

The Structural and Electrical Properties of Bismuth-based Pyrochlore Thin Films for embedded Capacitor Applications

Kyeong-Chan Ahn, Jong-Hyun Park, Jun-Ku Ahn, and Soon-Gil Yoon^a
 Department of Nano information Systems Engineering, Chungnam National University,
 220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea

^aE-mail : sgyoon@cnu.ac.kr

(Received March 27 2007, Accepted April 18 2007)

$\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$ (BZN), $\text{Bi}_2\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$ (BMN), and $\text{Bi}_2\text{Cu}_{2/3}\text{Nb}_{4/3}\text{O}_7$ (BCN) pyrochlore thin films were prepared on Cu/Ti/SiO₂/Si substrates by pulsed laser deposition and the micro-structural and electrical properties were characterized for embedded capacitor applications. The BZN, BMN, and BCN films deposited at 25 °C and 150 °C, respectively show smooth surface morphologies and dielectric constants of about 39 ~ 58. The high dielectric loss of the films deposited at 150 °C compared with films deposited at 25 °C was attributed to the defects existing at interface between the films and copper electrode by an oxidation of copper bottom electrode. The leakage current densities and breakdown voltages in 200 nm thick-BMN and BZN films deposited at 150 °C are approximately 2.5×10^{-8} A/cm² at 3 V and above 10 V, respectively. Both BZN and BMN films are considered to be suitable materials for embedded capacitor applications.

Keywords : $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$, $\text{Bi}_2\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$, $\text{Bi}_2\text{Cu}_{2/3}\text{Nb}_{4/3}\text{O}_7$, Embedded capacitor

1. INTRODUCTION

Embedding of passive components such as capacitors into polymer-based printed wiring boards (PWB) is becoming an important strategy for electronics miniaturization, device reliability, and manufacturing cost reduction. To date, much research has been involved in preparation of dielectric films directly on the PWB using ceramic/polymer composites[1,2] and polymers [3,4] with medium permittivity.

The bismuth-based pyrochlores were investigated by Safronov[5] and Cann[6]. Also, the preparation, characterization, and properties of bismuth-based dielectric thin films have been investigated by many research groups[7,8]. In our recent work,[9,10] dielectric properties and leakage current densities as well as structural properties in bismuth-based pyrochlore thin films were systematically investigated for embedded capacitor applications.

In this study, BZN, BMN, and BCN thin films were deposited on Cu/Ti/SiO₂/Si substrates at 25 °C and 150 °C by pulsed laser deposition. The structural and electrical properties of various films were investigated for film thicknesses of both 100 and 200 nm.

2. EXPERIMENTAL

Please BMN, BZN, and BCN thin films were prepared at 25 °C and 150 °C by pulsed laser deposition (PLD)

using a pulsed KrF excimer laser (248 nm, Lamda Physik COMPexPro 201). A ceramic of 1 inch diameter was used as a target. The base pressure of the chamber used was approximately 5.3×10^{-4} Pa. The laser density and repetition rate was 1.5 J/cm² and 4 Hz, respectively. The laser impacts the target at 45 ° to the surface and the substrate is centered along the target normal as shown in Fig. 1.

Oxygen was added into the chamber during deposition, and the oxygen pressure was maintained at 30 mTorr. Thin films were deposited on Cu/Ti/SiO₂/Si substrates at temperatures of 25 °C and 150 °C. 20-nm-thick Ti layers in Cu/Ti/SiO₂/Si substrates were used in order to improve the adhesion between Cu and SiO₂. Film thicknesses were constantly maintained at 100 and 200 nm at deposition temperatures of 25 °C and 150 °C, respectively. Surface morphologies were characterized by scanning electron microscopy (SEM). For electrical measurement, Pt top electrodes with dimensions of 100 x 100 μm² were exactly patterned by lift-off lithography and sputtered by dc magnetron sputtering. The dielectric properties of Pt/pyrochlore films/Cu capacitors were evaluated by impedance analyzer (HP 4194A). The leakage current characteristics of metal-insulator-metal (MIM) capacitors were investigated by HP 4156A semiconductor parameter analysis.

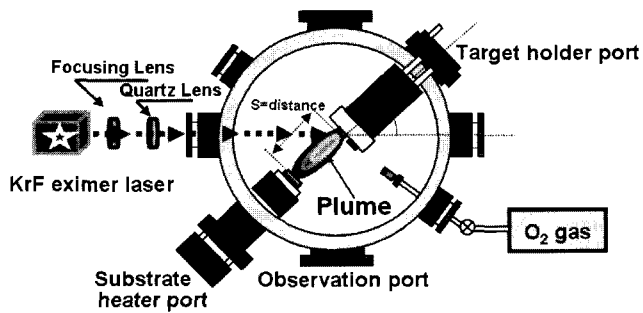


Fig. 1. A schematic diagram of pulsed laser deposition equipment.

3. RESULTS AND DISCUSSION

Figures 2(a), 2(b) and 2(c) show SEM surface images of 100nm thick-BZN, BMN, and BCN thin films, respectively, deposited at 25 °C. BMN and BZN films show smooth surface morphologies even though films are deposited at room temperature. On the other hand, BCN films show an inhomogeneous morphology because BCN target used in this study have a low density compared with other materials. Film quality deposited by PLD technique definitely depends on the target density. The grain size of BMN films deposited at room temperature was approximately 4 nm by XRD and TEM analysis[11].

The dielectric constant and dissipation factor of BZN, BMN, and BCN films deposited at 25 °C was shown in Fig. 3. As shown in Fig. 3, dielectric constant and dissipation factor of the films are varied from 39 to 53 and from 0.6 % to 0.8 %, respectively, depending on the materials. The reason that the films deposited at room temperature show a high dielectric constant is due to the crystalline phases crystallized partially within the films[11].

Figure 4 shows variations in leakage current density vs. applied voltage for films of various materials. Three different films show similar leakage current behaviors for an applied voltage. Leakage current densities of the samples were approximately 2×10^{-8} A/cm² at an applied deposited at 25 °C. voltage of 3 V.

The absolute leakage current density of the films was comparable to that of 1.3 μ m thick-Pb(Zr,Ti)O₃ films for embedded capacitor applications[12]. Bismuth-based pyrochlore thin films exhibited the breakdown strength of 300 kV/cm.

Figures 5(a), 5(b), and 5(c) show SEM surface images of 200 nm thick-BZN, BMN, and BCN thin films, respectively, deposited at 150 °C. Films deposited at 150 °C showed more dense and smooth morphologies than

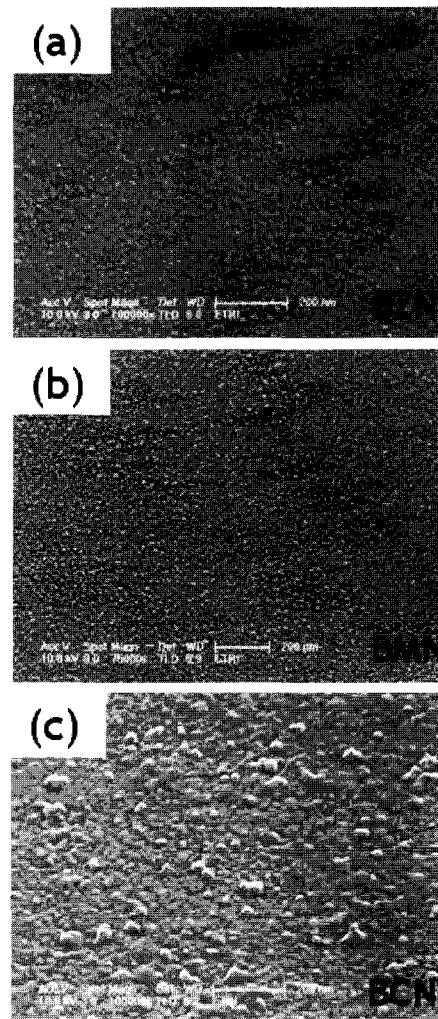


Fig. 2. SEM surface images of 100 nm thick-(a) BZN, (b) BMN, and (c) BCN films.

films deposited at room temperature shown in Fig. 2. An increase of deposition temperature produces the dense structure because molecules arrived at substrate surface easily migrate on the surface. The smooth morphologies of the films contribute for an improvement of leakage current characteristics. Figure 6 shows the relationship between dielectric constant and dissipation factor for three different films deposited at 150 °C. As shown in Fig. 6, the dielectric constant of the films was varied from 49 to 58 and dissipation factor was maintained at 1% irrespective of materials. An increase of dielectric constant by an increase of deposition temperature was related with an increase of grain size in the films. The BMN films deposited at 150 °C exhibit grain size of approximately 8.7 nm. An increase of dissipation factor in the films deposited at 150 °C was due to the increase of defects (such as oxygen vacancy) at interface between

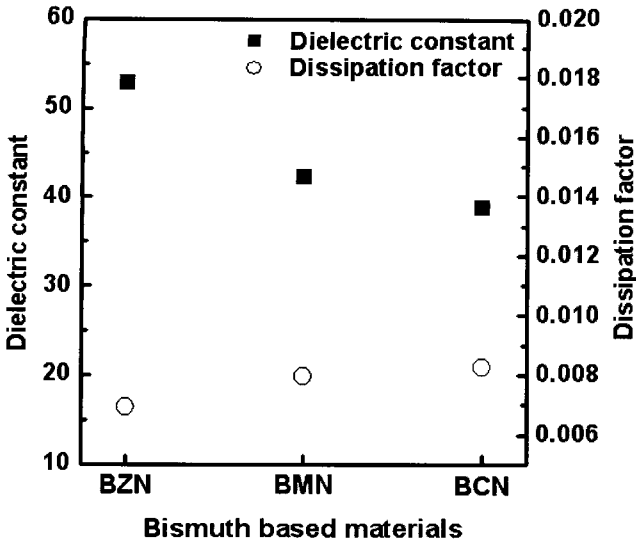


Fig. 3. Variations in dielectric constant and dielectric loss of 100 nm thick-BZN, BMN, and BCN films deposited at 25 °C.

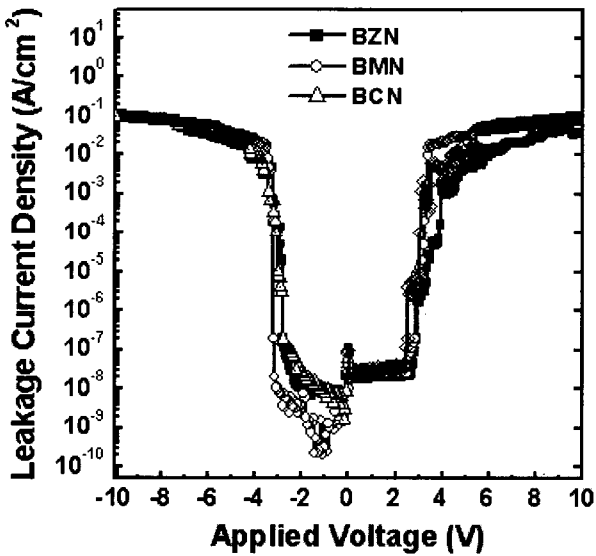


Fig. 4. The relationship between leakage current density and an applied voltage for various bismuth-based pyrochlore films with 100 nm thickness deposited at 25 °C.

films and copper by an oxidation of copper bottom electrode. An oxidation of copper electrode in films deposited at 150 °C was identified by TEM analysis[11]. An increase of dissipation factor in films deposited at 150 °C on Cu/Ti/SiO₂/Si substrates was compared with films deposited at 150 °C on Pt/TiO₂/SiO₂/Si substrates [13]. Films deposited at 150 °C on Pt bottom electrode show a dissipation factor of about 0.1 % smaller than those on copper electrode. This result suggests that the

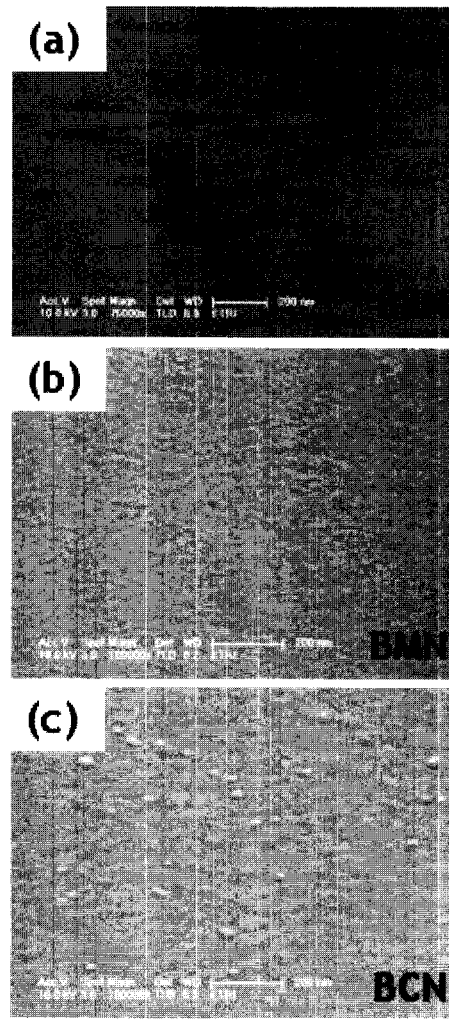


Fig. 5. SEM surface images of 200 nm thick-(a) BZN, (b) BMN, and (c) BCN films deposited at 150 °C

films deposited at 150 °C contain many defects such as oxygen vacancy at interface between the film and copper bottom electrode. Figure 7 shows the variations in leakage current density (at 3 V) and breakdown voltage for 200 nm thick-BZN, BMN, and BCN thin films deposited at 150 °C. The BMN and BZN films exhibit the low leakage current densities of approximately 2.5×10^{-8} A/cm² at an applied voltage of 3 V. On the other hand, BCN films show the high leakage current density of about 2×10^{-6} A/cm² as compared with BMN and BZN films. The high leakage current density of the BCN films may be attributed to the variation in copper valence in the films deposited in oxygen ambient at 150 °C. Both BZN and BMN films exhibit the breakdown voltages above 10 V, while BCN films show a low breakdown voltage of about 3 V. From these result, BZN and BMN films are considered to be suitable for embedded capacitor applications.

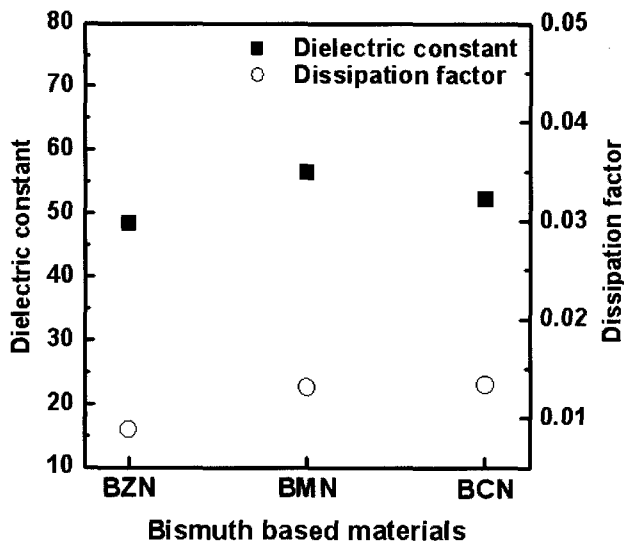


Fig. 6. Variations in dielectric constant and dielectric loss of 200 nm thick-BZN, BMN, and BCN films deposited at 150 °C.

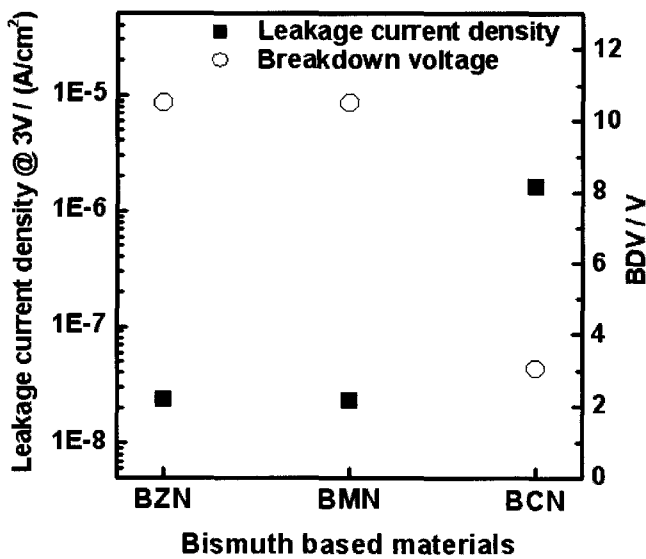


Fig. 7. Variations in leakage current density at 3 V and breakdown voltage of 200 nm thick-BZN, BMN, and BCN films deposited at 150 °C.

4. CONCLUSION

The microstructure and electrical properties of various bismuth-based pyrochlore films were characterized for embedded capacitor applications. The BZN, BMN, and BCN films deposited at 25 °C and 150 °C show smooth surface morphologies and dielectric constants of about 39 ~ 58. The high dielectric loss of the films deposited at 150 °C compared with films deposited at 25 °C was

attributed to the defects existing at interface between the films and copper electrode by an oxidation of copper bottom electrode. The leakage current densities and breakdown voltages in 200 nm thick-BMN and BZN films deposited at 150 °C are approximately 2.5×10^{-8} A/cm² at 3 V and above 10 V, respectively. Both BZN and BMN films are considered to be suitable materials for embedded capacitor applications.

ACKNOWLEDGMENTS

This work was financially supported by research foundation of the Samsung-Electro Mechanics Co. Ltd., by the Center for Ultramicrochemical Process Systems sponsored by KOSEF, by the Brain Korea 21 Project in 2006, and by the Korea Science and Engineering Foundation through the Research Center for Advanced Magnetic Materials at Chungnam National University.

REFERENCES

- [1] Y. Rao, S. Ogitani, P. Kohl, and C. P. Wong, "Novel high-dielectric constant nano-structure polymer-ceramic composite for embedded capacitor application", Proc. ECTC., Vol. 183, p. 183, 2000.
- [2] S. Ramesh, B. A. Shutzberg, C. Huang, J. Gao, and E. P. Giannelis, "Dielectric nanocomposites for integral thin film capacitors: Materials design, fabrication and integration issues", IEEE Trans. Adv. Packaging, Vol. 26, No. 1, p. 17, 2003.
- [3] D. G. Weiss, "Changes in the PCB world with new packaging technologies and the integration of passive components into the PCB", Circuit World, Vol. 24, No. 2, p. 6, 1998.
- [4] H. Pohl, "Superdielectrics polymers", IEEE Trans. Electrical Insulation, Vol. EI 21, No. 5, p. 683, 1986.
- [5] G. M. Safronov, V. N. Batag, T. V. Stepanyuk, and P. M. Fedorov, "Equilibrium diagram of bismuth oxide-zinc oxide system", Russ. J. Inorg. Chem., Vol. 16, p. 460, 1971.
- [6] D. P. Cann, C. A. Randall, and T. R. Shrout, "Investigation of the dielectric properties of bismuth pyrochlores", Solid State Commun., Vol. 100, p. 529, 1996.
- [7] J. Lu and S. Stemmer, "Low-loss, tunable bismuth zinc niobate films deposited by RF magnetron sputtering", Appl. Phys. Lett., Vol. 83, p. 2411, 2003.
- [8] S. W. Wang, W. Lu, N. Li, Z. F. Li, H. Wang, M. Wang, and X. C. Shen, "Insulating properties of rapid thermally processed Bi₂Ti₂O₇ thin films by a chemical solution decomposition technique", Mater. Res. Bull., Vol. 37, p. 1691, 2002.

- [9] J. H. Park, W. S. Lee, N. J. Seong, S. G. Yoon, S. H. Son, H. M. Chung, J. S. Moon, H. J. Jin, S. E. Lee, J. W. Lee, H. D. Kang, Y. K. Chung, and Y. S. Oh, "Bismuth-zinc-niobate embedded capacitors grown at room temperature for printed circuit board applications", *Appl. Phys. Lett.*, Vol. 88, p. 192902, 2006.
- [10] J. H. Park, C. J. Xian, N. J. Seong, S. G. Yoon, S. H. Son, H. M. Chung, J. S. Moon, H. J. Jin, S. E. Lee, J. W. Lee, H. D. Kang, and Y. K. Chung, "Bismuth-based pyrochlore thin films deposited at low temperatures for embedded capacitor applications", *Jpn. J. of Applied Physics part 1*, Vol. 45, p. 7325, 2006.
- [11] J. H. Park, C. J. Xian, N. J. Seong, S. G. Yoon, S. H. Son, H. M. Chung, J. S. Moon, H. J. Jin, S. E. Lee, J. W. Lee, H. D. Kang, Y. K. Chung, and Y. S. Oh, "Realization of a high capacitance density in $\text{Bi}_2\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$ pyrochlore thin films deposited directly on polymer substrates for embedded capacitor applications", *Appl. Phys. Lett.*, Vol. 89, No. 23, p. 232910, 2006.
- [12] T. Kim, A. I. Kingon, J. P. Maria, and R. T. Croswell, "Ca-doped lead zirconate titanate thin film capacitors on base metal nickel on copper foil", *J. Mater. Res.*, Vol. 19, No. 10, p. 2841, 2004.
- [13] C. J. Xian, J. H. Park, K. C. Ahn, S. G. Yoon, J. W. Lee, W. C. Kim, S. T. Lim, S. H. Sohn, J. S. Moon, H. M. Jung, S. E. Lee, I. H. Lee, Y. K. Chung, M. K. Jeon, and S. I. Woo, "Electrical properties of $\text{Bi}_2\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$ (BMN) pyrochlore thin films deposited on Pt and Cu metal at low temperatures for embedded capacitor applications", *Appl. Phys. Lett.*, Vol. 90, p. 052903, 2007.