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MOCVD growth and characterization of $BiFeO_3$–$Bi(Zn_{1/2}Ti_{1/2})O_3$ ferroelectric films

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ABSTRACT

xBi$(Zn_{1/2}Ti_{1/2})O_3$–$(1-x)$BiFeO$_3$ films with x = 0–0.68 were prepared on (1 0 0)$SrTiO_3$ and (1 0 0)$_c$$SrRuO_3$||(1 0 0)$SrTiO_3$ substrates by pulsed metalorganic chemical vapor deposition. Effects of the composition, x, on the constituent phases and their electrical properties were systematically investigated. {1 0 0}-oriented epitaxial films were ascertained to be grown and three series of peaks with x = 0–0.23 (*Peak A*), x = 0.15–0.44 (*Peak B*) and x = 0.23–0.68 (*Peak C*) were observed. Leakage current density monotonously decreased with increasing x. On the other hand, maximum relative dielectric constant of the films was observed at x = 0.20, almost corresponding to the compositional boundary of the x between *Peaks A* and *C*.

1. Introduction

Piezoelectric materials have been used for wide range of applications, such as sensor and actuator. Among these applications, the microelectromechanical system (MEMS) using piezoelectric films have been great interesting [1]. Lead-based materials, such as $Pb(Zr,Ti)O_3$, are widely investigated for these applications due to the large piezoelectric response and the high Curie temperature. However, it is well known that lead has toxicity for environment. Thus, the lead-free materials have been highly required for environmental friendly and lead-free alkali metals-based piezoelectric materials are widely investigated [2,3]. However, alkali metals-based materials are not suitable especially for MEMS application because Si-based processes are mainly used to fabricate to MEMS application and the diffusion of alkali metals into Si becomes severe problem for the device performance. Therefore, we focus our attention to Bi-based perovskite materials. Use of the composition located at phase boundary is known to be useful for the enhancement of the piezoelectricity, such as $Pb(Zr_{0.52}Ti_{0.48})O_3$ located at phase boundary between rhombohedral and tetragonal symmetry [4]. In addition, it was reported that (Bi,RE)FeO_3 (RE = Nd, Sm, Gd) solid-solution have phase boundary between rhombohedral and orthorhombic symmetry [5–8]. Especially (Bi,Sm)FeO_3 system indicated maximum value of d_{33} at phase boundary [5]. In recent years, $BiCoO_3$ and $Bi(Zn_{1/2}Ti_{1/2})O_3$ having tetragonal symmetry have been prepared by high pressure synthesis [9,10]. Phase boundary between tetragonal $BiCoO_3$ and rhombohedral $BiFeO_3$ similar to $Pb(Zr,Ti)O_3$ system was discovered for the epitaxial films by metal organic chemical vapor deposition (MOCVD) [11,12]. However, it is difficult to measure electrical properties at room temperature owing to the large leakage current. This result motivates us to use another tetragonal $Bi(Zn_{1/2}Ti_{1/2})O_3$ instead of $BiCoO_3$ because Zn^{2+} and Ti^{4+} have d^{10} and d^0 ion state, respectively. In the present study, we tried to grow the epitaxial films of $Bi(Zn_{1/2}Ti_{1/2})O_3$–$BiFeO_3$ solid-solution by MOCVD and investigated the crystal structure as well as the electrical properties.

2. Experimental

xBi$(Zn_{1/2}Ti_{1/2})O_3$–$(1-x)$BiFeO$_3$ epitaxial films (x = 0–0.68) were grown on (1 0 0)$SrTiO_3$ and (1 0 0)$_c$$SrRuO_3$||(1 0 0)$SrTiO_3$ substrates by pulsed-MOCVD at relative high temperature of 770 °C to get highly crystallized films. We selected MOCVD as preparation method because of its growth ability of the high quality films with low process damage. $Bi[(CH_3)_2(2\text{-}(CH_3)_2NCH_2C_6H_4)]$, $Zn(C_{12}H_{25}O_2)$, $Ti(O\cdot i\text{-}C_3H_7)_4$, $Fe(C_2H_5C_5H_4)_2$ were used as Bi, Zn, Ti and Fe source materials, respectively, and oxygen gas was used as an oxidant. Films were deposited using pulse introduction of the mixture gases of Bi, Zn, Ti and Fe sources in a cold-wall type vertical reactor maintained at a 530 Pa. Film composition was changed by controlling the input gas flow rate of each source gases based on the theoretical input gas flow rate, $R(\text{source}) = [P(T) \times l]/P_v$, where $P(T)$, l, and P_v were respective vapor pressure of the sources at fixed the temperature, gas flow rate of the carrier gas and the pressure of the source vessel [13].

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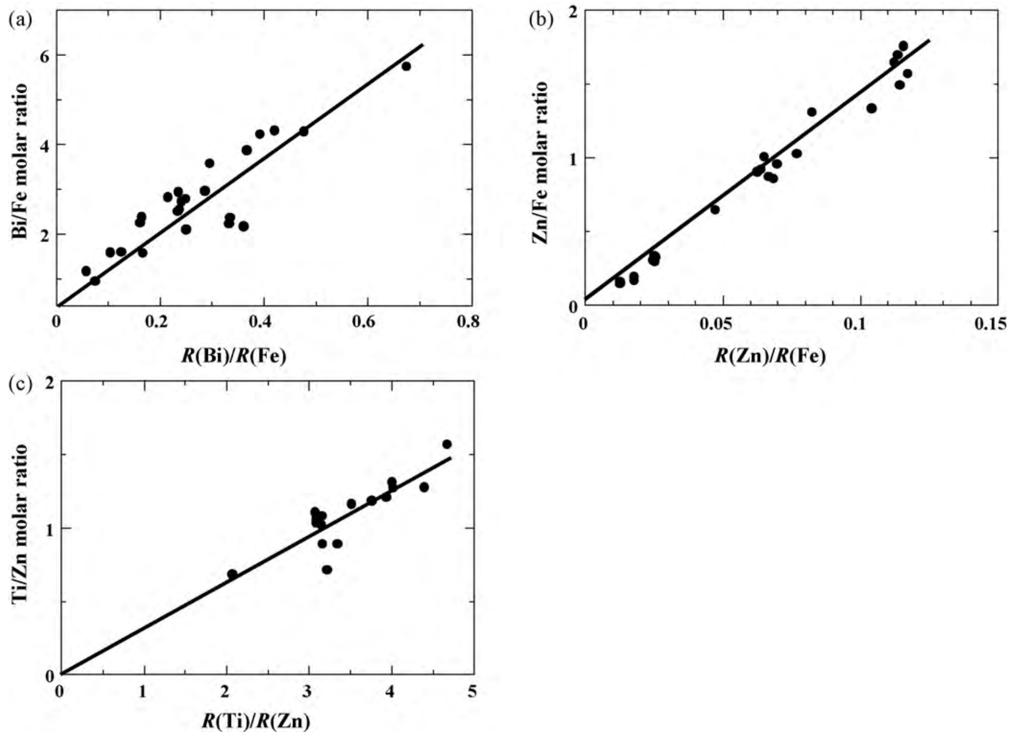

Fig. 1. Molar ratio of constituted element as a function of theoretical gas flow rate ratio of the source gas, *R*(source): (a) Bi/Fe, (b) Zn/Fe and (c) Ti/Zn.

The film composition was determined by X-ray fluorescence (XRF). Phase identification and the lattice spacing, *d*, measurements were carried out using X-ray diffraction (XRD). The electrical properties were measured at room temperature and 80 K using Pt/xBi($Zn_{1/2}Ti_{1/2}$)O_3–(1 − x)$BiFeO_3$/$SrRuO_3$ capacitor structure after making Pt top electrode (100 μm in diameter) by electric beam evaporation.

3. Results and discussion

3.1. Composition control in MOCVD process

Fig. 1(a) shows the molar ratio of the Bi/Fe, Zn/Fe and Ti/Zn in the films as a function of the corresponding ratio of the theoretical input gas flow rate. Almost linear relationship across zero was observed between the molar ratio in the film and the corresponding ratio of the theoretical input gas flow rate. These results reveal that the composition in the films can be controlled by the theoretical input gas flow rate.

3.2. Crystal structure

Fig. 2(a) shows the XRD patterns of xBi($Zn_{1/2}Ti_{1/2}$)O_3–(1 − x)$BiFeO_3$ films with various x value (x = 0–0.68) prepared on (1 0 0)$SrTiO_3$ substrates. The pure perovskite structure with {1 0 0}-orientation was observed without impurity phase for all compositions which were also ascertained by the X-ray pole figure measurement.

Fig. 2(b) shows the enlarged XRD patterns from 2θ range between 38° and 47°. There are three series of film peaks labeled as *Peak A*, *Peak B* and *Peak C*.

Fig. 3 plotted the composition dependency of the lattice spacing, *d* value, calculated from these three peaks. In addition, *d* values obtained from the films on $(1\,0\,0)_c SrRuO_3 || (1\,0\,0)SrTiO_3$ substrates are also shown in Fig. 3 because those are basically the same on

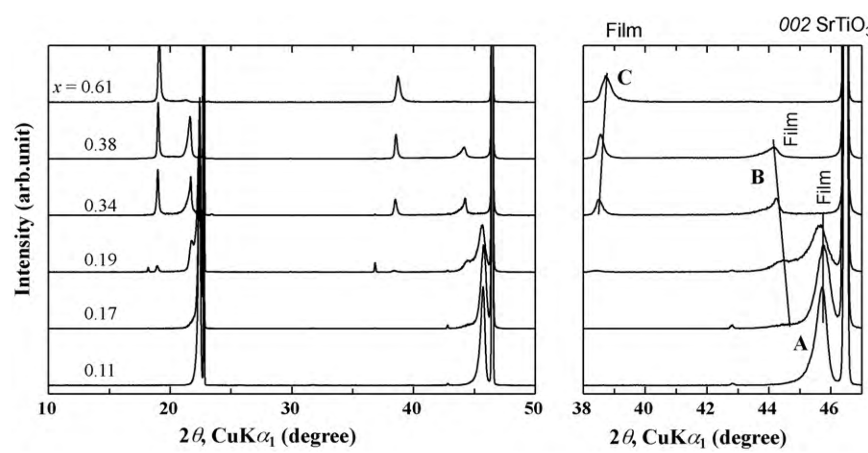

Fig. 2. XRD θ–2θ patterns of xBi($Zn_{1/2}Ti_{1/2}$)O_3–(1 − x)$BiFeO_3$ films with various x value prepared on (1 0 0) $SrTiO_3$ substrates. 2θ: (a) 10–50° and (b) 38–47°