

Micro-Raman Study of BiFeO₃ Thin Films Fabricated by Chemical Solution Deposition Using Different Bi/Fe Ratio Precursors

T. NAKAMURA, H. FUKUMURA, N. HASUIKE, H. HARIMA

Department of Electronics, Kyoto Institute of Technology, Kyoto 606-8585, Japan

Y. NAKAMURA

Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan

K. KISODA

Department of Physics, Wakayama University, Wakayama 640-8510, Japan

S. NAKASHIMA AND M. OKUYAMA

Graduate School of Engineering Science, Osaka University, Osaka 560-8531, Japan

BiFeO₃ thin films were grown by chemical solution deposition using precursors with different elemental ratios, Bi/Fe = 1.1/1.0, 1.0/1.0 and 1.0/1.1. All the samples consisted of two easily distinguishable components of crystalline and amorphous phases. We have found that the electric properties of BiFeO₃ thin films are closely connected to the crystallinity of the films.

PACS numbers: 78.30.Hv, 63.20.D-, 78.30.-j

1. Introduction

There has been increasing interest in the so-called multiferroic materials, showing unique features due to coexistence of two or more ferroic orderings (ferroelectricity, ferromagnetism and ferroelasticity). For example, coexistence of ferroelectricity and ferromagnetism may yield a magnetoelectric effect: the magnetization is controlled by the applied electric field. Such materials may lead us to future innovative electronic devices. BiFeO₃ is a very promising candidate from this point of view because it shows ferroelectric and weak ferromagnetic orderings above room temperature simultaneously (Curie temperature $T_C = 1103$ K and Néel temperature $T_N = 643$ K) [1–3].

Recently, growth technique of BiFeO₃ thin films have gathered much attention because pulsed laser deposition (PLD) provided films with excellent ferroelectric properties compared to bulk samples [4, 5]. Chemical solution deposition is another attractive candidate for low-cost and efficient growth of BiFeO₃ films [6]. To elucidate the potential for future device production, we were studying basic properties of BiFeO₃ films prepared by chemical solution deposition. We have recently revealed by surface morphology observation that the films consisted of two different phases with dimensions of μm , changing with the Bi/Fe ratio in the precursor solution [7, 8]. We have demonstrated there that micro Raman scattering is a very powerful technique to investigate lattice properties

of the two μm -sized regions separately. In this study, we will characterize crystallinity of these regions in detail by micro Raman scattering as a function of Bi/Fe ratios.

2. Experiment

The BiFeO₃ thin films were prepared by chemical solution deposition using different Bi/Fe ratio precursor solutions of #1: Bi/Fe = 1.1/1.0 (10 mol% Bi-excess), #2: Bi/Fe = 1.0/1.0 (stoichiometric) and #3: Bi/Fe = 1.0/1.1 (10 mol% Fe-excess) compositions. The solution of 0.2 mol/l using 2-ethylhexanoate bismuth [Bi(OCO(CH)(C₂H₅)C₄H₉)₃] and trisacetylacetonato iron [Fe(C₅H₇O₂)₃] (Toshima MFG Co., Ltd.) was spin-coated on a Pt/TiO₂/SiO₂/Si substrate at 3000 rpm for 30 s and dried at 250°C for 5 min in air. This processes was repeated 20 times to obtain film thickness of 250 nm. Then, the films were annealed at 450°C for 15 min in N₂ atmosphere.

The micro Raman measurement was conducted by using an Ar⁺ laser at $\lambda = 514.5$ nm for excitation. The scattered light was collected in the backscattering geometry by the same objective lens, fed to a double monochromator of focal length 85 cm for dispersion, and the spectra were detected by a liquid-nitrogen-cooled charge-coupled-device (CCD) camera. The laser beam was focused by an objective lens with N/A (numerical aperture) = 0.90. The beam waist could be conventionally calculated as $\phi = 1.2 \lambda/\text{NA} = 0.7 \mu\text{m}$. In this experiment,

actually, we have elongated the beam linearly to a size roughly $1\ \mu\text{m} \times 20\ \mu\text{m}$ on the sample surface by using a cylindrical lens. This is to avoid excess heating problem of the sample and also for easy comparison over a large area.

3. Results and discussion

Figure 1 shows typical X-ray diffraction (XRD) patterns of the BiFeO₃ samples. Let us note that strong signals marked with S derive from the substrate. The result shows that all the samples consisted of polycrystalline phases containing BiFeO₃ perovskite units. Careful comparison of the (010) and (110) peak intensities between the samples shows that sample #1, giving the most intense signals, may have the highest crystalline quality in the samples, and the quality deteriorates in the order of #1, 2 and 3. Remnant polarizations P_r measured in our separate electrical measurement at room temperature supports this view and suggests strong correlation between the crystallinity and ferroelectric properties: we obtained $P_r = 85, 38$ and $30\ \mu\text{C}/\text{cm}^2$ for #1, #2 and #3, respectively.

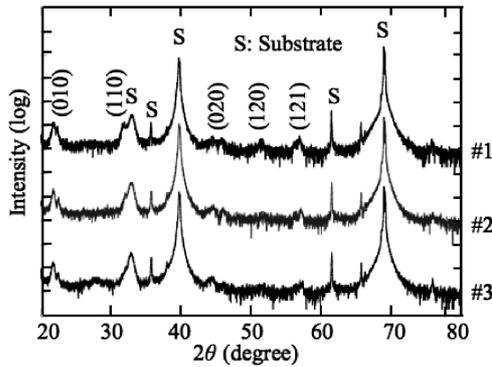


Fig. 1. XRD patterns of BiFeO₃ films prepared by different precursor solutions with Bi/Fe = 1.1/1.0 (#1), 1.0/1.0 (#2) and 1.0/1.1 (#3) [7].

Figure 2 shows Raman spectra of three samples. In sample #1, eight phonon peaks were identified and classified as A_1 and E modes with reference to the previous results [9, 10]. In the inferior quality samples #2 and #3, a broad signal at $\approx 640\ \text{cm}^{-1}$ was observed. Recalling that the XRD signals (Fig. 1) showed no impurity phases in #2 and 3, we attribute this broad signal to some very defective phase or amorphous phase of BiFeO₃.

Figures 3a, b and c show optical microscope images of samples #1, #2 and #3, respectively. As easily noticed in all samples, the images consisted of two different components; bright region (I) and dark one (II) as marked in Fig. 3a. Similar morphology has been reported in other ferroelectric films prepared by sol-gel method such as PbZrO₃ [11, 12]. Here we find that the area ratio of bright region to dark one, I/II, clearly decreases from (a) for #1 to (c) for #3. We believe therefore that the

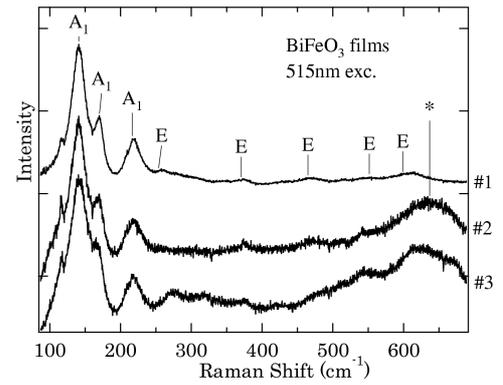


Fig. 2. Raman spectra of BiFeO₃ films prepared by different precursor solutions with Bi/Fe = 1.1/1.0 (#1), 1.0/1.0 (#2) and 1.0/1.1 (#3).

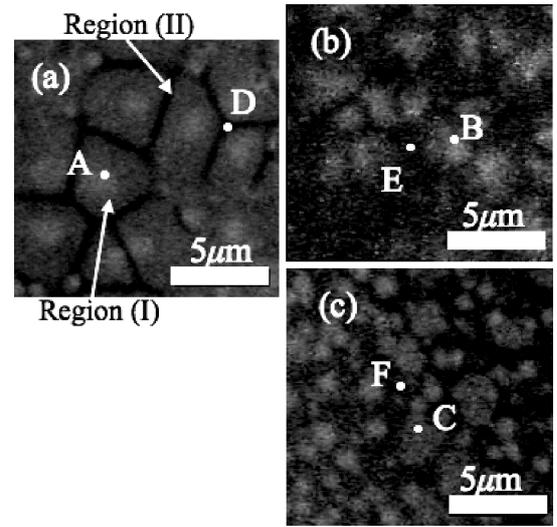


Fig. 3. Optical microscope images of the BiFeO₃ samples prepared by different precursor solutions with (a) Bi/Fe = 1.1/1.0 for #1, (b) 1.0/1.0 for #2 and (c) 1.0/1.1 for #3.

area ratio I/II is closely correlated with the ferroelectric properties and the overall crystalline quality. We then examined local Raman spectrum at white dotted positions A to F.

Figures 4a and b compare local Raman spectra in the bright (I) and dark regions (II), respectively, of Fig. 3. In Fig. 4a, only sharp phonon peaks of BiFeO₃ perovskite structure can be observed and furthermore, position A in #1 gives sharper phonon peaks compared to B in #2 and C in #3. This is clearly correlated with the superior crystalline quality suggested already by XRD (Fig. 1) and Raman scattering (Fig. 2). On the contrary, in Fig. 4b, no clear phonon peaks are observed except for the broad one at $\approx 640\ \text{cm}^{-1}$. The Raman spectra suggest that the dark regions (II) are mainly amorphous. We can conclude from Figs. 3 and 4 that, as the area ratio I/II

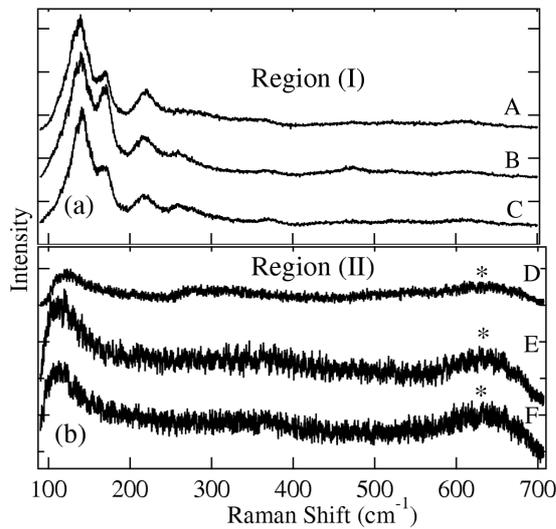


Fig. 4. Local Raman spectra of BiFeO₃ films of (a) region (I) and (b) region (II). A–F correspond to white dot positions in Fig. 3.

becomes higher, the crystalline quality of the samples will be improved and the ferroelectric property likewise. In the present experiment, sample #1 was prepared with the 10 mol% Bi-excess condition. It may reflect a relatively evaporative property of Bi in our process condition.

4. Conclusion

BiFeO₃ thin films grown by chemical solution deposition using precursor solutions with different Bi/Fe ratios were studied by X-ray diffraction, micro-Raman scattering and surface morphology observation by optical mi-

croscopy. The samples consisted of two regions: highly crystalline region containing BiFeO₃ perovskite units and amorphous region. The ferroelectric properties of the films are strongly correlated with the volume ratio of these regions.

References

- [1] G. Smolenskii, V. Yudin, E. Sher, Y.E. Stolypin, *Sov. Phys. JETP* **16**, 622 (1963).
- [2] Y.N. Venevtsev, G. Zhadanov, S. Solov'ev, *Sov. Phys. Crystallogr.* **4**, 538 (1960).
- [3] G. Smolenskii, V. Isupov, A. Agranovskaya, N. Kranik, *Sov. Phys. Solid State* **2**, 2651 (1961).
- [4] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh, *Science* **299**, 1719 (2003).
- [5] K.Y. Yun, D. Ricinchi, T. Kanashima, M. Okuyama, *Appl. Phys. Lett.* **89**, 192902 (2006).
- [6] S.K. Singh, H. Ishiwara, K. Maruyama, *Appl. Phys. Lett.* **100**, 064102 (2006).
- [7] Y. Nakamura, K.Y. Yun, S. Nakashima, M. Okuyama, *Integrated Ferroelectrics* **95**, 226 (2007).
- [8] Y. Nakamura, S. Nakashima, Dan Ricinchi, M. Okuyama, *Funct. Mater. Lett.* **1**, 19 (2008).
- [9] H. Fukumura, S. Matsui, H. Harima, T. Takahashi, T. Itoh, K. Kisoda, M. Tamada, Y. Noguchi, M. Miyayama, *J. Phys., Condens. Matter* **19**, 365224 (2007).
- [10] M.K. Singh, H.M. Jang, S. Ryu, M.H. Jo, *Appl. Phys. Lett.* **88**, 042907 (2006).
- [11] E.M. Alkoy, S. Alkoy, T. Shiosaki, *Jpn. J. Appl. Phys.* **44**, 6654 (2005).
- [12] E.M. Alkoy, S. Alkoy, T. Shiosaki, *Jpn. J. Appl. Phys.* **44**, 8606 (2005).