

# Studies of physical properties in BiFeO<sub>3</sub> thin films

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## ABSTRACT

BiFeO<sub>3</sub>(BFO) thin films were grown by radio frequency(RF) magnetron sputter deposition on a (111) SrTiO<sub>3</sub>(STO) substrate., These films were grown with Fe:Bi ratio =1:1.02 of target,, and at different argon environmental pressures and different growth time to grow, the growth of pressure used in the experiments were  $20 \times 10^{-2}$  torr. and  $60 \times 10^{-2}$  torr., the substrate temperature of 600 under the growth of this film. By X-ray diffraction for analysis, observed perpendicular to the films surface of the X-ray diffraction, showing the BFO thin film of STO (111) epitaxial properties , BFO lattice parameter matching (111) peak, the diffraction peak of the angle is  $40^\circ$  , the growth of the BFO film with time will affect the structure, the growth in the relatively long time under the BFO thin film structure will be more obvious, the film growth will significantly affect the pressure structural phase BFO with the mixed phase (Bi<sub>25</sub>FeO<sub>40</sub> , Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>), the growth in the low pressure of the growth of the BFO film with the structure will be better, and also in the mixed phase is relatively good improvement on the film surface analysis using atomic force microscope (AFM) and scanning electron microscopy (SEM) to do measurements, we found that crystallization and surface roughness at a relatively low under the pressure of growth are more favorable, and in the electrical aspects of the I-V curves show only films with Ohmic nature of the relationship, the other part of the activation energy of the film in a relatively high growth under the pressure of a relatively high activation energy. Keywords: magnetron sputter, epitaxial, atomic force (AFM) , scanning electron microscope ( SEM)

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## REFERENCES

【1】張文智，利用射頻磁控濺鍍系統製備BiFeO<sub>3</sub>複鐵式薄膜及相關物性研究，國立成功大學材料及工程學系碩士班，碩士論文，2008。

【2】R. Ramesh, "Thin Film Ferroelectric Materials and Devices", Kluwer Academic, London, Chap1-3,1997. 【3】J.F. Scott, and C.A. Araujo, "Ferroelectric Memory", Science, 246,1400,1989. 【4】B.Price, "Emerging Memories-Technologies a Trend", Kluwer Academic Publishers, 4,2002. 【5】富士通與東京工業大學聯手開發FeRAM的新型材料，電子工程專輯，2006。【6】H.S.Nalwa, "Ferroelectric and dielectric thin films", (Academic press, New York, 2002). 【7】H.Uchida, R.Ueno, H.Nakaki, H.Funakubo and S.Koda, "Ion Modification for Improvement of Insulating and Ferroelectric Properties of BiFeO<sub>3</sub> Thin Films Fabricated By chemical Solution Deposition", J.J.Appl.Phys., 44 (18), L1561-1563, 2005. 【8】M.M.Kumar and V.R.Palkar, "Ferroelectricity in pure BiFeO<sub>3</sub> ceramic", Appl.Phys.Lett.76, 2764 (2000). 【9】C.Michel, "The atomic structure of BiFeO<sub>3</sub>" Solid State Communication 7, 701 (1969). 【10】V.A.Murashov, D.N.Rakov, V.M.Ionov, I.S.Dubenko, Y.U.Titov, Ferroelectric, 162,11, 1994. 【11】Y.F.Popov, A.M.Kadomtseva, G.P.Vorobev, A.K.Zvezdin, "The Nature of Dielectric and Magnetic Properties of BiFeO<sub>3</sub>", Ferroelectrics, 162,135, 1994. 【12】呂正傑，詹世雄，鐵電記憶體簡介，奈米通訊，第五卷第四期(1998)。【13】鄭佩慈，真空技術組，儀器科學中心簡訊，68期，中華民國九十四年4月30日出版。【14】R.J.H.Voorhoeve, Advanced Mate.Catal.; Academic Press: New York (1977)。【15】Y.Xu, "Ferroelectric Materials and their Applications", North Holland, Amsterdam, 1991. 【16】G.shirane, F.Jona, and R.Pepinsky, Proc.I.R.E., 42, 1738 (1955)。【17】J.Wang, "Deposition and Characterization of Multiferroic BiFeO<sub>3</sub> Thin Films".PhD dissertation, University of Maryland,Department of Materials Science and Engineering, 2005. 【18】Kingery, Bowen, uhlmann, 陶瓷材料概論，?園出版社，初版，1988年4月。【19】M.E.Lines and A.M.Glass, "Principles and applications of Ferroelectrics and related materials", (Oxford University, New York, 2001)。【20】B.H.Park, B.S.Kang, S.D.Bu, T.W.Noh,J.Lee and W.Jo, "Lanthanum-substituted bismuth titanate for use in non-volatile memories", Nature 401, 682 (1999)。【21】C.Kittel, "Introduction to solid state physics", 7th ed. (John Wiley & Sons, New York, 1996)。【22】J.A.C.Bland and B.Heinrich, "Ultrathin Magnetic Structure I", Springer-verlag, Chap.3,1994. 【23】M.Barsoum, Fundamentals of ceramics, (McGraw Hill, New York, 1994)。【24】林麗娟，X光繞射原理及其應用，工業材料86期，83年2月。【25】W.D.Kingery, H.KBrown,and D.R.UhLmann, "Introduction to Ceramics", 2nd Ed., John Wiley and Sons, New York, Chper.2, 1976. 【26】M.E.Lines and A.M.Glass, "Principles and application of Ferroelectrics and related materials", Oxford University Press, New York, Chap.2-5, 2001. 【27】S.M.Sze, Physics of Semiconductor Devices, New York:Wiley, 1981. 【28】Y.S.Yang, S.J.Lee, S.H.Kim, B.G.Chae, and M.S.Jang, "Schottky barrier effect in the electronic conduction of Sol-gel derived lead zirconate titanate thin film Capacitors", J.J.Appl.Phys.84[9]5005-5011 (1998)。【29】Stolichnovb and A. Tagantsev, "Space-charge influenced- Injection model for conduction in Pb (ZrxTil-x) O3 thin Films", J.J.Appl.Phys. 84[6]3216-3225 (1998) 【30】K.Y.Yun, M.Noda and M. Okuyama, "Prominent Ferroelectricity of BiFeO<sub>3</sub> thin films prepared by pulsed- Laser deposition", Appl.Phys.Lett 83, 3981 (2003)。【31】F.Kubel and H.Schmid, "Structure of a ferroelectric and Ferroelatic monodomain crystal of the pervskite BiFeO<sub>3</sub>", Actacryst.B46, 698 (1990)。【32】J.M.Moreau and C.Michel, "Ferroelectric BiFeO<sub>3</sub> X-ray and Neutron diffraction study", J.Phys.Chem.Solid 32,1315 (1971)。【33】O.Muller and R.Roy, "The Major Ternary Structural Families", Springer,New York, 1974. 【34】N.N.Krainik, Sov.Phys.8, 654, 1966. 【35】M.I.Morozov, N.A.Lomanova, and V.V.Gusarov. "Specific features of BiFeO<sub>3</sub> formation in a mixture of bismuth (III) and iron (III) oxides".Russian Journal of Gener Chemistry, 73 (11) :1676-1680, 2003.Translated from Zhurnal Obshchei Khimi. 【36】劉純宇，碩士論文，BiFeO<sub>3</sub>鐵電薄膜之製備與特性研究，成功大學材料科學與工程學系，2005。【37】J.Wang, "Deposition and characterization of Multiferroic BiFeO<sub>3</sub> Thin Films".PhD dissertation,University of Maryland,Department of Materials Science and Engineering, 2005. 【38】吳奇錕，鐵酸鈹與鈷鐵氧體之複合材料電性與磁性研究，清華大學材料科學與工程學系，2007。【39】J.R.Teague, R.Gerson, and W.J.James, "Dielectric hysteresis in single crystal", Solid State Comm.12, 1073, 1970. 【40】K.Y.Yun,M.Noda, and M.Okuyama H.SaeKi, H.Tabata.and K.Saito, "Structural and multiferroic properties of BiFeO<sub>3</sub> thin films at room Temperature", J.J.Appl.Phys.96,3399-3403,2004. 【41】Y.P.Wang, L.Zhou, M.F.Zhang, X.Y.Chen, J.M.Liu, and Z.G.Liu, "Room-temperature saturated ferroelectric polarization in BiFeO<sub>3</sub> ceramics synthesized by rapid liquid phase sintering", Appl.Phys. Lett, 84, 1731-1733, 2004. 【42】V.R.Palkar,K.G.Kumara, S.K.Malik, "Observation of room-temperature magnetoelectric coupling in pulsed-laser-deposited Bi<sub>0.6</sub>Tb<sub>0.3</sub>La<sub>0.1</sub>FeO<sub>3</sub> thin films", J.Phys.58, 1003, 2002. 【43】Y.E.Roginskaya, Y.Y.Tomashpol'skiy, Y.N.Venevtsev, V.M.Petrov, and G.S.Zhdanov, "The Nature of the Dielectric and Magnetic Properties of BiFeO<sub>3</sub>", Soviet Phys.JETP, 44, 1418, 1966. 【44】H.S.Gu, J.M.Xue, Gao, J.Wang, "Doping effect of BiFeO<sub>3</sub> in layered Pervoskite SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>", Materials Chemistry and Physics, 75, 105, 2002. 【45】X.Qi, J.Dho, R.Tomov, M.G. Blamire, J.L.MacManus-Driscoll, "Greatly reduced leakage current and conduction mechanism in aliovalent-ion-doped BiFeO<sub>3</sub>" Appl.Phys.Lett.86, 06290 (2005)。【46】B.Ruette, S.Zv yagin, A.P.Pytakov, A.Bush,J.F.Li, V.I.Belotelov, A.K.Zvezdin,and D.Viehland. "Magnetec-field induced phase transition in BiFeO<sub>3</sub> observed by high-Field electron spin resonance":cycloidal to homogenous spin order. Physical Review B,69:064114-1-064114-7,2004. 【47】Gippius,D.F.Khozeev,E.N.Morozova,and V.Zalesky,Phys . stat.sol.196 (1) ,221,2003. 【48】張志嘉，摻雜釷、矽之鐵酸鈹多鐵性薄膜製備與特性之研究，國立成功大學材料及工程學系碩士班，碩士論文，2006。【49】http:web.nchu.edu.tw/~pinlin/ 【50】D.C.Look,Semiconductors and Semimetals edited by R.K. Willardson and A.C.Berr, (Academic,New York,1983)，Vol.19,chap 2. 【51】張耕銘，氧化鋅-氧化鈹複層薄膜之微結構與非歐姆性質之研究，國立成功大學材料及工程學系碩士班，碩士論文，2004