JLMN-Journal of Laser Micro/Nanoengineering Vol. 2, No. 3, 2007

Dielectric Properties of Ba(Zr, Ti)O_3 Thin Films Fabricated by Pulsed Laser Deposition

Takanori Hino*, Minoru Nishida**, Takao Araki**, Takahiro Ohno***, Toshio Kawahara***,
Masakazu Murasugi***, Hitoshi Tabata*** and Tomoji Kawai***

** Department of Materials Science and Engineering, Niihama National College of Technology,*
7-1 Yagumo, Niihama, Ehime 792-8580, Japan
E-mail: hino@mat.niihama-nct.ac.jp
*** Department of Materials Science and Engineering, Ehime University,*
3 Bunkyo, Matsuyama, Ehime 792-8580, Japan
**** The Institute of Scientific and Industrial Research, Osaka University,*
8-1 Mihogaoka, Ibaraki. Osaka 567-0047, Japan

A KrF excimer laser with wavelength of 248nm and pulse width of 22ns was irradiated on rotating sintered $BaZr_xTi_{1-x}O_3$ (BZT) (x=0.00, 0.25, 0.50, 0.75, 1.00) target at fluence of 3.0J/cm^2 and pulse frequency of 2Hz. The single layer BZT films were deposited on Nb-doped $SrTiO_3$ (111) substrate at temperature of 973K in O_2-8%O_3 atmospheric gas pressure of 0.1, 1 and 8Pa. The BZT super lattice films were also fabricated at same conditions of single layer BZT films. The films were oriented to (111) direction. The 2-theta peak position of BZT (111) decreased as the x value increased. In the case of x>0.5, the dielectric constant was hardly changed by atmospheric gas pressure. The dielectric constant of the BZT solid solution film decreased as x value increases. In the case of x<0.5, the dielectric properties were different at each atmospheric gas pressure. The temperature dependences of dielectric constant in BZT film at 100mPa and 1Pa were almost constant, however the film at 8Pa was not stable. The oxygen pressure influenced dielectric properties in particular composition region (x=0.25) where relaxor phenomenon existed.

DOI: 10.2961/jlmn.2007.03.0001

Keywords: dielectric properties, Ba(Zr, Ti)O_3 films, pulsed laser deposition

1. Introduction

In these days, the ferroelectrics are widely applied to the memory IC cards, the chip capacitor and flash memory in our common life. Especially, the chip capacitors called multi layer ceramic capacitor (MLCC) are used for most compact electric apparatus such as notebook computer, PDA, and mobile phone. This passive component is indispensable part for propagations of ubiquitous computing life in the near future.

ABO_3 perovskites of the included lead and different valence state of B-site ion such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ [1] and $Pb(Sc_{1/2}Ta_{1/2})O_3$ [2] had been attracted as ferroelectric materials with relaxor phenomenon. The relaxor phenomenon originates large dielectric constant in wide temperature range above 100K due to the disorder of the electric dipole polarization caused by fluctuation of the crystal phase in the compound [3]. This peculiar phenomenon is also controlled by the ordered and disordered structure for $A(B'_{1/2}B''_{1/2})O_3$ along to <111> direction of the crystal [4]. However it is not cleared enough about the phenomenon what is dominant factor. On the other hand, by limiting the Pb use in electric products, the dielectrics of non-lead perovskite compound with the relaxor phenomenon are actively developed. Recently, relaxor phenomenon of non-lead ferroelectrics, which has two B-site ions with same ion valence of 4^+ was reported.

It is well known that pulsed laser deposition (PLD) with an excimer laser can fabricate functional thin films of oxides from bulk targets [5]. We can also control the crystal growth in the atomic scale by counting the pulse number of laser, because the deposited layer at a laser pulse is less than an atomic monolayer. Utilizing these advantages, the development of the new oxides such as superconductors [6], ferromagnets [7] and ferroelectrics [8] is suitable in comparison to other film formation methods. The PLD has recently been noticed as a high-speed research and development system for the new materials.

In this study, we aimed at development of thin film capacitor instead of the MLCC fabricated by sintering. It is necessary to improve of dielectric properties of $BaTiO_3$ film. The effect of atmospheric gas pressure on the dielectric characteristics of solid solution $BaZr_xTi_{1-x}O_3$ films that are suggested relaxor phenomenon is discussed. The super lattice $BaZr_xTi_{1-x}O_3$ films were also prepared to compare the dielectric characteristics with solid solution films.

2. Experiment procedures

The deposition targets were prepared by sintering of compacts, which consisted of high purity $BaTiO_3$ (BTO) (99.8%; Kishida Chemical) and $BaZrO_3$ (BZO) (98%; Kojyundo Chemical) powders. The composition of sintered $BaZr_xTi_{1-x}O_3$ (BZT) targets were varied in mixture ratio of $BaTiO_3$ and $BaZrO_3$ as x=0.00, 0.25, 0.50, 0.75 and 1.00, where the sintering temperature were set at 1523K, 1623K, 1673K, 1773K and 1773K, respectively.

BZT films with a thickness of 200nm were fabricated by using a pulsed laser depositon (PLD) with KrF excimer laser. The laser was irradiated on rotating target at fluence of $3.0J/cm^2$ and pulse frequency of 2Hz. The single laser BZT films were deposited on 1%Nb-doped $SrTiO_3$ (111) substrate of $0.5x0.5x0.5mm^3$ by using BZT target at the temperature of 973K in O_2-8%O_3 atmospheric gas pressure of 100m, 1 and 8Pa. A distance from target to substrate was kept at 50mm. The two kinds of BZT super lattice films were also fabricated by repeat alternate laser ablation of two kinds of BZT targets at same conditions in case of single layer BZT films. The super lattice film with the average composition of x=0.25 was deposited by using BZT (x=0.00) target and BZT (x=0.50) target, and the super lattice film with the average composition of x=0.50 was deposited by using BZT (x=0.25) target and BZT (x=0.75). These structures were obtained by repeating deposition of each layer 20 times.

The crystal structure was examined by X-ray diffraction using CuKα radiation. The 2θ was scanned from 20 degree to 120 degree at scan speed of 1 degree/min. The electrical measurements were conducted by configuration of platinum/BZT film/STO substrate. The platinum electrodes were deposited by sputtering through a metal shadow mask with an area of $0.25mm^2$. Capacitance and dielectric loss tangent were measured by using a LCR meter (HP4284A) at frequency from 100Hz to 1MHz and temperature from 250K to 400K.

3. Results and discussions

The deposition rate of the films deposited at 100mPa and 1Pa was about 3.0nm/min. That of the films deposited at 8Pa were about 2.3nm/min. The XRD peaks of the BZT single layer thin films were observed at the position of lower angle than substrate of STO (111). There was hardly changed of the peak positions in different gas pressure. The films had only the diffraction peak from BZT (111) and grown oriented to substrate. The peak position of BTO film at x=0.0 was very close to substrate. The position of diffraction angle shifted to lower angle as composition x increased. The spacing of (111) plane (d (111) value) calculated from diffraction angle of BZT (111) is related to composition x and was changed linearly. In Fig. 1, the spacing of (111) plane obtained from the JCPDS card and result of XRD for BZT targets were also described. These d (111) values gradually increased in linearly relationship the increase the increase in the composition x, following Vegard's law. The gradient of these straight lines was almost the same. The d (111) value of the single layer films was larger than that of bulk target. The supper lattice has more interface than the single layer film. This suggested that the lattice of the films was expanded to <111> direction by compressive strain due to lattice mismatch at the interface. While the d(111) of the supper lattice films was almost same as the single layer films.

In the case of super lattice BZT films, the satellite peaks in addition to the main peak from BZT (111) were observed as shown Fig. 2. These satellite peaks were denoted by the number of *i* which corresponds to the *i^th^* satellite peak. The presence of higher order satellite peaks adjacent to the main peak indicates the formation of a new structure having a periodic modulation of the structure and a coherently grown film with the one of in-plane lattice parameter throughout the entire film thickness. The main peak of BZT (x=0.25) and BZT (x=0.50) super lattice films appeared slightly lower angle than the each single layer films as shown Fig. 1. These were thought that the effect of the compressive strain enlarged because the interface was increased by formation of super lattice. This increment of the plane lattice parameter means growth of films with the lattice expanded in <111> direction because of stacking strain at interfaces by super lattice structure. The plane lattice parameter calculated from main peak and satellite peaks was almost agreement with setting values, which were 12.4nm and 13nm for BZT (x=0.25) and BZT (x=0.50) super lattice films respectively.

Fig. 3 shows the relationship between the dielectric permittivity and composition x in single layer BZT films deposited at 100mPa. The dielectric permittivity of BTO film at 1MHz was almost constant, while that at 10kHz was dispersion in the high temperature region. The frequency and temperature dependences of dielectric permittivity for the film at larger than x=0.25 were stable within the range of the measurement in this study. The BZT film of x=0.25 had the largest value. It was reported that BZT (x>0.2) bulk ceramics had large dielectric constant due to

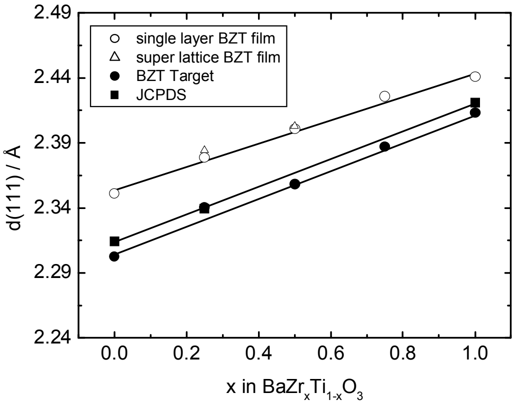

Fig. 1 The spacing of (111) plane of BZT films.

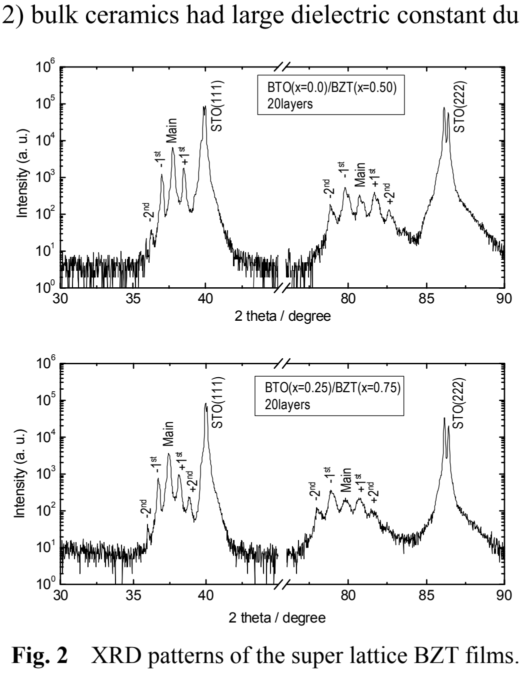

Fig. 2 XRD patterns of the super lattice BZT films.

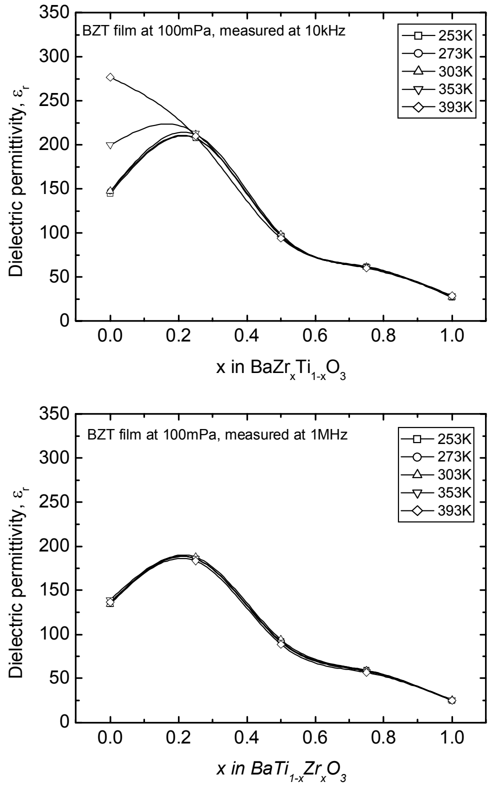

Fig. 3 Dielectric permittivity of the BZT films deposited at 100mPa.

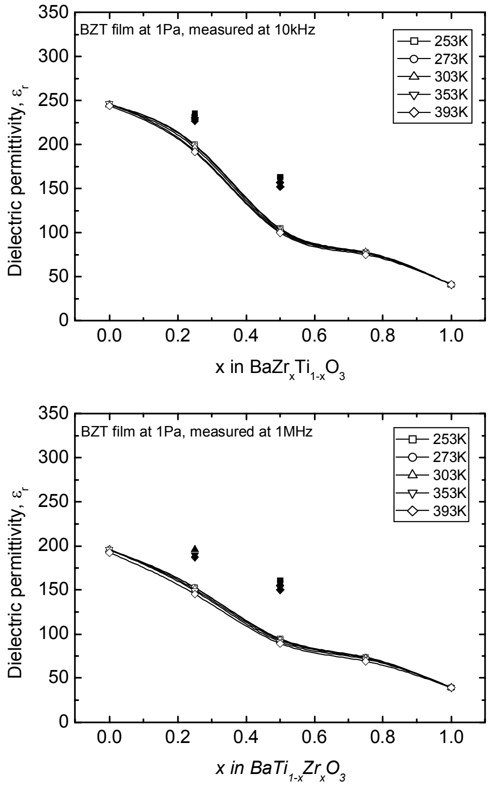

Fig. 4 Dielectric permittivity of the BZT films (open symbol; single layer, closed symbol; supper lattice) deposited at 1Pa.

relaxor behavior with diffuse phase transition [9-10]. The dielectric permittivity of the BZT films decreased with an increase of composition x in the region where x is larger than 0.25. There was a clear difference in the composition dependence of the dielectric permittivity on the BZT films deposited at 1Pa compared with that of 100mPa as shown Fig. 4. There were no increase of the dielectric permittivity at x=0.25 as seen for the films deposited at 100mPa. The dielectric permittivity of the BZT films decreased with an increase of composition x. The dielectric permittivity of BTO film and BZT (0.25) film decreased about 20% as the frequency increases from 10kHz to 1MHz. The temperature dependence of dielectric permittivity for the films hardly changed. The closed symbols in the Fig. 4 denoted the dielectric permittivity of the super lattice whose average composition was 0.25 and 0.50. The super lattice films had larger dielectric permittivity than single layer films. The super lattice films had the structure that lattices expand more than the single layer films in <111> that is the direction of the film thickness. In this <111> direction, the voltage was applied when dielectric characteristics measurement, and a great difference existed in the polarization between the single layer films and the super lattice films. The permittivity of the film made with 8Pa was the maximum at x=0.25 as well as 100mPa, however temperature dependence dispersed, as shown in Fig. 5. The permittivity of single layer BZT (0.25) deposited at 8Pa was larger than that of super lattice at 1Pa.

To discuss the influence of pressure on a dielectric characteristics at x=0.25, the composition ratio of Ba/(Zr+Ti) was analyzed by an Auger electron spectroscopy (AES). However, any differences could not be confirmed to the composition ratio of Ba/Ti+Zr by each deposition pressure. In addition, the full width at half- maximum (FWHM) of the (111) diffraction peak was substituted in the Sherrer equation and then the crystallite size was estimated. Here, it was assumed that the lattice strain of the film deposited at 100mPa, 1Pa and 8Pa was also the same because the plane lattice parameters of these films were almost same as aforementioned. The crystallite size of the film deposited at 100mPa and 1Pa was about 34nm and that at 8Pa was 24nm. This was thought that the crystallite size became smaller than film thickness because the films were epitaxial growth. In the films made with 1Pa that had the peculiar dielectric characteristics, there was no remarkable difference in the crystallite size. While the crystallite size at 8Pa was smaller due to increase of collision frequency among ablation particles at 8Pa. The surface oxidation was the main at 100mPa and the collision oxidation was the main at 8Pa from the relationship between pressure and the mean free path [11-12] On the other hand, it became the pressure region where the surface oxidation and the collision oxidation are caused at 1Pa. It is thought that the PLD process had some influences on the growth of the film though the factor that the permittivity increases at x=0.25 was not clearly understood.

Fig. 6 shows relationship between dielectric permittivity and O_3-O_2 gas pressure. In the case of x>0.5, the dielectric constant was hardly changed by atmospheric gas pressure. The dielectric constant of the single layer BZT films decreased as x value increases. In the case of x<0.5, the dielectric properties were different at each atmospheric gas pressure. The temperature dependences of dielectric constant in BZT film at 100mPa and 1Pa were almost

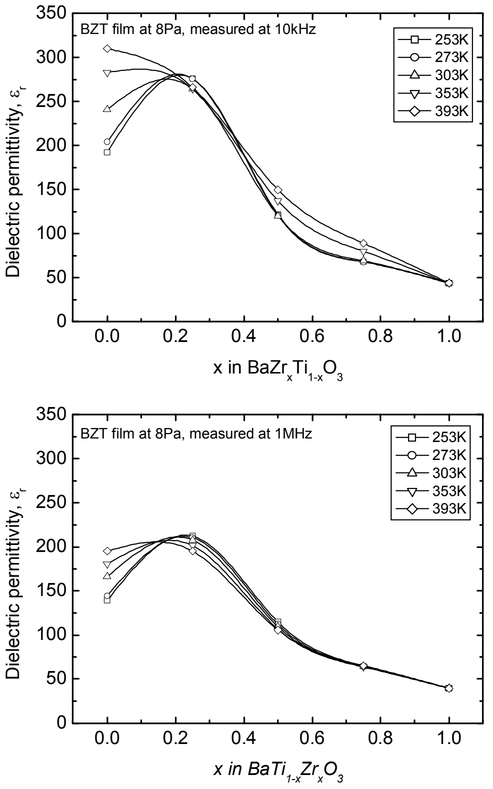

Fig. 5 Dielectric permittivity of the BZT films deposited at 8Pa.

constant, however the film at 8Pa was dispersion. BZT film fabricated at 100mPa had large dielectric constant at x=0.25. We considered that the oxygen pressure was most important factor, which influenced dielectric properties in particular composition region (x=0.25) where relaxor phenomenon existed.

4. Conclusions

The single layer films had only the diffraction peak from BZT (111) and grown oriented to Nb-STO(111) substrate. In the case of super lattice BZT films, the satellite peaks in addition to the main peak from BZT (111) were observed. The main peak of BZT (x=0.25) and BZT (x=0.50) super lattice films appeared slightly lower angle than the each single layer films. This increment of the plane lattice parameter means growth of films with the lattice expanded in <111> direction because of stacking strain at interfaces by super lattice structure.

The dielectric permittivity of the single layer BZT film deposited at 100mPa and 8Pa had the largest value at x=0.25. The dielectric permittivity of the single layer BZT film deposited at 1Pa was decreased with composition of x. The temperature dependences of dielectric constant in BZT film at 100mPa and 1Pa were almost constant, however the film at 8Pa was dispersed.

The super lattice films had larger dielectric permittivity than single layer films. The super lattice films had the structure that lattices expand more than the single layer films in <111> that is the direction of the film thickness. By controlling atmospheric gas pressure, the permittivity of single layer film at 8Pa was larger than super lattice at 1Pa. We considered that the oxygen pressure was most important factor, which influenced dielectric properties in particular composition region of x=0.25.

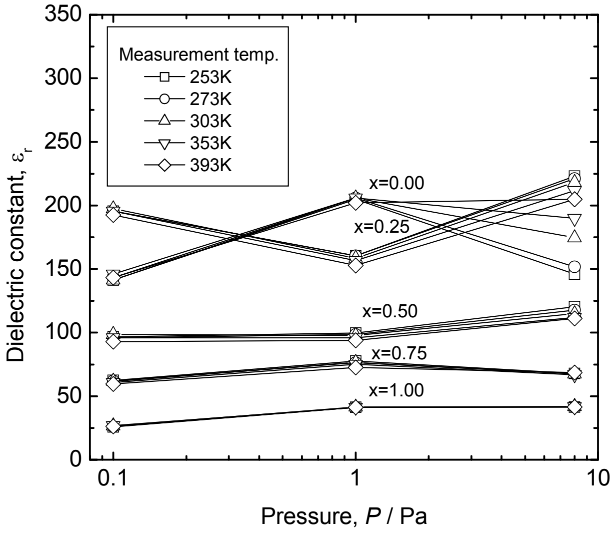

Fig. 6 Dielectric properties of the BZT films.

Acknowledgments

The experiments were supported by the nanotechnology support project of Ministry of Education, Culture, Sport, Science and Technology, Japan. We also thank Dr H. Aono of Ehime University for his helpful to measure AES.

References

[1] G. A. Smolensky and A. I. Agranovskaja: Sov. Phys. Tech. 3 (1958) 1380.
[2] N. Setter and L. E. Cross: J. Appl. Phys. 51 (1980) 4356.
[3] L. E. Cross: J. Appl. Phys. 34 (1995) 2525.
[4] Y. Hotta, G. W. J. Hassink, T. Kawai and H. Tabata: Jpn. J. Appl. Phys. 42 (2003) 5908.
[5] H. Tabata, T. Kawai and S. Kawai: Appl. Phys. Lett. 58 (1991) 1443.
[6] H. Tabata, T. Kawai and S. Kawai: Appl. Phys. Lett. 70 (1993) 2633.
[7] H. Tabata, T. Kawai, IEICE trans. Electron. 7 (1997) 918.
[8] H. Tabata, T. Kawai and S. Kawai: Appl. Phys. Lett. 65 (1994) 1970.
[9] J. Ravez, C. Broustera and A. Simon: J. Mater. Chem. 9 (1999) 1609.
[10] Z. Yu, C. Ang, R. Guo and A. S. Bhalla: J. Appl. Phys. 92 (2002) 2655.
[11] T. Hino, M. Nishida, T. Araki, T. Ooie, T. Yano, M. Yoneda, M. Katsumura: Proceedings ot the ICALEO'97 (1997) 185.
[12] T. Hino, M. Nishida, T. Araki: Appl. Surf. Sci. 189 (2002) 1.

(Received: May 17, 2006, Accepted: June 25, 2007)