Development of Novel Piezoelectric Materials for Si-based MEMS Application

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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)O₃ 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)O₃ 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 material and properties of Bi(Zn₀.₅Ti₀.₅)O₃ - Bi(Mg₀.₅Ti₀.₅)O₃ - BiFeO₃ solid solution systems, such as rhombohedral one and shows the maximum piezoelectric response.

In 2006, BiCoO₃ [1] and Bi(Zn₀.₅Ti₀.₅)O₃ [2] having tetragonal symmetry were reported using high pressure synthesis technique. We investigated Bi perovskite materials, such as Bi(Zn₀.₅Ti₀.₅)O₃ - BiFeO₃[3,4], BiCoO₃ - BiFeO₃[5-9] and Bi(Zn₀.₅Ti₀.₅)O₃ - Bi(Mg₀.₅Ti₀.₅)O₃ - BiFeO₃ 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(Zn₀.₅Ti₀.₅)O₃ - Bi(Mg₀.₅Ti₀.₅)O₃ - BiFeO₃ films were systematically investigated as a function of the film composition and kinds of substrates.

2. Experimental Procedure

Epitaxial Bi(Zn₀.₅Ti₀.₅)O₃ - Bi(Mg₀.₅Ti₀.₅)O₃ - BiFeO₃ films with about 300 nm thickness were grown at 700°C on (100) SrRuO₃//(100) SrTiO₃, (110) SrRuO₃//(110) SrTiO₃, and (111) SrRuO₃//(111) SrTiO₃ substrates by pulsed MOCVD using Bi[(CH₃)₂(2-(CH₃)₂NCH₂)CH₄] (Tosoh Co. Ltd), Zn(C₂H₅O₂)₂, Mg(C₁₀H₁₄O₂)₂, TiO(C₂H₅)₂CH₃, Fe(C₂H₅CH₂)₂ and oxygen gas as the source materials. SrRuO₃ 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 HiSTAR, Bruker AXS.

Pr[(Bi(Zn₀.₅Ti₀.₅)O₃ - Bi(Mg₀.₅Ti₀.₅)O₃ - BiFeO₃)] films grown on (100), (110), and (111) SrRuO₃//SrTiO₃ substrates were examined using XRD. Single phase of the perovskite phase without impurity phase was observed for all films grown on (100), (110), and (111) oriented SrRuO₃//SrTiO₃ 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) SrRuO₃//(100) SrTiO₃ substrates that the only tetragonal phase 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) SrRuO₃//(111) SrTiO₃ substrates. High temperature XRD-RSM measurement was carried out to investigate the temperature stability of the constituent phase.

F i g u r e s 3 (a) and (b) show X R D - R S M s of (2/3)(1-x)Bi[(Zn₀.₅Ti₀.₅)O₃ - Bi(Mg₀.₅Ti₀.₅)O₃ - BiFeO₃] films grown on (100), (110), and (111) SrRuO₃//SrTiO₃ substrates measured at 30°C and 900°C. Vertical and lateral axes respective correspond to $\theta-2\theta$ and $\phi$ direction. Right brightest spot is from SrTiO₃ 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
(a) (100), (b) (110) and (c) (111) c-oriented SrRuO3//SrTiO3 substrates.

[(a),(b)] 0.57 and [(c),(d)] 1.00 grown on (100), (110) and (111)-oriented SrRuO3//SrTiO3 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) SrRuO3//SrTiO3 substrates was above 900°C. Maximum observed longitudinal piezoelectric coefficient, $AFM-d_{33,obs}$ measured by PFM was about 300 pm/V.

**Fig. 1** XRD RSMs around [(a),(c)] 002 and [(b),(d)] 103 diffractions of (2/3)(1-x)Bi(Zn1/2Ti1/2)O3 - xBi(Zn1/2Ti1/2)O3 - (1/3)BiFeO3 films grown on (a) (100), (b) (110), and (c) (111)-oriented SrRuO3//SrTiO3 substrates.

**Fig. 2** XRD-RSMs around [(a),(c)] 002 and [(b),(d)] 103 diffractions of (2/3)(1-x)Bi(Zn1/2Ti1/2)O3 - xBi(Zn1/2Ti1/2)O3 - (1/3)BiFeO3 films with x = [a] 0.57 and [c] 1.00 grown on (100)SrRuO3//(100)SrTiO3 substrates. Open and closed circles correspond to SrTiO3 and SrRuO3 diffractions, respectively.

**Fig. 3** XRD-RSM of (2/3)(1-x)Bi(Zn1/2Ti1/2)O3 - xBi(Zn1/2Ti1/2)O3 - (1/3)BiFeO3 films with x = 0.79 grown on (110)SrRuO3//(110)SrTiO3 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(Zn1/2Ti1/2)O3 - xBi(Zn1/2Ti1/2)O3 - (1/3)BiFeO3 films grown on (a) (100), (b) (110) and (c) (111)-oriented SrRuO3//SrTiO3 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(Zn1/2Ti1/2)O3 - xBi(Zn1/2Ti1/2)O3 - (1/3)BiFeO3 films grown on (100), (110), and (111)-oriented SrRuO3//SrTiO3 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)O3 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(Zn1/2Ti1/2)O3 - Bi(Mg1/2Ti1/2)O3 - BiFeO3, were successfully grown on (100), (110), and (111)-oriented SrRuO3//SrTiO3 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) SrRuO3//SrTiO3 substrates was above 900°C. Maximum observed longitudinal piezoelectric coefficient, $AFM-d_{33,obs}$ measured by PFM was about 300 pm/V.

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