

Hiroshi Funakubo, Prof.

Department of Innovative and Engineered Materials

1. Main Research Results

1) Development of Lead Free Piezoelectric Material

Additional novel lead-free system was also developed this year based on the same concept developed last year. This indicates that a lot of novel system can be found based on our material design.

2) Characterization of Polar-axis oriented PZT Thick Films

Electrical and piezoelectric properties of polar-axis oriented-PZT agreed well with the prediction from the theory. This indicates that the obtained film can be regard as the single crystal.

3) Growth of Tunable Capacitor

Material design induced large tunability, i.e. the change of the capacitance with electrical field, was developed.

2. List of Publications (original article, comment/book)

1) Original Paper

- (1) "Temperature Dependency of Dielectric Properties in Epitaxially Grown $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ Films with Different Orientation", Hiroshi Funakubo Muneyasu Suzuki, Kenji Takahashi, and Takayuki Watanabe, *Key Eng. Mater.*, 368-372 (2008) pp. 1811-1813
- (2) "Structural modulation in bismuth cuprate superconducting film with continuous epitaxial growth", Satoru Kaneko, Kensuke Akiyama, Takeshi Ito, Yoshitada Shimizu, Yasuo Hirabayashi, Seishiro Ohya, Hiroshi Funakubo, and Mamoru Yoshimoto, *J. Crystal Growth*, 310 (2008) pp.1713–1717
- (3) "Epitaxial growth of (100) Fe_3Si thin films on insulating substrates", Kensuke Akiyama, Teiko Kadowaki, Satoru Kaneko, Azusa Kyoduka, Yutaka Sawada, and Hiroshi Funakubo, *J. Crystal Growth*, 310 (2008) pp1703–1707
- (4) "In-Plane Rotated Crystal Structure in Continuous Growth of Bismuth Cuprate Superconducting Film", Satoru Kaneko, Kensuke Akiyama, Takeshi Ito, Yasuo Hirabayashi1, Hiroshi Funakubo, and Mamoru Yoshimoto, *Solid State Pheno.* 139 (2008) pp 53-58
- (5) "Low strain sensitivity of the dielectric property of pyrochlore Bi-Zn-Nb-O films", Hiroshi Funakubo, Shingo Okaura, Muneyau Suzuki, Hiroshi Uchida, Seiichiro Koda, Rikyu Ikariyama, and Tomoaki Yamada, *Appl.Phys.Lett.*, 92 (2008) pp.182901-1 – 3
- (6) "Single domain epitaxial growth of yttria-stabilized zirconia on Si(111) substrate", S. Kaneko, K. Akiyama, T. Ito, Y. Hirabayashi, S. Ohya, T. Oguni, Y. Sawada, H. Funakubo and M. Yoshimoto, *Ceram. Inter.*, 34(4) (2008) pp.1047-1050
- (7) "Enhancement of ferroelectric and magnetic properties in BiFeO_3 films by small amount of cobalt addition", Hiroshi Naganuma, Nozomi Shimura, Jun Miura, Hiromi Shima, Shintaro Yasui, Ken Nishida, Takashi Katoda, Takashi Iijima, Hiroshi Funakubo, and Soichiro Okamura, *J.Appl.Phys.*, 103 (2008) pp.07E314-1-3

- (8) "Step coverage study of indium-tin-oxide thin films by spray CVD on non-flat substrates at different temperatures", T. Kondo, Y. Sawada, K. Akiyama, H. Funakubo, T. Kiguchi, S. Seki, M.H. Wang, and T. Uchida, *Thin Solid Films*, 516 (2008) pp.5864–5867
- (9) "X-ray Analysis of Strain Relaxed Domain Structure in (100)/(001)-oriented epitaxial PbTiO₃ thick films grown on (100)SrTiO₃ substrates", Hiroshi Nakaki, Yong Kwan Kim, Shintaro Yokoyama, Rikyu Ikariyama, Hiroshi Funakubo, S. K. Streiffer, Ken Nishida, and Keisuke Saito, *Mater. Res.Soc.Proc.*, 1034 (2008) pp.1034-K10-35
- (10) "Epitaxial Growth of Fe₃Si Thin Films on (100) Magnesia Substrates", Kensuke Akiyama, Satoru Kaneko, Teiko Kadowaki, Yasuo Hirabayashi, Azusa Kyoduka, Yutaka Sawada, Yoshihiko Kobayashi, Kichizo Asai, and Hiroshi Funakubo, *Mater. Res.Soc.Proc.* 1032 (2008)pp. 1032-I14-10-1 - 1032-I14-10-5.
- (11) "In-situ observation of strain accumulation and relaxation in PbTiO₃ film during thermal process using Raman spectroscopy", Ken Nishida, Hiroshi Funakubo, Takashi Yamamoto, and Takashi Katoda, *Integ. Ferro.*, 99 (2008) pp.23-30
- (12) "Supercell Structure on Continuous Growth of Bi₂Sr₂Ca₁Cu₂O_x Film", Satoru Kaneko, Kensuke Akiyama, Takeshi Ito, Yasuo Hirabayashi, Hiroshi Funakubo, and Mamoru Yoshimoto, *Jpn. J. Appl. Phys.*, 47 (2008) pp.5602-5604
- (13) "Thick Epitaxial Pb(Zr_{0.35},Ti_{0.65})O₃ Films Grown on (100)CaF₂ Substrates with Polar-axis-orientation", Takashi Fujisawa, Hiroshi Nakaki, Rikyu Ikariyama, Hitoshi Morioka, Tomoaki Yamada, Keisuke Saito, and Hiroshi Funakubo, *Apply. Phy. Express.* 1 (2008) 085001-1-3
- (14) "X-ray diffraction study of polycrystalline BiFeO₃ thin film under electric field", Seiji Nakashima, Osami Sakata, Yoshitaka Nakamura, Takeshi Kanashima, Hiroshi Funakubo, and Masanori Okuyama, *Apply. Phy. Lett.*, 93 (2008) 042907-1-3
- (15) "Crystal Structure and Electrical Properties of {100}-Oriented Epitaxial BiCoO₃-BiFeO₃ Films Grown By Metalorganic Chemical Vapor Deposition", Shintaro Yasui, Hiroshi Naganuma, Soichiro Okamura, Ken Nishida, Takashi Yamamoto, Takashi Iijima, Masaki Azuma, Hitoshi Morioka, Keisuke Saito, Mutsuo Ishikawa, Tomoaki Yamada, and Hiroshi Funakubo, *Jpn. J. Appl. Phys.*, 47 (2008) pp.7582-7585
- (16) "Rhombohedral-Tetragonal Phase Boundary with High Curie Temperature in (1-x) BiCoO₃ – xBiFeO₃ Solid Solution", Masaki Azuma, Seiji Niitaka, Naoaki Hayashi, Kengo Oka, Mikio Takano, Hiroshi Funakubo, and Yuichi Shimakawa, *Jpn. J. Appl. Phys.*, 47 (2008) pp. 7579-7581
- (17) "Annealing Temperature Dependences of Ferroelectric and Magnetic Properties in Polycrystalline Co-Substituted BiFeO₃ Films", Hiroshi Naganuma, Jun Miura, Mitsumasa Nakajima, Hiromi Shima, Soichiro Okamura, Shintaro Yasui, Hiroshi Funakubo, Ken Nishida, Takashi Iijima, Masaki Azuma, Yasuo Ando, Kenji Kamishima, Koichi Kakizaki, and Nobuyuki Hiratsuka, *Jpn. J. Appl. Phys.*, 47 (2008) pp. 7574-7578
- (18) "Langmuir-Blodgett Fabrication of Nanosheet-Based Dielectric Films without an Interfacial Dead Layer", Minoru Osada, Kosho Akatsuka, Yasuo Ebina, Yoshinori Kotani, Kanta Ono, Hiroshi

- Funakubo, Shigenori Ueda, Keisuke Kobayashi, Kazunori Takada, and Takayoshi Sasaki, *Jpn. J. Appl. Phys.*, 47 (2008) pp. 7556-7560
- (19)“Electrooptic And Piezoelectric Properties Of (Pb,La)(Zr,Ti)O₃ Filmswith Various Zr/Ti Ratios”, Hiromi Shima, Takashi Iijima, Hiroshi Funakubo, Takashi Nakajima, Hiroshi Naganuma, and Soichiro Okamura, *Jpn. J. Appl. Phys.*, 47 (2008) pp. 7541-7544
- (20)“In-Plane Lattice Strain Evaluation in Piezoelectric Microcantilever By Two-Dimensional X-Ray Diffraction”, Hitoshi Morioka, Keisuke Saito, Takeshi Kobayashi, Toshiyuki Kurosawa, and Hiroshi Funakubo, *Jpn. J. Appl. Phys.*, 47 (2008) pp. 7537-754
- (21)“Raman Spectroscopy Study of Oxygen Vacancies in PbTiO₃ Thin Films Generated Heat-treated in Hydrogen Atmosphere”, Ken Nishida, Minoru Osada, Hironari Takeuchi, Yoshiaki Ishimoto, Joe Sakai, Nobuaki Ito, Rikyu Ikariyama, Takafumi Kamo, Takashi Fujisawa, Hiroshi Funakubo, Takashi Kotoda, and Takashi Yamamoto, *Jpn. J. Appl. Phys.*, 47 (2008) pp. 7510-7513
- (22)“Experimental evidence of strain relaxed domain structure in (100)/(001)-oriented epitaxial lead titanate thick films grown by metalorganic chemical vapor deposition”, Hiroshi Nakaki, Yong Kwan Kim, Shintaro Yokoyama, Rikyu Ikariyama, Hiroshi Funakubo, S.K. Streiffer, Ken Nishida, Keisuke Saito, and Alexei Gruverman, *J. Appl. Phys.*, 104 (2008) pp. 064121-1 – 6
- (23)“1 V - Saturated Pb(Zr, Ti)O₃ films with (111) orientation using lattice-matched (111)SrRuO₃/(111)Pt bottom electrode prepared by pulsed metal organic chemical vapor deposition”, Hiroki Kuwabara, Nicolas Menou, and Hiroshi Funakubo, *Appl.Phys.Lett.*, 93 (2008) 152901-1 – 3
- (24)“Growth Mechanism of Indium-Tin-Oxide Transparent Conducting Films Prepared by Spray CVD”, Takeshi Kondo, Takeshi Aoyama, Chikako Kobayashi, Shigeyuki Seki, Takayuki Uchida, Yoshiyuki Seki, Hiroyuki Enta, Hiroshi Funakubo, Kouji Ninomiya, Aki Iwasawa, Riko Ozao, Toetsu Shishido, and Yutaka Sawada, *J. Flux Growth*, 3(1) (2008) 14-17
- (25)“Novel Highly Volatile MOCVD Precursors for Ta₂O₅ and Nb₂O₅ Thin Films”, T. Yotsuya, H. Chiba, T. Furukawa, T. Yamamoto, K. Inaba, K. Tada, T. Suzuki, K. Fujimoto, H. Funakubo, T. Yamakawa, and N. Oshima, *ECS Trans.*, 16(5)243-251(2008)
- (26)“Bandwidth-Controlled Insulator-Metal Transition and Correlated Metallic State in 5d Transition Metal Oxides S_{m+1}Ir_nO_{3n+1} (n=1, 2, and∞)”, S.J. Moon, H. Jin, K.W. Kim, W.S. Choi, Y.S. Lee, J. Yu, G. Cao, A. Sumi, H. Funakubo, C. Bernhard, and T.W. Noh, *Pys. Rev. Lett.*, 101(2008)226402-1-4
- (27)“Effect of the Annealing Temperature on Dielectric Properties of Bi_{1.5}Zn_{1.0}Nb_{1.5}O₇ Films Prepared by MOCVD”, Hiroshi Funakubo, Shingo Okaura, Muneyau Suzuki, Hiroshi Uchida and Seiichiro Koda, *Key Eng. Mater.*, 388(2009)175-178.
- (28)“Strain-relaxed structure in (001)/(100)-oriented epitaxial Pb(Zr,Ti)O₃ films grown on (100) SrTiO₃ substrates by metal organic chemical vapor deposition”, Hiroshi Nakaki, Yong Kwan Kim, Shintaro Yokoyama, Rikyu Ikariyama, Hiroshi Funakubo, Ken Nishida, Keisuke Saito, Hitoshi Morioka, Osami Sakata, Hee Han, and Sunggi Baik, *J. Appl. Phys.*, 105 (2009) 014107-1-5
- (29)“Domain structure of (100)/(001)- oriented epitaxial PbTiO₃ thick films with various volume fraction of (001) orientation grown by metal organic chemical vapor deposition”, Satoru Utsugi , Takashi

- Fujisawa, Rikyu Ikariyama, Shintaro Yasui, Hiroshi Nakaki, Tomoaki Yamada, Mutsuo Ishikawa, Masaaki Matsushima, and Hiroshi Funakubo, *Appl.Phys. Lett.*, 94(2009) 052906-1 -3.
- (30)“Deposition of undoped indium oxide thin films on stripe-patterned substrates by spray CVD”, T.Kondo, H.Funakubo, K.Akiyama, H.Enta, Y.Seki, M.H.Wang, T.Uchida, and Y.Sawada, *J. Crystal Growth*, 311 (2009) 642-646
- (31)“Growth of Epitaxial Potassium Niobate Film on (100)SrRuO₃/(100)SrTiO₃ by Hydrothermal Method and their Electromechanical Properties”, Mutsuo Ishikawa, Shintaro Yasui, Satoru Utsugi, Takashi Fujisawa, Tomoaki Yamada, Takeshi Morita, Minoru Kurosawa, and Hiroshi Funakubo, *Mater. Res. Soc. Symp. Proc.*, 1139(2009)GG03-52.
- (32)“Fabrication of conductive oxide polycrystalline BaPbO₃ films by chemical solution deposition and their electrical resistivity”, Hiroshi Naganuma, Kayoko Yamada, Hiromi Shima, Kensuke Akiyama, Takashi Iijima, Hiroshi Funakubo, and Soichiro Okamura, *J Electroceram*, *In press*.
- (33)“Effect of bottom electrode on dielectric property of sputtered-(Ba,Sr) TiO₃ films”, Shinichi Ito, Tomoaki Yamada, Kenji Takahashi, Shoji Okamoto, Takafumi Kamo, Hiroshi Funakubo, Ivoyl Koutsaroff, Marina Zelner, and Andrew Cervin-Lawry, *J.Appl.Phys.*, *In press*.
- (34)“Composition control and thickness dependence of {100}-oriented epitaxial BiCoO₃-BiFeO₃ films grown by metalorganic chemical vapor deposition”, Shintaro Yasui, Mitsumasa Nakajima, Hiroshi Naganuma, Soichiro Okamura, Ken Nishida, Takashi Yamamoto, Takashi Iijima, Masaki Azuma, Hitoshi Morioka, Keisuke Saito, Mutsuo Ishikawa, Tomoaki Yamada, and Hiroshi Funakubo, *J.Appl.Phys.*, *In press*.
- (35)“Crystal Structure and Electrical Property Comparisons of Epitaxial Pb(Zr, Ti)O₃ Thick Films Grown on (100)CaF₂ and (100)SrTiO₃ Substrates”, Takashi Fujisawa, Hiroshi Nakaki, Rikyu Ikariyama, Tomoaki Yamada, Mutsuo Ishikawa Hiroshi Funakubo, and Hitoshi Morioka, *J.Appl.Phys.*, *In press*.
- (36)“Polarized Raman study for epitaxial PZT thick film with the mixture orientation of (100)/(001).”, Mitsumasa Nakajima, Takashi Fujisawa, Ken Nishida, Takashi Yamamoto, Minoru Osada, Hiroshi Naganuma, Soichiro Okamura, and Hiroshi Funakubo, *Key Eng. Mater.*, *In press*.
- (37)“Effect of incubation time on deposition behavior of Ruthenium films by MOCVD using (2,4-Dimethylpentadienyl)(ethylcyclopentadienyl) Ruthenium”, Masaki Hirano, Kazuhisa Kawano, and Hiroshi Funakubo, *Key Eng. Mater.*, *In press*
- (38)“Low Temperature Preparation of (111)-oriented Pb(Zr, Ti)O₃ Films Using Lattice – matched (111)SrRuO₃/Pt Bottom Electrode by Metal Organic Chemical Vapor Deposition”, Hiroki Kuwabara, Akihiro Sumi, Shoji Okamoto, Hiromasa Hoko, Jeffrey S. Cross, and Hiroshi Funakubo, *Jpn. J. Appl. Phys.*, *In press*.
- (39)“Growth of Epitaxial Pb(Zr,Ti)O₃ Thick Films on (100)CaF₂ Substrates with Perfect Polar-axis-orientation and Their Electrical and Mechanical Property Characterization”, Takashi Fujisawa, Hiroshi Nakaki, Rikyu Ikariyama, Mitsumasa Nakajima, Tomoaki Yamada, Mutsuo Ishikawa, Hitoshi Morioka, Takashi Iijima, and Hiroshi Funakubo, *Mater. Res. Soc. Symp. Proc.*, *In press*.

- (40) “Composition dependency of epitaxial $\text{Pb}(\text{Zr,Ti})\text{O}_3$ films with different film thickness”, Shintaro Yokoyama, Hiroshi Funakubo, Hitoshi Morioka, Keisuke Saito, Tomoaki Yamada, and Mutsuo Ishikawa, *Ferroelectrics*, *in press*.
- (41) “Good conformability of indium-tin-oxide thin films prepared by spray chemical vapor deposition”, Takeshi Kondo, Yutaka Sawada, Hiroshi Funakubo, Kensuke Akiyama, Takanori Kiguchi, Meihan Wang Wang, and Takayuki Uchida, *Electrochem. Solid-State Lett.*, *in press*.

2) Review & Book

- (1) “Epitaxially grown ferroelectric thin films for memory applications (ferroelectric random access memories)”, Hiroshi Funakubo, Takahiro Oikawa, Shintaro Yokoyama, Kuniharu Nagashima, Hiroshi Nakaki, Takashi Fujisawa, Rikyu Ikariyama, Shintaro Yasui, Keisuke Saito, Hitoshi Morioka, Hee Han, Sunggi Baik, Yong Kwan Kim, and Toshimasa Suzuki, *Phase Transition*, Vol. 81 (7) (2008) 667 – 678.
- (2) “Recent Development of Thin films of Perovskite Oxide”, Hiroshi Funakubo and Tomoaki Yamada, *Ceramics*, Vol.43 (8) (2008) 634-638
- (3) “Degradation-free Dielectric Property Using Bismuth Layer-structure Dielectrics Having Natural Superlattice Structure”, Hiroshi Funakubo, *J. Ceram. Soc. Jpn.*, 116(12) (2008) 1249-1254.
- (4) “Self-assembled Growth of Ferroelectric-Dielectric Oriented Nanocomposite Films and Their Tunable Properties”, Tomoaki Yamada, Nava Setter, and Hiroshi Funakubo, *Ceramics data Book*, 2008/2009 Vol.36 (90) 2008, pp.37-40
- (5) “Chemical vapor deposition of ferroelectric thin films: a critical review”, Hiroshi Funakubo, Shintaro Yasui, Mutsuo Ishikawa, and Tomoaki Yamada, “Ferroelectric Thin Films at Microwave Frequencies”, *in press*

3. Invited/Plenary Talks in Conference

1) International Conference or Workshop

- (1) H. Funakubo, H. Nakaki, R. Ikariyama, N. Menou, K. Nishida, H. Morioka, K. Saito, K. Fukuda, O. Sakata, and S. Kimura, “Strained-relaxed Novel Domain Structure of Epitaxial $\text{Pb}(\text{Zr,Ti})\text{O}_3$ Thick Films Grown by Metal Organic Chemical Vapor Deposition and Their Contribution to Piezoresponse”, 2008 U.S. Navy Workshop on Acoustic Transduction Materials and Devices, The Penn State Conference Center Hotel, State College, PA, U.S.A., May 13, 2008, III-7.
- (2) Hiroshi Funakubo, Shingo Okaura, Muneyau Suzuki, Hiroshi Uchida, Seiichiro Koda, Rikyu Ikariyama, Tomoaki Yamada, and Minoru Osada “Dielectric Tunability Design in Paraelectric Bi-Zn-Nb-O Pyrochlore Films”, Joint Conferences of the 2nd International Conference on the Science and Technology for Advanced Ceramics (STAC) and The 1st International Conference on Science and Technology of Solid Surface and Interface (STSI), OVTA (Chiba), Japan, May 30, 2008, 1B05, p.117.
- (3) Hiroshi Funakubo, Rikyu Ikariyama, Shintaro Yasui, Tomoaki Yamada, Kobayashi, Kichizo Asai, Keisuke Saito, and Hitoshi Morioka, “Growth of Epitaxial Pyrochlore Conductor for Electronic Film Devices.”, MRS International Materials Research Conference, Chongqing, China, June 11, 2008, F22,1 p252-3.

- (4) Hiroshi Funakubo, Shintaro Yokoyama, Satoshi Okamoto, Tomoaki Yamada, Mutsuo Ishikawa, Hitoshi Morioka, Keisuke Saito, Takashi Iijima, Ken Nishida, Takashi Katoda, Joe Sakai, Takashi Yamamoto, and Hirotake Okino, "Materials Comparison of Piezoelectric Epitaxial Thick Films Grown by MOCVD", 9th European Conference on Application of Polar Dielectrics, Roma, Italy, August 27, 2008, I10, p.65.
- (5) Hiroshi Funakubo, Takayuki Watanabe, Nicolas Menou, and Tomoaki Yamada, "Overview and Future Challenges of Advanced Materials for FeRAM", 2008 International Conference on Solid State Devices and Materials, Tsukuba, Japan, September 26, 2008, J-8-1, p.1154-1155.
- (6) Hiroshi Funakubo, Rikyu Ikariyama, Shintaro Yasui, and Tomoaki Yamada, Keisuke Saito, and Hitoshi Morioka, Tetsuya Kaneko, Yoshihiko Kobayashi, and Kichizo Asai, "Growth of Epitaxial Bi-Zn-Nb-O Pyrochlore Thin films on Epitaxial Pyrochlore Bottom Electrode and Their Electrical Properties", Materials Science & Technology 2008 Conference, PA, U.S.A., October 6, 2008, p.59.
- (7) Hiroshi Funakubo, "Metal-Organic Chemical Vapor Deposition and Property of High Quality Dielectric Thin Films", Materials Science & Technology 2008 Conference, PA, U.S.A., October 7, 2008, p.89. [Richard M. Fulrath Award Lecture]
- (8) Hiroshi Funakubo, Hiroshi Nakaki, Rikyu Ikariyama, Nicolas Menou, Ken Nishida, Minoru Osada, Hitoshi Morioka, Keisuke Saito, Osami Sakata, Kazunori Fukuda, and Shigeru Kimura, "Novel Mechanism for Large Piezoelectric Response Observed in Epitaxial Pb(Zr,Ti)O₃ Thick films", 6th Asian Meeting on Electroceramics(AMEC-6), Tsukuba Japan, Oct. 22-24, 2008, I-1C-02.
- (9) Hiroshi Funakubo, Shintaro Yasui, Keisuke Yazawa, Tomoaki Yamada, Mutsuo Ishikawa and Hiroshi Uchida, "Novel candidate of lead-free piezoelectric materials developed by epitaxial film", Piezo 2009, Electroceramics for End users IV, 1-4 March, 2009, 1, March, Belvedere Hotel, Zakopane, Poland, I02

2) Domestic Conferences

Total 6

4. Patent

Total 10 (Japan, 2008)

5. Award

Total 8 including

- 1) The American Ceramic Society, Richard M. Fulrath Award, "Metal-Organic Chemical Vapor Deposition and Property of High Quality Dielectric Thin Films",
- 2) Tetsu Miyoshi, The 6th Asian meeting on Electroceramics Young Scientist Awards
- 3) Masaki Hirano, The 6th Asian meeting on Electroceramics Young Scientist Award
- 4) Mitsumasa Nakajima, The 6th Asian meeting on Electroceramics Young Scientist Awards
- 5) Takashi Fujisawa, Best Presentation Awards of Master Thesis.

6. Others

Topics presentation in Annual Meeting of Japan Ceramic Society; 1C31L “Growth of Perfectly Polar-axis Oriented Tetragonal PZT Thick Films”: Hiroshi Funakubo, Takashi Fujisawa, Hiroshi Nakaki, Rikyu Ikariyama, Keisuke Saito, and Hitoshi Morioka, 20th March, 2008, 1C31L, p.19