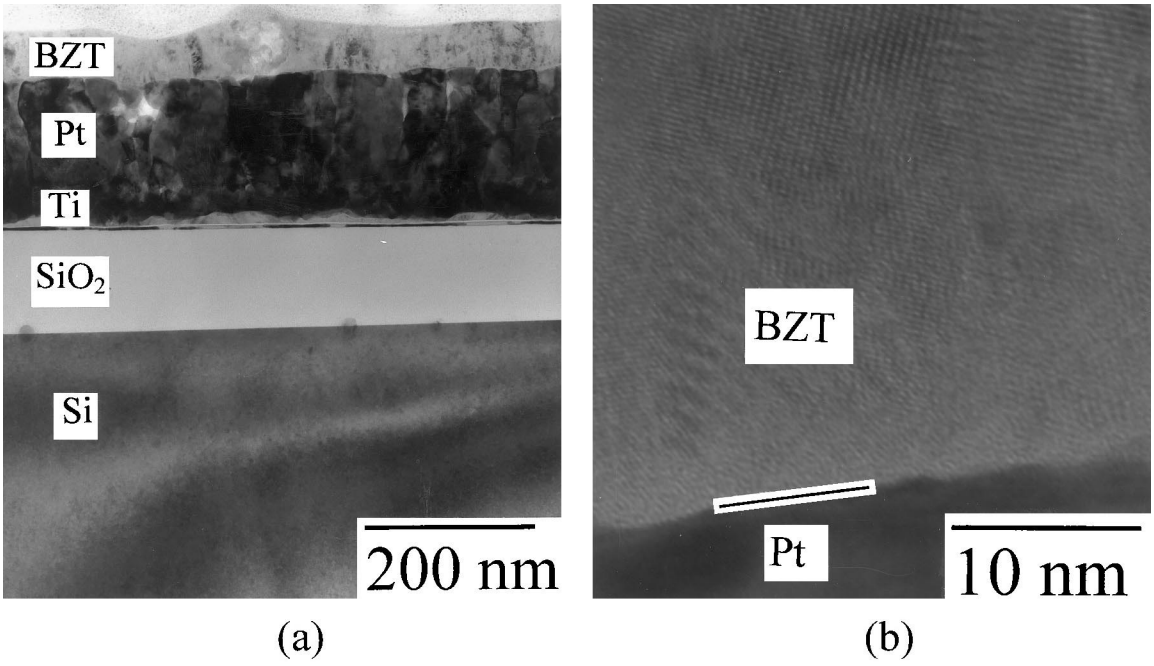

Fig. 3. Transmission electron micrographs of BZT thin film deposited on Pt: (a) cross-sectional micrograph, and (b) lattice image.

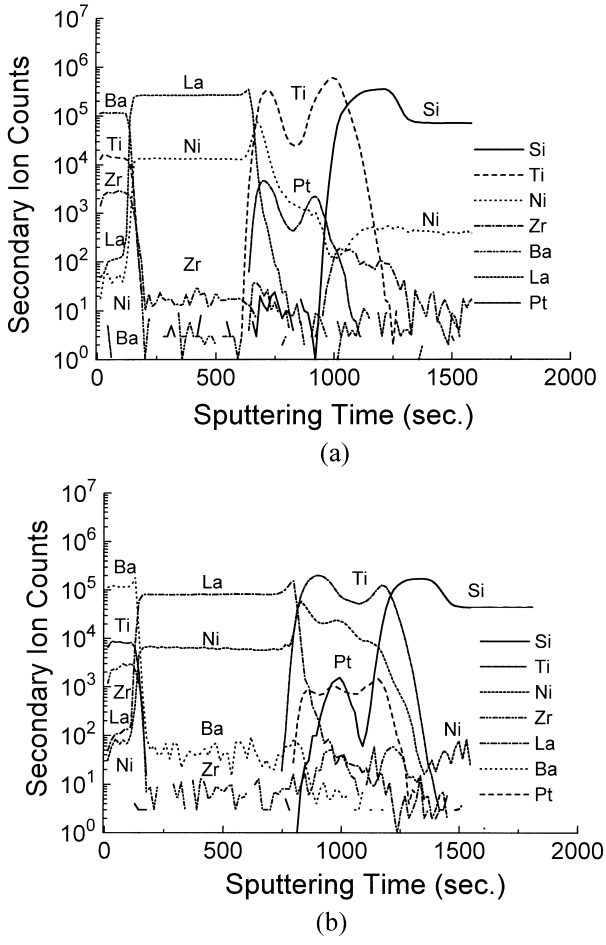

Fig. 4. The SIMS depth profiles of BZT thin film deposited on $LaNiO_3$ at: (a) 300°C, and (b)550°C.

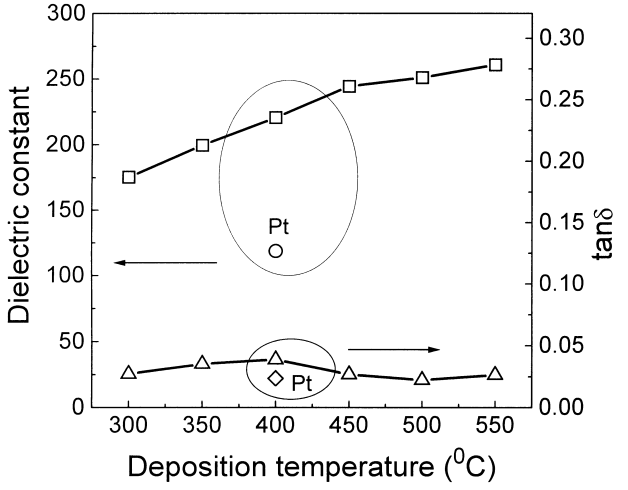

Fig. 5. The change of dielectric constant of BZT thin films on $LaNiO_3$ and Pt with respect to the deposition temperature.

that the interdiffusion between the BZT and $LaNiO_3$ during the film deposition was quite low.

The change of the dielectric constant of the BZT films on $LaNiO_3$ with respect to the increase of deposition temperature is shown in Fig. 5, along with the one of the film deposited on Pt at 400°C. The dielectric constant increased from 175 to 270 with increasing the deposition temperature from 300 to 550°C, and all the values were significantly higher for the film deposited on Pt, i.e. 125. The result is obviously consistent with the previous XRD observation that the crystallization of the BZT films was greatly enhanced by deposition on the $LaNiO_3$ electrode.

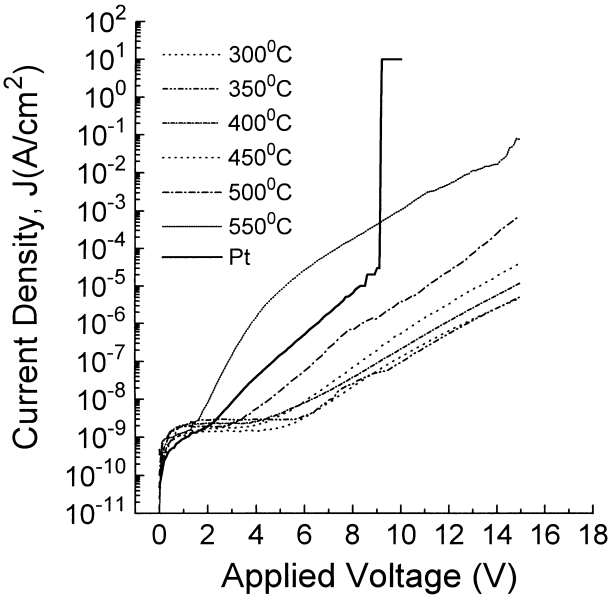

Fig. 6. The current–voltage curves of Pt/BZT/$LaNiO_3$ and Pt/BZT/Pt capacitors with BZT films deposited on $LaNiO_3$ at different temperatures and that deposited on Pt at 400°C.

The current–voltage relations of Pt/$LaNiO_3$/BZT capacitors, as well of Pt/BZT/Pt, are shown in Fig. 6. A low leakage current less than 10^{-9}A/cm^2 was measured in the low bias regime before the onset of high current emission, and the onset voltage raised with decreasing the deposition temperature of the BZT films. Moreover, an onset voltage of ~5 V, which corresponded to a high field of ~1MV/cm, could be obtained for the films deposited on $LaNiO_3$ at temperatures below 500°C. However, the film deposited on Pt only had a relatively low onset voltage of 2 V. Fig. 7 shows the relation of $\ln(J/T^2)$ vs. $V^{1/2}$ for the high current emission measured at different ambient temperatures (T) from the film deposited on $LaNiO_3$ at 400°C, in which J and V are the current density and the biasing voltage of measurement, respectively. A quite good linearity was found from the plots in the region of high current emission, which indicates that the mechanism of Schottky emission was followed. According to the equation of Schottky emission, the barrier height, ϕ_B, of electron emission from $LaNiO_3$ to BZT was evaluated from the slope of the plot, $\ln(J/T^2)_{V=0}$ vs. $1/T$, shown in Fig. 8. A high value of $\phi_B = 0.73$ eV was obtained.

The above results clearly revealed the significant effects of $LaNiO_3$ electrode on improving the crystallization ability and electrical properties, i.e. the dielectric constant and the onset voltage of high current emission, of the deposited BZT thin films. The high dielectric constant obviously resulted from the better crystallinity of the films. On the other hand, the high onset voltage was most likely related to the flat interface as well as the high Shottky barrier formed between BZT and $LaNiO_3$. For the former, the localized enhancement

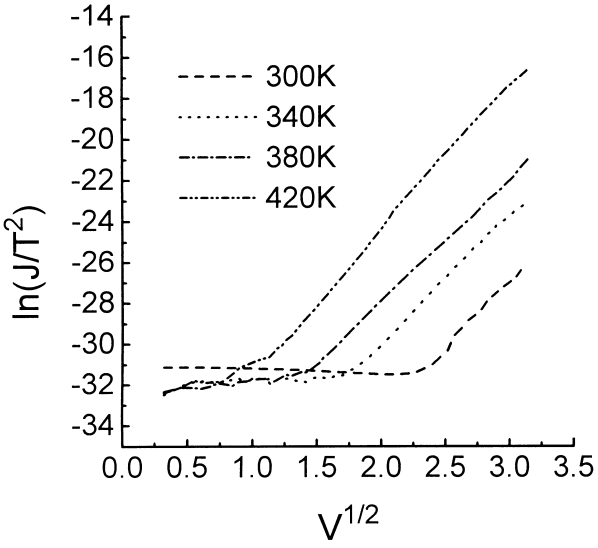

Fig.7. The relations of $\ln(J/T^2)$ vs. $V^{1/2}$ of the BZT Film deposited on $LaNiO_3$ at 400°C and measured at different ambient temperatures.

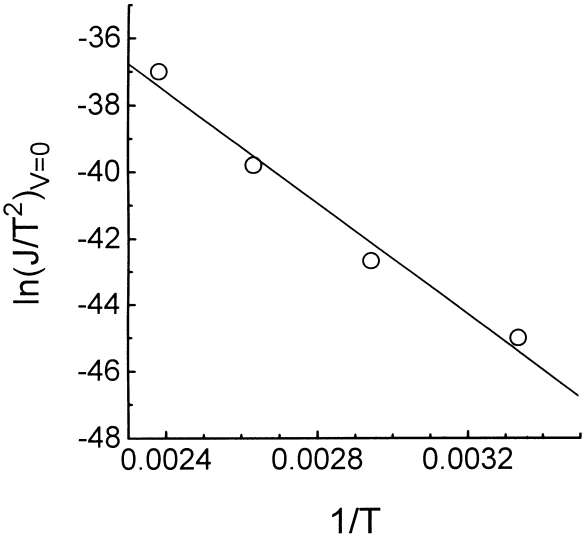

Fig. 8. The plot of $\ln(J/T^2)_{V=0}$ vs. $1/T$ with data taken from Fig. 7.

of current emission induced by a nonuniform distribution of biasing field at the interface could be avoided.

4. Conclusions

(100)-textured $LaNiO_3$ electrode was used for the deposition of $Ba(Zr_{0.12}Ti_{0.88})O_3$ (BZT) thin films by rf magnetron sputtering. Highly crystallized and (100)-oriented perovskite thin films of BZT were obtained by deposition at temperatures from 300 to 550°C, and the film was epitaxially bonded to the $LaNiO_3$ electrode with a very flat interface formed between them. Satisfactory dielectric constant of about 220~270 was obtained for 50 nm thick films deposited at a low temperature of 400~550°C. More importantly, the films had a very

good insulating characteristic against biasing voltage, i.e. a low leakage current of $\leqslant 10^{-9}$ A/cm^2 was maintained before the onset of an abrupt current emission at a voltage as high as 5V which corresponds to a high electric field of 1 MV/cm. It was also found that the current emission behavior of the BZT films deposited on $LaNiO_3$ followed the mechanism of Schottky emission, and a high Schottky barrier of about 0.73 eV was evaluated from the temperature dependence of current–voltage relation.

Acknowledgements

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References

[1] R. Abe, S. Komatsu, J. Appl. Phys. 77 (1995) 6461.
[2] T. Nakamura, Y. Yamanaka, A. Morimoto, T. Shimizu, Jpn. J. Appl. Phys. 34 (1995) 5150.
[3] T. Kawahara, M. Yamamuka, A. Yuuki, K. Ono, Jpn. J. Appl. Phys. 35 (1996) 4880.
[4] T.B. Wu, C.M. Wu, M.L. Chen, Appl. Phys. Lett. 69 (1996) 2659.
[5] S. Hoffmann, R. Waser, Integrated Ferroelectrics 17 (1997) 141.
[6] M. Tsukada, M. Mukaida, S. Miyazawa, Jpn. J. Appl. Phys. 35 (1996) 4908.
[7] H. Ichinose, Y. Shiwa, M. Nagano, Jpn. J. Appl. Phys. 33 (1994) 5903.
[8] C.C. Yang, M.S. Chen, T.J. Hong, C.M. Wu, J.M. Wu, T.B. Wu, Appl. Phys. Lett. 66 (1995) 2643.
[9] M.S. Chen, J.M. Wu, T.B. Wu, Jpn. J. Appl. Phys. 34 (1995) 4870.
[10] T.F. Tseng, K.S. Liu, T.B. Wu, I.N. Lin, Appl. Phys. Lett. 68 (1996) 2505 .