Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp1055-1056

I-3-1(Invited)

Development of Novel Piezoelectric Materials for Si-based MEMS Application

Hiroshi Funakubo[1], Shintaro Yasui[1], Keisuke Yazawa[1], Jun-ichi Nagata[1], Takahiro Oikawa[1], Hitoshi Morioka[2], Tomoaki Yamada[3, 4] and Hiroshi Uchida[5]

[1]Tokyo Institute of Technology,
J2-43, Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan
Phone: +81-45-924-5446, E-mail: funakubo.h.aa @m.titech.ac.jp
[2]Bruker AXS,
3-9-B-6F Moriya-cho, Kanagawa-ku, Yokohama 221-0022, Japan
[3]Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan
[4]PRESTO, Japan Science and Technology Agency,
5 Sanban-cho, Chiyoda-ku, Tokyo 102-0075, Japan
[5]Sophia University
7-1, Kioi-cho, Tiyoda-ku Tokyo, 102-8554, Japan

1. Introduction

MEMS devices using piezoelectric materials are one of the promising filed for the miniaturization of the MEMS devices. Most widely investigated piezoelectric material is $Pb(Zr,Ti)O_3$ that has been used not only bulk form, but also film form. However, the toxicity of lead enhance the development of lead-free materials having compatible piezoelectric property with $Pb(Zr,Ti)O_3$ as well as the temperature for usage.

Most of present candidate of lead-free piezoelectric oxide materials include Li, Na and K. However, these elements are not suitable for Si semiconductor devices. We focused our attention to the Bi-based oxide materials. Because Bi-based materials are already integrated on Si and commercialized as ferroelectric random access memories (FeRAMs). To obtain large piezoelectricity, we focus on the materials having morphtropic phase boundary (MPB) like $Pb(Zr,Ti)O_3$, that is the phase boundary by composition between the tetragonal and non-tetragonal symmetries, such as rhombohedral one and shows the maximum piezoelectric response.

In 2006, $BiCoO_3$ [1] and $Bi(Zn_{1/2}Ti_{1/2})O_3$ [2] having tetragonal symmetry were reported using high pressure synthesis technique. We investigated Bi perovskite materials, such as $Bi(Zn_{1/2}Ti_{1/2})O_3$ - $BiFeO_3$[3,4], $BiCoO_3$ - $BiFeO_3$[5-9] and $Bi(Zn_{1/2}Ti_{1/2})O_3$ - $Bi(Mg_{1/2}Ti_{1/2})O_3$ - $BiFeO_3$ solid solution systems, epitaxially grown by metalorganic chemical vapor deposition (MOCVD). Crystallographic analysis revealed that the crystal symmetry of the films changes from rhombohedral to tetragonal with composition of the films.

In the present study, the crystal structure and piezoelectric property of $Bi(Zn_{1/2}Ti_{1/2})O_3$ - $Bi(Mg_{1/2}Ti_{1/2})O_3$ - $BiFeO_3$ films were systematically investigated as a function of the film composition and kinds of substrates.

2. Experimental Procedure

Epitaxial $Bi(Zn_{1/2}Ti_{1/2})O_3$ - $Bi(Mg_{1/2}Ti_{1/2})O_3$ - $BiFeO_3$ films with about 300 nm thickness were grown at 700°C on $(100)_cSrRuO_3$//(100)$SrTiO_3$, $(110)_cSrRuO_3$//(110)$SrTiO_3$ and $(111)_cSrRuO_3$//(111)$SrTiO_3$ substrates by pulsed MOCVD using $Bi[(CH_3)_2(2\text{-}(CH_3)_2NCH_2C_6H_4)]$ (Tosoh Co. Ltd), $Zn(C_{14}H_{25}O_2)_2$, $Mg(C_{11}H_{19}O_2)_2$, $Ti(O\cdot i\text{-}C_3H_7)_4$, $Fe(C_2H_5C_5H_4)_2$ and oxygen gas as the source materials. $SrRuO_3$ films were grown by RF magnetron sputtering method.

Film thickness and composition were confirmed by X-ray fluorescence (XRF) calibrated using standard samples. Crystal structure was characterized by X-ray diffraction (XRD) analysis. High temperature XRD - reciprocal space mappings (XRD-RSMs) were carried out using D8 Discover SSS with Hi-STAR, Bruker AXS.

Pt/[$Bi(Zn_{1/2}Ti_{1/2})O_3$ - $Bi(Mg_{1/2}Ti_{1/2})O_3$ - $BiFeO_3$]/$SrRuO_3$ capacitor structure was used for the electrical measurements after making circular Pt top electrodes of 100 μm in diameter, which were deposited by e-beam evaporation. Piezoresponse mappings and longitudinal piezoelectric coefficient (*AFM*-d_{33}) was measured using piezoresponse force microscopy (PFM).

3. Results and Discussion

XRD θ-2θ patterns of (2/3)[(1-x)$Bi(Zn_{1/2}Ti_{1/2})O_3$-$x$$Bi(Mg_{1/2}Ti_{1/2})O_3$]-(1/3)$BiFeO_3$ films grown on (100), $(110)_c$ and $(111)_cSrRuO_3$//$SrTiO_3$ substrates are shown in Fig. 1. Single phase of the perovskite phase without impurity phase was observed for all films grown on (100), $(110)_c$ and $(111)_c$ - oriented $SrRuO_3$//$SrTiO_3$ substrates. All films were ascertained to be epitaxially grown with substrate from XRD pole figure analysis.

XRD-RSM shown in Fig. 2 reveals for the films on $(100)_cSrRuO_3$//(100)$SrTiO_3$ substrates that the only tetragonal structure and mixture phase of tetragonal and rhombohedral were obtained for the films with x = 0.57 and 1.00, respectively. For the films on $(110)_cSrRuO_3$//(110)$SrTiO_3$ substrates, similar change of crystal symmetry with Mg/(Zn+Mg) ratio was observed. On the other hand, the mixture of tetragonal and rhombohedral phases were observed for all composition between x = 0.5 and 1.0 in case of films on $(111)_cSrRuO_3$//(111)$SrTiO_3$ substrates.

High temperature XRD-RSM measurement was carried out to investigate the temperature stability of the constituent phase. Figures 3 (a) and (b) show XRD-RSMs of (2/3)[(1-x)$Bi(Zn_{1/2}Ti_{1/2})O_3$-$x$$Bi(Zn_{1/2}Ti_{1/2})O_3$] - (1/3)$BiFeO_3$ films with x = 0.79 grown on $(110)_cSrRuO_3$//(110)$SrTiO_3$ substrates measured at 30°C and 900°C. Vertical and lateral axes respective correspond to θ-2θ and Chi direction. Right brightest spot is from $SrTiO_3$ *110* diffraction and center spot and left two spots with off axis along substrate surface normal are from rhombohedral and tetragonal symmetry phase of the film. There is no big change and the only the shift of each peak position to lower angle was observed between 30°C and 900°C. This result indicates that Curie temperature of the film having mixture phase

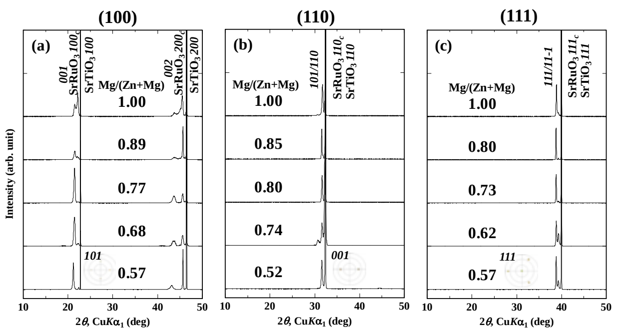

Fig. 1 XRD θ-2θ patterns of (2/3)[(1-x)Bi($Zn_{1/2}Ti_{1/2}$)O_3 - xBi($Zn_{1/2}Ti_{1/2}$)O_3]-(1/3)$BiFeO_3$ films grown on (a) (100), (b) $(110)_c$ and (c) $(111)_c$-oriented $SrRuO_3$//$SrTiO_3$ substrates.

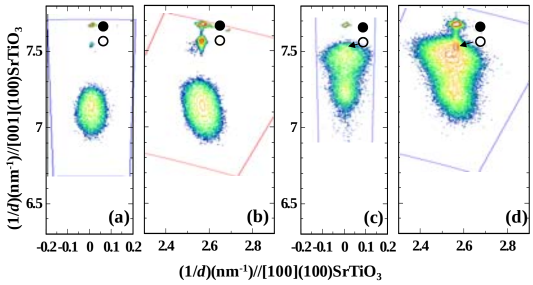

Fig. 2 XRD-RSMs around [(a),(c)] *003* and [(b),(d)] *103* diffractions of (2/3)[(1-x)Bi($Zn_{1/2}Ti_{1/2}$)O_3-xBi($Zn_{1/2}Ti_{1/2}$)O_3] – (1/3)$BiFeO_3$ films with x = [(a),(b)] 0.57 and [(c),(d)] 1.00 grown on (100)$SrRuO_3$//(100)$SrTiO_3$ substrates. Open and closed circles correspond to $SrTiO_3$ and $SrRuO_3$ diffractions, respectively.

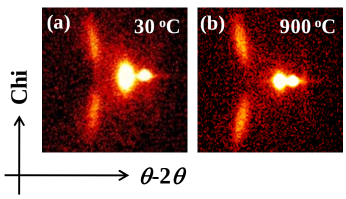

Fig. 3 XRD-RSM of (2/3)[(1-x)Bi($Zn_{1/2}Ti_{1/2}$)O_3- xBi($Zn_{1/2}Ti_{1/2}$)O_3] - (1/3)$BiFeO_3$ films with x = 0.79 grown on $(110)_c SrRuO_3$//(110)$SrTiO_3$ substrates measured at (a) 30°C and (b) 900°C.

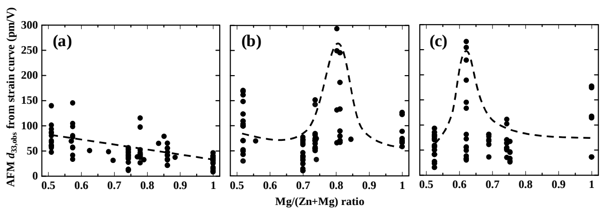

Fig. 4 Observed longitudinal piezoelectric coefficient ($d_{33,obs}$) as a function of Mg/(Zn+Mg) ratio for (2/3)[(1-x)Bi($Zn_{1/2}Ti_{1/2}$)O_3-xBi($Zn_{1/2}Ti_{1/2}$)O_3]-(1/3)$BiFeO_3$ films grown on (a) (100), (b) (110) and (c) $(111)_c$-oriented $SrRuO_3$//$SrTiO_3$ substrates.

is higher than 900°C.

Figure 4 represents observed longitudinal piezoelectric coefficient measured by PFM (*AFM*-$d_{33,obs}$) for (2/3)[(1-x)Bi($Zn_{1/2}Ti_{1/2}$)O_3 - xBi($Zn_{1/2}Ti_{1/2}$)O_3] - (1/3)$BiFeO_3$ films grown on (100), $(110)_c$ and $(111)_c$ -oriented $SrRuO_3$//$SrTiO_3$ substrates as a function of Mg/(Zn+Mg) ratio. *AFM*-$d_{33,obs}$ of the films on (100) substrates slightly decreased with increasing x. In contrast, a local maximum were observed for the films on (110) and (111) substrates neighbor phase boundary. Maximum *AFM*-$d_{33,obs}$ of about 300 pm/V was observed at x = 0.79 near phase boundary on (110) substrate. Absolute value of *AFM*-$d_{33,obs}$ was almost or higher than epitaxial Pb(Zr,Ti)O_3 films with same film thickness on the same substrates. These characteristics are also observed for the one-axis oriented films prepared on (100)Si substrates. This indicates that this composition is a novel candidate of lead-free piezoelectric materials integrated with Si semiconductor devices.

4. Conclusions

Bi-perovskite films, Bi($Zn_{1/2}Ti_{1/2}$)O_3 - Bi($Mg_{1/2}Ti_{1/2}$)O_3 - $BiFeO_3$, were successfully grown on (100), $(110)_c$ and $(111)_c$-oriented $SrRuO_3$//$SrTiO_3$ substrates by MOCVD. Crystal structure in the films changed tetragonal to rhombohedral with film compositions. Curie temperature of the films with mixture of tetragonal and rhombohedral symmetries on $(110)_c SrRuO_3$//$SrTiO_3$ substrates was above 900°C. Maximum observed longitudinal piezoelectric coefficient, *AFM*-$d_{33,obs}$, measured by PFM was about 300 pm/V.

Acknowledgement

This research is partially granted by the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)," initiated by the Council for Science and Technology Policy (CSTP) and Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] A. A. Belik, S. Iikubo, K. Kodama, N. Igawa, S. Shamoto, S. Niitaka, M. Azuma, Y. Shimakawa, M. Takano, F. Izumi and E. Takayama-Muromachi, Chem. Mater. **18**, (2006) 798.
[2] M. R. Suchomel, A. M. Fogg, M. Allix, H. Niu, J. B. Claridge and M. J. Rosseinsky, Chem. Mater. **18**, (2006) 4987.
[3] K. Yazawa, S. Yasui, M. Matsushima, H. Uchida, and H. Funakubo, Mater. Sci. Eng. B **173** (2010) 14.
[4] K. Yazawa, S. Yasui, H. Morioka, T. Yamada, H. Uchida, A. Gruverman, and H. Funakubo, J. Ceram. Soc. Jpn. **118** (2010) 659.
[5] S. Yasui, K. Nishida, H. Naganuma, S. Okamura, T. Iijima and H. Funakubo, Jpn. J. Appl. Phys., **46** (2007) 6948 (.
[6] S. Yasui, H. Naganuma, S. Okamura, K. Nishida, T. Yamamoto, T. Iijima, M. Azuma, H. Morioka, K. Saito, M. Ishikawa, T. Yamada, and H. Funakubo, Jpn. J. Appl. Phys., **47** (2008) 7582.
[7] S. Yasui, M. Nakajima, H. Naganuma, S. Okamura, K. Nishida, T. Yamamoto, T. Iijima, M. Azuma, H. Morioka, K. Saito, M. Ishikawa, T. Yamada, and H. Funakubo, J. Appl. Phys., **105** 061620-1-5 (2009).
[8] S. Yasui, O. Sakata, M. Nakajima, S. Utsugi, K. Yazawa, T. Yamada, and H. Funakubo, Jpn. J. Appl. Phys., **48** (2009) 09KD06.
[9] S. Yasui, K. Yazawa, T. Yamada, K. Nishida, H. Uchida, M. Azuma, and H. Funakubo, Jpn. J. Appl. Phys., **49** (2010) 09MB04.