Dependence of Ferroelectric and Magnetic Properties on Measuring Temperatures for Polycrystalline BiFeO3 Films

著者	永沼　博
journal or publication title	IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control
volume	55
number	5
page range	1046-1050
year	2008
URL	http://hdl.handle.net/10097/46542

doi: 10.1109/TUFFC.2008.754

Dependence of Ferroelectric and Magnetic Properties on Measuring Temperatures for Polycrystalline $BiFeO_3$ Films

Hiroshi Naganuma, Yosuke Inoue, and Soichiro Okamura

***Abstract*—A multiferroic $BiFeO_3$ film was fabricated on a $Pt/Ti/SiO_2/Si(100)$ substrate by a chemical solution deposition (CSD) method, and this was followed by postdeposition annealing at 923 K for 10 min in air. X-ray diffraction analysis indicated the formation of the polycrystalline single phase of the $BiFeO_3$ film. A high remanent polarization of 89 $\mu C/cm^2$ was observed at 90 K together with a relatively low electric coercive field of 0.32 MV/cm, although the ferroelectric hysteresis loops could not be observed at room temperature due to a high leakage current density. The temperature dependence of the ferroelectric hysteresis loops indicated that these hysteresis loops lose their shape above 165 K, and the nominal remanent polarization drastically increased due to the leakage current. Magnetic measurements indicated that the saturation magnetization was less than 1 emu/cm^3 at room temperature and increased to approximately 2 emu/cm^3 at 100 K, although the spontaneous magnetization could not appear. The magnetization curves of polycrystalline $BiFeO_3$ film were nonlinear at both temperatures, which is different with $BiFeO_3$ single crystal.**

I. Introduction

$BiFeO_3$ has been predicted to possess a high remanent polarization, for example, theoretical calculated values of ∼100 $\mu C/cm^2$ have been reported [1]. In fact, the films, as well as bulk forms of $BiFeO_3$ showed a remanent polarization of 50 to 100 $\mu C/cm^2$ at room temperature [2]–[5]. Therefore, the ferroelectric properties of the $BiFeO_3$ films have been extensively investigated in the recent past [2], [6]–[8]. In these reports, the values of the remanent polarization for the polycrystalline $BiFeO_3$ films were different. One of the reasons for these differences could be the high leakage current density in the $BiFeO_3$ films due to the absence of the Schottky-barrier interface between the Pt electrode and the $BiFeO_3$ layer [9], [10] and/or the existence of the bivalent iron in the film bodies [11]. A method to measure the accurate ferroelectricity of $BiFeO_3$ films is to decrease the measuring temperature to reduce the leakage current density. However, the critical temperature, which could suppress the leakage current component, is not clearly known. It is better to discuss the value of the remanent polarization below the critical temperature. In this study, we fabricated a polycrystalline $BiFeO_3$ film by a chemical solution deposition (CSD) and investigated the temperature dependence of both ferroelectric and magnetic properties. We found that the leakage current begins to increase at 165 K in the polycrystalline $BiFeO_3$ film.

Manuscript received May 26, 2007; accepted February 19, 2008. This study was partly supported by the Grant-in-Aid for Young Scientist (start-up program, Grant No. 18860070) from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by the Sasakawa Scientific Research Grant from the Japan Society (Grant No. 19-216).

The authors are with the Department of Applied Physics, Tokyo University of Science, Tokyo, Japan (e-mail: naganuma@rs.kagu.tus.ac.jp).

Digital Object Identifier 10.1109/TUFFC.2008.754

II. Experimental Procedure

A $BiFeO_3$ film was fabricated by the CSD method on $Pt/Ti/SiO_2/Si(100)$ substrates. The Pt electrodes at the bottom and top were deposited by RF magnetron sputtering and electron beam evaporation, respectively. The specimen was annealed at 923 K for 10 min in air. The film thickness of the $BiFeO_3$ layer was approximately 180 nm. The crystal structure was determined by conventional X-ray diffraction (XRD) ($2\theta/\theta$, Cu-Kα; X'Pert PRO MRD, PANalytical, Almelo, The Netherlands). The surface morphology of the film was observed by atomic force microscopy (AFM). The magnetic properties at low temperature were measured by a superconducting quantum interface device (SQUID; MPMS-XL, Quantum Design, San Diego, CA) magnetometer, and at room temperature were measured by vibrating sample magnetometer (VSM; TM-VSM311483-HGC, Tamagawa, Hiyagi, Japan) in the in-plane direction. The temperature dependence of the ferroelectric hysteresis loops were measured by using a ferroelectric tester (TF-2000, aixACCT Systems GmbH, Aachen, Germany) with a single triangular pulse of 1 kHz. A driving voltage was applied to the bottom electrode during the measurement of the electrical properties.

III. Results and Discussion

A. Film Structure

Fig. 1 shows the XRD pattern of the specimen annealed at 923 K for 10 min in air. Many diffraction peaks that could be attributed to the $BiFeO_3$ phase were observed and no secondary phases appeared; this indicated the formation of the polycrystalline single phase of the $BiFeO_3$ film.

Fig. 2 shows the AFM images of the $BiFeO_3$ film with the various magnifications. In the low-magnification AFM

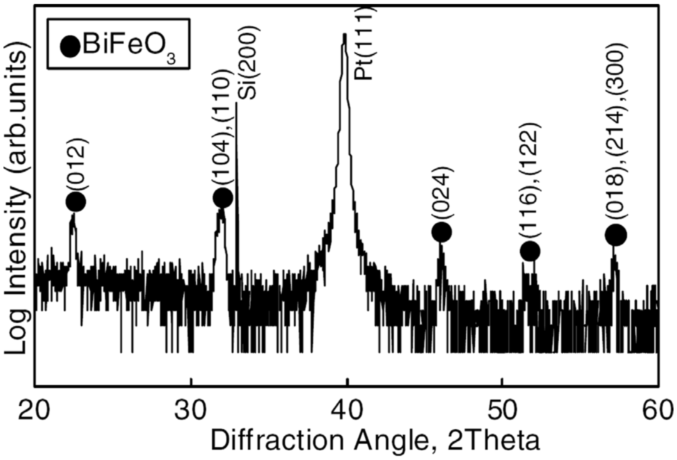


Fig. 1. XRD pattern of the specimen annealed at 923 K for 10 min in air.

image seen in Fig. 2(a), the grains with a diameter of 1∼2 μm could be observed. When the AFM images were magnified, small grains with a diameter of around a few hundred nanometers were observed to have formed on the surface of the large grains with a size of 1∼2 μm. In the cross-sectional TEM observation, it was revealed that both of large and small grains had $BiFeO_3$ structure, and the small grains appeared only on the surface of the film [12].

B. Ferroelectric Properties

Fig. 3(a) shows a plot of the leakage current density against the electric field characteristic of the $BiFeO_3$ film measured at room temperature. A fairly high leakage current density of around 10^{-1} A/cm^2 at 0.15 MV/cm was observed at room temperature. When measured at 90 K, as shown in Fig. 3(b), the leakage current density was found to be drastically reduced to the order of 1×10^{-7} A/cm^2 at 0.15 MV/cm. Further, the leakage current could be measured up to 1.1 MV/cm ($\sim 4\times10^{-6}$ A/cm^2) due to the reduction of the Joule heat damage. The leakage current density of $BiFeO_3$ film was strongly affected by measuring temperature which indicated the electric conduction due to defect of oxygen and/or bismuth because the calculated band gap of $BiFeO_3$ is 2.8 eV [13].

Fig. 4 shows the temperature dependence of the ferroelectric hysteresis loops for the $BiFeO_3$ film that was determined by using a single triangular pulse of 1 kHz. Because of the ease of dielectric breakdown at high measuring temperatures, we applied an insufficient electric field when measuring the temperature dependence of the ferroelectric hysteresis loops. Below the measuring temperature of 150 K, ferroelectric hysteresis loops with a relatively high squareness ratio were obtained. However, the ferroelectric hysteresis loops start expanding above 165 K due to increase of leakage current density and dielectric breakdown at 203 K. The results suggest that it is necessary to measure the temperature dependence of ferroelectric hysteresis loops and to find the temperature that showed high squareness hysteresis loops when discussing the remanent polarization for the specimens with high-leakage-current materials such as $BiFeO_3$ films.

To discuss the ferroelectricity without the leakage current component, the ferroelectric hysteresis loops were measured at 90 K. The result is shown in Fig. 5(a). In this experiment, we could apply a higher electric field as compared with that in the case of the temperature dependence of ferroelectricity (Fig. 4) due to the low measuring temperature. The ferroelectric hysteresis loop measured at 90 K showed a high squareness with a high remanent polarization of 89 μC/cm^2 and a relatively low electric coercive field of 0.32 MV/cm at an applied electric field of 1.33 MV/cm. Fig. 5(b) shows the electric field dependence of remanent polarization estimated from ferroelectric hysteresis loops. It should be noted that the remanent polarization had a tendency to increase by an increase in the applied electric field, although the leakage current was sufficiently suppressed at 90 K. This result indicated that the polycrystalline $BiFeO_3$ films require electric fields that are quite high to achieve the saturated polarization.

C. Magnetic Properties

Fig. 6 shows the magnetization curves for the $BiFeO_3$ film measured at both room temperature using VSM and 100 K using the SQUID magnetometer. Because the film is a weak ferromagnetic material, magnetic fields with the machine-limited maximum values of 15 kOe for VSM and 50 kOe for SQUID were applied. The saturation magnetization at room temperature was less than 1 emu/cm^3, and the saturation magnetization was increased to approximately 2 emu/cm^3 by decreasing the temperature to 100 K, although the spontaneous magnetization did not appear. The small saturation magnetization is attributed to the antiferromagnetic spin structure [1], [3], [5]. When we compared the magnetization curve with $BiFeO_3$ single crystals, the shape of the magnetization curves is different. The polycrystalline $BiFeO_3$ film showed nonlinear magnetization curves at both room temperature and 100 K, although the magnetization curves above 100 K were linear for the $BiFeO_3$ single crystals [5]. In our other study, secondary phases could not be observed in the TEM observation [12], therefore, the reason of nonlinearity of magnetization curves might be not the effect of impurity phases. Thus, although the further discussion is necessary, nonlinearity of magnetization curves can be attributed to the imperfect antiferromagnetic cycloidal spin structure due to the polycrystalline structure [14] and/or existence of bivalence iron due to deficiency of oxygen.

IV. Conclusion

A single phase of a polycrysalline $BiFeO_3$ film was fabricated by the CSD method, and this was followed by postdeposition annealing at 923 K for 10 min in air; the electric, ferroelectric, and magentic properties of the film showed a temperature dependence. The temperature dependence of the ferroelectric hysteresis loops of the $BiFeO_3$

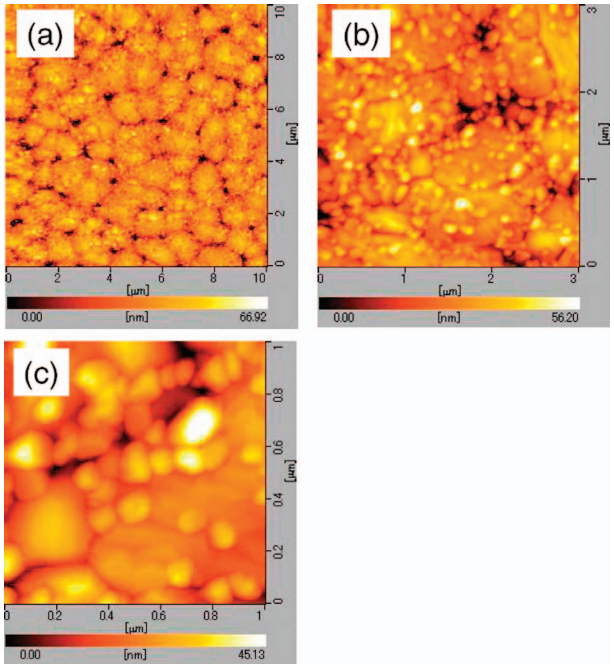


Fig. 2. Various magnifications of the AFM images of the $BiFeO_3$ film.

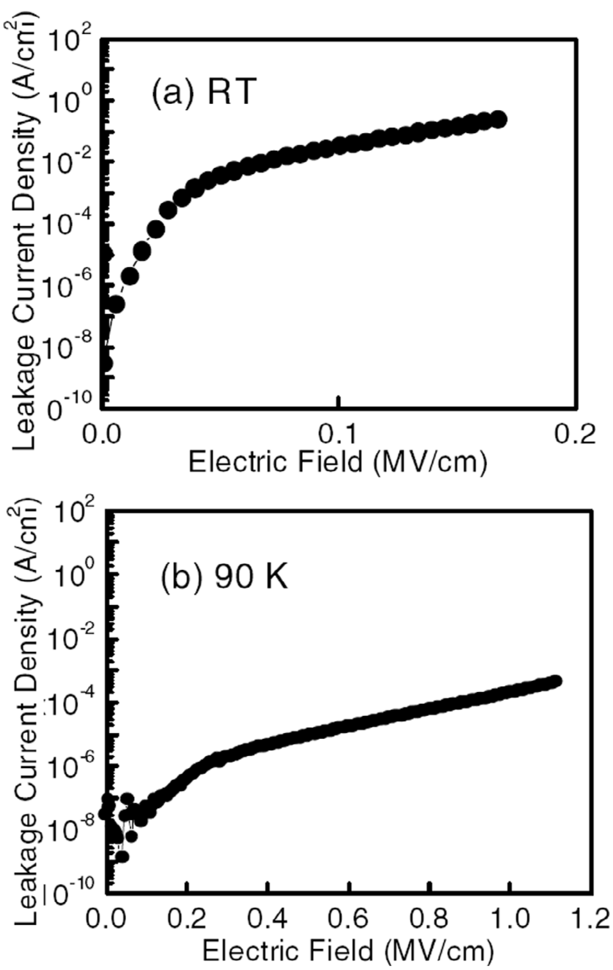


Fig. 3. Leakage current density vs. electric field characteristic of the $BiFeO_3$ film measured (a) at room temperature and (b) 90 K.

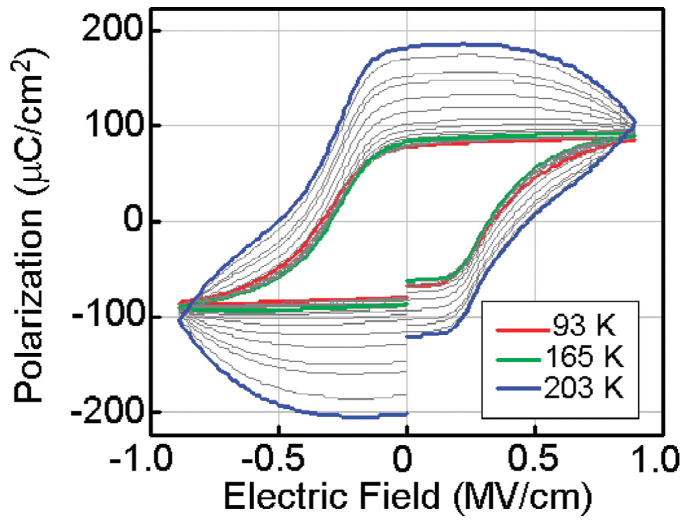


Fig. 4. Temperature dependence of the ferroelectric hysteresis loops of the $BiFeO_3$ film.

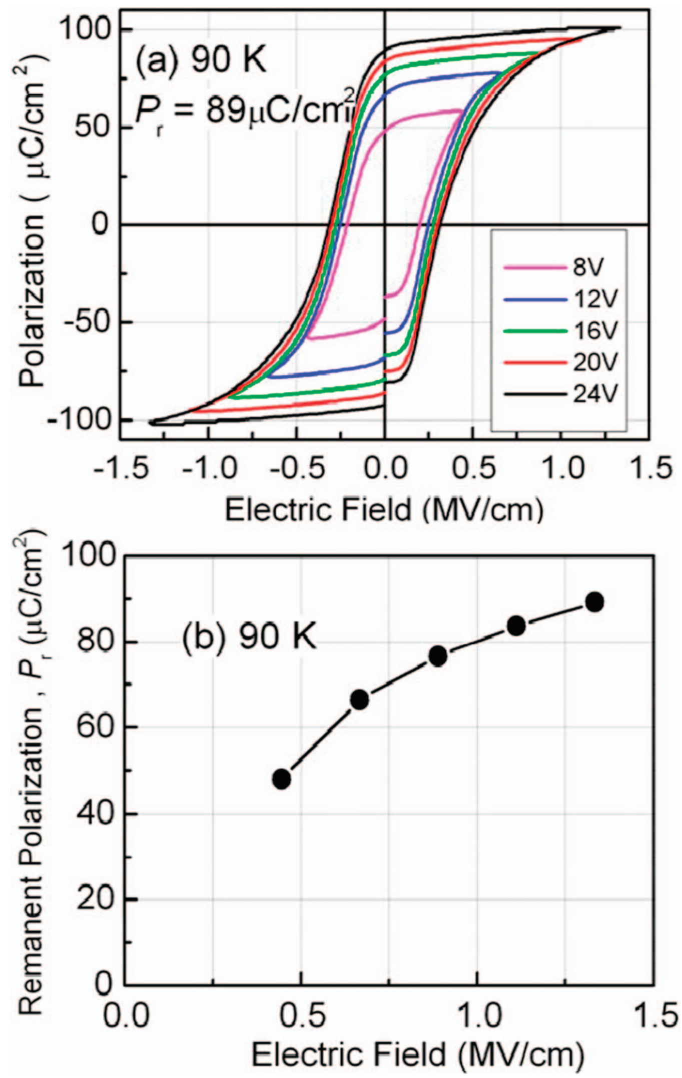


Fig. 5. Ferroelectric hysteresis loop (a) measured at 90 K, and (b) electric field dependence of remanent polarization.

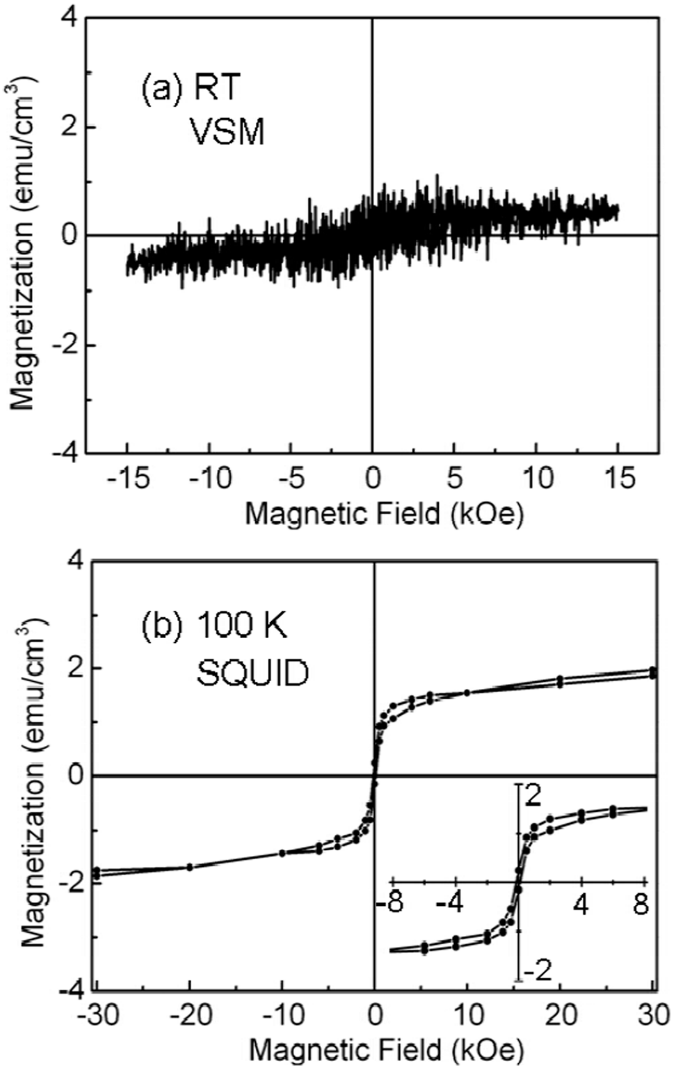


Fig. 6. Magnetization curves for the $BiFeO_3$ film measured at both (a) room temperature using the VSM and (b) 100 K using the SQUID magnetometer.

film revealed that, when an electric field of 0.9 MV/cm was applied, the remanent polarizations were constant, below 155 K, and the nominal remanent polarization drastically increased above 165 K due to the summation of the leakage current component. This suggests that the remanent polarization of the high-leakage-current materials such as $BiFeO_3$ films should be estimated by ferroelectric measurements related to the temperature. At 90 K, when leakage current components could not be considered, a high remanent polarization of 89 $\mu C/cm^2$ was observed together with a relatively low electric coercive field of 0.32 MV/cm under an appled electric field of 1.33 MV/cm. However, the remanent polarization had a tendency to increase according to the P_r vs. E curve, indicating that the polycrystalline $BiFeO_3$ films require quite high electric fields to achieve the saturated polarization. The saturation magnetization at room temperature was less than 1 emu/cm^3 and increased to approximately 2 emu/cm^3 at 100 K. The spontaneous magnetization could not appear both at room temperature and 100 K. It should be noted that the magnetization curves were nonlinear against the magnetic field, which is different with $BiFeO_3$ single crystals.

Acknowledgments

The authors would like to thank Prof. Yoshihiko Hirotsu, Osaka University, and Prof. Nobuyuki Hiratsuka, Saitama University, for measuring the magnetic properties by using the SQUID and VSM. We also wish to express gratitude to Prof. Hiroshi Funakubo, Tokyo Institute of Technology, for observing the surface morphology using AFM.

References

[1] J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, "First-principles study of spontaneous polarization in multiferroic $BiFeO_3$," *Phys. Rev. B*, vol. 71, art. no. 014113, 2005.

[2] 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, and R. Ramesh, "Epitaxial $BiFeO_3$ multiferroic thin film heterostructures," *Science*, vol. 299, pp. 1719–1722, 2003.

[3] W. Eerenstein, F. D. Morrison, J. Dho, J. F. Scott, M. Blamire, and N. D. Mathur, "Comment on 'Epitaxial $BiFeO_3$ multiferroic thin film heterostructure'," *Science*, vol. 307, p. 1203a, 2005.

[4] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruette, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, "Dramatically enhanced polarization in (001), (101), and (111) $BiFeO_3$ thin films due to epitiaxial-induced transitions," *Appl. Phys. Lett.*, vol. 84, pp. 5261–5263, 2004.

[5] D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, "Room-temperature coexistence of large electric polarization and magnetic order in $BiFeO_3$ single crystals," *Phys. Rev. B*, vol. 76, art. no. 024116, 2007.

[6] K. Y. Yun, D. Ricinschi, T. Kanashima, and M. Okuyama, "Enhancement of electrical properties in polycrystalline $BiFeO_3$ thin films," *Appl. Phys. Lett.*, vol. 89, art. no. 192902, 2006.

[7] S. K. Singh, H. Ishiwara, and K. Maruyama, "Enhanced polarization and reduced leakage current in $BiFeO_3$ thin films fabricated by chemical solution deposition," *J. Appl. Phys.*, vol. 100, art. no. 064102, 2006.

[8] A. Z. Simões, A. H. M. Gonzalez, L. S. Cavalcante, C. S. Riccardi, E. Longo, and J. A. Varela, "Ferroelectric characteristics of $BiFeO_3$ thin films prepared via a simple chemical solution deposition," *J. Appl. Phys.*, vol. 101, art. no. 074108, 2007.

[9] W. G. Pabst, L. W. Martin, Y.-H. Chu, and R. Ramesh, "Leakage mechanisms in $BiFeO_3$ thin films," *Appl. Phys. Lett.*, vol. 90, art. no. 072902, 2007.

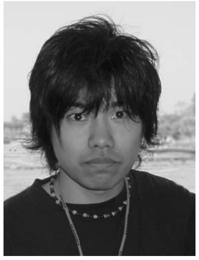
[10] H. Naganuma and S. Okamura, "Structural, magnetic and ferroelectric properties of multiferroic $BiFeO_3$ film fabricated by chemical solution deposition," *J. Appl. Phys.*, vol. 101, art. no. 09M103, 2007.

[11] Y. Wang, Q.-H. Jiang, H.-C. He, and C.-W. Nana, "Multiferroic $BiFeO_3$ thin films prepared via a simple sol-gel method," *Appl. Phys. Lett.*, vol. 88, art. no. 142503, 2006.

[12] H. Naganuma, Y. Inoue, A. Kovacs, A. Hirata, Y. Hirotsu, J. Balogh, T. Higuchi, and S. Okamura, "Magnetic and ferroelectric properties of polycrystalline $BiFeO_3$ films on annealing," to be published.

[13] S. J. Clark and J. Robertson, "Band gap and Schottky barrier heights of multiferroic $BiFeO_3$," *Appl. Phys. Lett.*, vol. 90, art. no. 132903, 2007.

[14] A. M. Kadomtseva, A. K. Zvezdin, Y. F. Popov, A. P. Pyatakov, and G. P. Vorob'ev, "Space-time parity violation and magnetoelectric interactions in antiferromagnets," *JETP Lett.*, vol. 79, pp. 571–581, 2004.



Hiroshi Naganuma was born in Tokyo, Japan, on February 17, 1976. In 2004, he received a Ph.D. degree from Osaka University.

In 2004, he was employed as a postdoctoral student by the Institute of Science Industrial Research of Osaka University. Since 2006, he has been an assistant professor in the Faculty of Science, Department of Applied Physics, Tokyo University of Science. Specific areas of interest include fabrication and evaluation of the Bi-based multiferroic thin films.

Dr. Naganuma is a regular member of the Japan Society of Applied Physics, the Magnetic Society of Japan, and the Japan Institute of Metals.

Yosuke Inoue was born in Tokyo, Japan, on March 5, 1985. He received the B.S. degree from Tokyo University of Science, Tokyo, Japan, in 2007. He is presently a student of the master's course in the Department of Applied Physics at Tokyo University of Science.

His research interests include fabrication and evaluation of the Bi-based multiferroic thin films.

Mr. Inoue is a student member of the Japan Society of Applied Physics.

Soichiro Okamura was born in Kochi, Japan, on September 12, 1959. In 1989, he received a Ph.D. degree from Science University of Tokyo. From 1989 to 1992, he was an assistant professor in the Department of Electronic Engineering, Science University of Tokyo, Yamaguchi College. From 1992 to 1995, he was an assistant professor in the Department of Applied Physics, the Faculty of Science, Science University of Tokyo. From 1995 to 1998, he was a lecturer in the Department of Electronic Engineering, the Faculty of Fundamental Engineering, Yamaguchi Tokyo University of Science. From 1998 to 2005, he was an associate professor in the Graduate School of Materials Science, Nara Institute of Science and Technology. Since 2005, he has been a professor in the Department of Applied Physics, Faculty of Science, Tokyo University of Science.

He has developed the electron-beam-induced micropatterning technique for composite oxides. His present interests are in the properties of ferroelectric thin films and the fabrication of nanostructures of ferroelectrics.

Professor Okamura is a regular member of the Japan Society of Applied Physics and the Ceramics Society of Japan.