Journal of Nano Research
ISSN: 1661-9897, Vol. 1, pp 59-63
doi:10.4028/www.scientific.net/JNanoR.1.59

Online: 2008-01-01

Orientation Preferred Structures in $BaTiO_3$ Thin Films on Ni Substrates

J.C. Jiang[1,a], E.I. Meletis[1,b], Z. Yuan[2,c], J. Liu[2,d], J. Weaver[2,e], C.L. Chen[2,3,f], B. Lin[4,g], V. Giurgiutiu[4,h], R.Y.Guo[5,i], A.S. Bhalla[5,j], D. Liu[6,k] and K. W. White[6,l]

[1]Department of Material Science and Engineering, University of Texas at Arlington, Arlington, TX 76019 USA

[2]Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, TX 78249 USA

[3]The Texas Center for Superconductivity, University of Houston, TX 77204 USA

[4]Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208 USA

[5]Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802 USA

[6]Department of Mechanical Engineering, University of Houston, TX 77204 USA

[a]jiang@uta.edu (corresponding author), [b]meletis@uta.edu, [c]tresses@gmail.com, [d]jianliu.1@gmail.com, [e]weaver.jenny@gmail.com, [f]cl.chen@utsa.edu, [g]LINBIN@engr.sc.edu, [h]giurgiut@engr.sc.edu, [i]ryguo@psu.edu, [j]abhalla@psu.edu, [k]liuduo@sina.com, [l]kwwhite@uh.edu

[Submitted June 11, 2007]

Keywords: transmission electron microscopy, oxide thin films, Orientation preferred structures, metallic substrate.

Abstract. We report the fabrication of the orientation preferred structures in $BaTiO_3$ thin films on Ni substrates using pulsed laser deposition. Transmission electron microscopy studies showed that the films consist of crystalline structures of tetragonal $BaTiO_3$. More than 60% of $BaTiO_3$ grains in the films exhibit nearly the same crystallographic orientation with their ***a***-axis lying in the film plane and the [011] direction parallel to the growth direction. Such orientation preferred structures were grown on a Ni nanocrystalline buffer layer. This result demonstrated the possibility of approximating an oriented single crystalline ceramic oxide structures on metallic substrates.

Introduction

Ferroelectric $BaTiO_3$ (BTO) has a high dielectric constant, large electro-optic and non-linear optic coefficients and good ferroelectric and piezoelectric properties [1,2,3,4,5]. $BaTiO_3$ thin films have been attracting tremendous interest as promising materials for many device applications such as ferroelectric random access memories, optical modulators and switches, waveguides and microelectromechanical systems (MEMS) [6,7,8,]. The excellent piezoelectric properties of ferroelectric BTO thin films make them great candidates for the development of the unobtrusive piezoelectric wafer active sensor arrays for structural health monitoring [9,10].

BTO thin films have been deposited on various non-metallic substrates, including oxide single crystals and semiconductor substrates, using a variety of techniques such as pulsed laser deposition, hydrothermal methods and metal-organic chemical vapor deposition [3,11,12,13,14,15]. However, deposition of polycrystalline ferroelectric BTO thin films on structural metals such as steel, nickel, aluminum had not been reported until our very recent successful fabrication of BTO thin films directly deposited on Ni, a typical structural material, using pulsed laser deposition [16]. Our achievement opens the real option for the deposition of BTO thin films on structural metals for unobtrusive piezoelectric wafer active sensor arrays for structural health monitoring.

The dielectric and ferroelectric properties of the BTO thin films deposited on MgO were found to strongly depend on the microstructure of the films [4]. The highly orientation-preferred structure may enable tailoring the dielectric constant, charge storage parameters, nonlinear optical susceptibility and refractive index for many applications [17]. In this paper, we report our recent achievements of the fabrication of highly orientation-preferred structures of ferroelectric BTO thin films on Ni substrates.

Experimental

BTO thin film deposition was conducted by using a KrF excimer pulsed laser deposition (PLD) system with a wavelength of 248 nm. A layer of NiO with the thickness of 50 to 80 nm was synthesized via *in-situ* oxidation treatment of the Ni tape in oxygen atmosphere of 300 Torr at 800^{o}C for 3 min. Ferroelectric BTO thin film growth on Ni tape required a laser repetition rate of 5Hz in an oxygen pressure of 300 mTorr at 800^{o}C. The typical growth rate was about 10 nm/min. After film growth, 300 Torr of oxygen was introduced into the deposition chamber for a 10 minute anneal, prior to cooling at 5^{o}C/min to room temperature. For the transmission electron microscopy (TEM) studies, plan-view and cross-section TEM specimens were prepared by mechanical grinding, polishing and dimpling followed by Ar-ion milling. Electron diffraction analysis and dark-field imaging were employed to study the grain orientation of the film.

Results and Discussion

Fig. 1(a) is a bright-field TEM image with an inset of the selected-area electron diffraction (SAED) pattern of a plan-view BTO film showing a crystalline grain structure. The size of the grains in Fig. 1(a) varies from 50 nm to 150 nm in diameter with the majority of the grain size being about 75 nm. The inset SAED pattern clearly shows sharp diffraction spots indicating crystalline structure of the film. Further, the inhomogeneous distribution of spot intensities along the diffraction rings suggests a preferred orientation (texture). It can be found by careful examination that the SAED pattern is a superposition of a polycrystalline diffraction pattern and a single crystal diffraction pattern of the tetragonal BTO (space group P4mm, a=3.992Å and c=4.036 Å). The $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ reflections in the SAED pattern have a lattice spacing of 4.0 Å and 2.84 Å and can be identified as the (100) and (011) reflections of BTO, respectively. The zone axis of this single crystal diffraction pattern is along the $[0\bar{1}1]$ direction of BTO. The ***a***- axis of BTO lies in the film plane, while the ***c***- axis is out of the film plane with an inclination angle of ~45º with respect to the film plane.

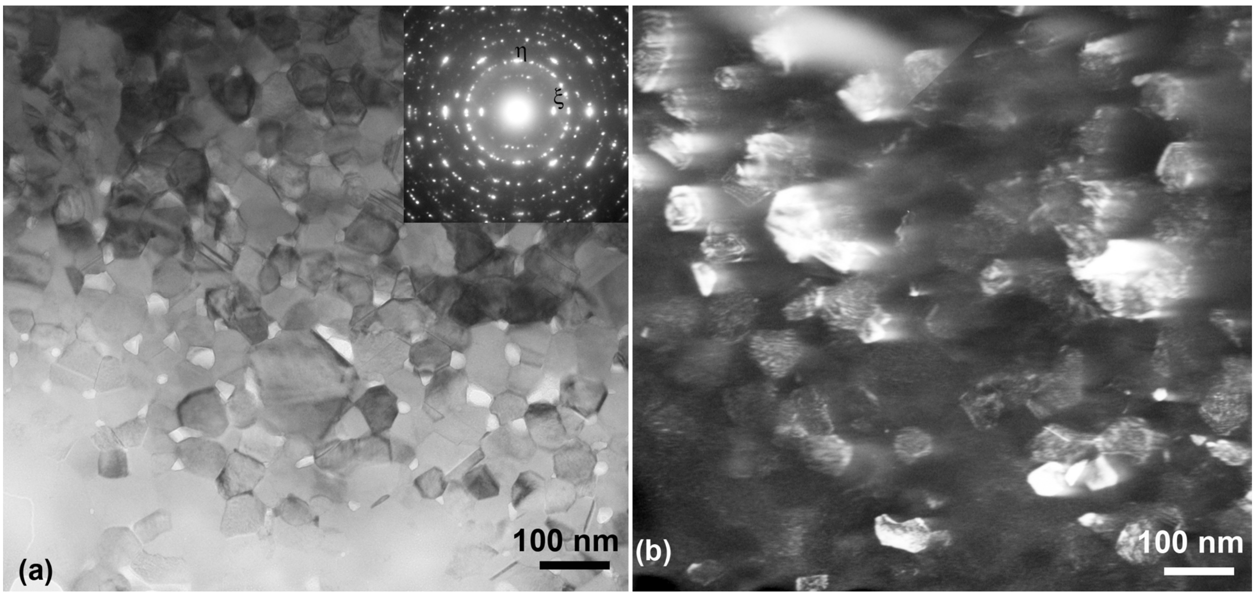

Fig. 1. (a) Plan-view TEM image and SAED pattern (inset) of the BTO film, (b) dark-field image obtained using the reflection ξ in the SAED pattern.

The dark-field micrograph of Fig. 1(b), imaged through the ξ reflection of the SAED pattern, shows nearly the same area as Fig. 1(a). Here, more than 60% of the area shows bright contrast, indicating the common agreement with the ***a***-axis lying in the film plane and the [011] axis perpendicular to the film plane.

Fig. 2(a) is a cross-sectional TEM image showing the interface structure of the BTO films on Ni tapes. The BTO film has a thickness of about 200 nm and consists of nanopillar structures with lateral dimensions of about 100 nm, which is close to the value obtained from the plan-view TEM. The intermediate (IM) layer between the BTO film and Ni substrate shows nanocrystalline structure. Fig. 2(b) is a plan-view TEM image and the SAED pattern (inset) of the IM layer, in which the nanostructures show different characteristics from that shown in Fig. 1(a). The grain size of the nanostructures varies from 30 to 100 nm in diameter and is smaller than that of the BTO grains. The nanostructures in the IM layer were found to be pure Ni (fcc, a=3.52 Å) as identified by the electron diffraction analysis. For example, diffraction rings 1, 2, 3 and 4 have a lattice spacing of 2.03 Å, 1.76 Å, 1.25 Å and 1.06 Å, respectively, which can be identified as the (111), (200), (220) and (311) reflection of Ni.

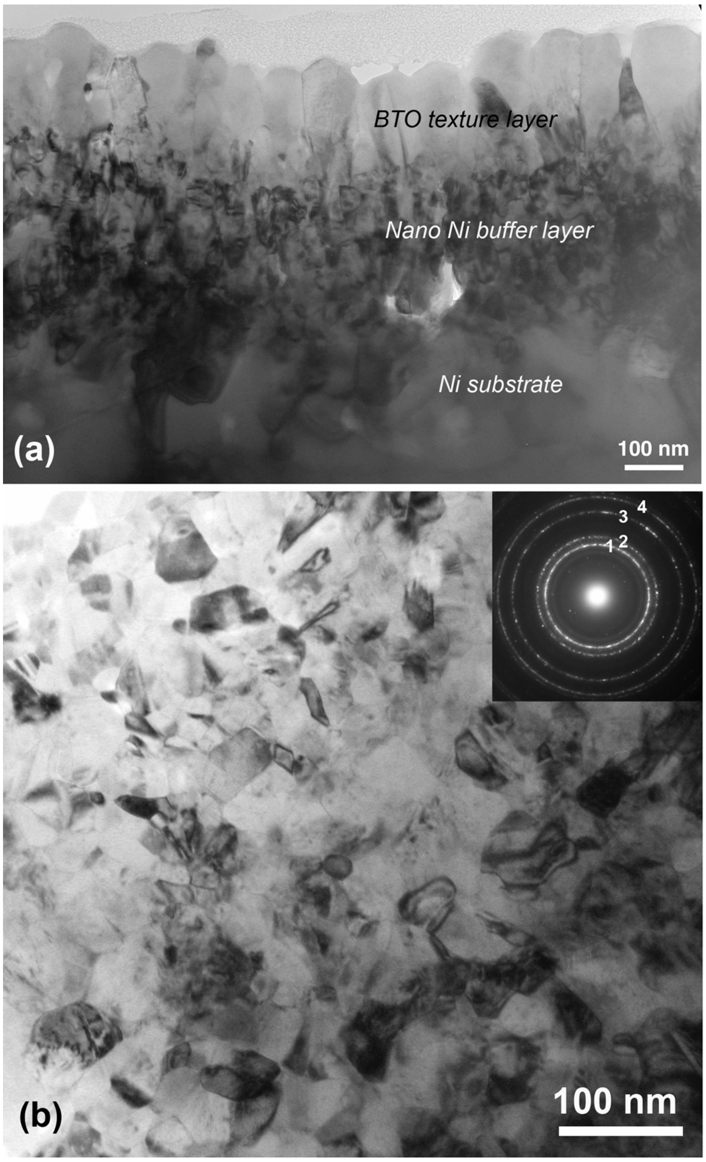

Fig. 2. (a) Cross-sectional TEM of BTO/Ni showing film and interface structure, (b) plan-view TEM image and SAED pattern (inset) of the intermediate layer in (a).

The observation of nanostructured pure Ni intermediate layer is different from the NiO layer that was synthesized prior to the deposition of the BTO films. Such difference can be understood by looking into the entropy and the free energy of BTO and NiO. The NiO has an entropy of -240 $JK^{-1}mol^{-1}$ and a free energy of -212 $JK^{-1}mol^{-1}$, which are higher than the entropy (-1634 $JK^{-1}mol^{-1}$) and free energy (-1529 $JK^{-1}mol^{-1}$) of BTO. Therefore, it can be speculated that during the deposition, oxygen atoms in NiO intermediate layer migrated to the BTO film layer.

We have employed Piezoelectric Response Microscopy (PRM) to study the physical property of such BTO films with preferred orientation. Fig. 3 is a PRM image of such a BTO film. It can be observed that over the 1 μm x 1 μm image, over 60% of the area shows uniform contrast, indicating good alignment of the polarization vectors associated with these nano-sized grains. These results agree well with the dark-field TEM results of Fig. 1(b).

Summary

In conclusion, we have demonstrated feasibility to grow single crystalline oriented structures of ferroelectric and ferromagnetic oxide films on metallic substrates by optimizing the growth

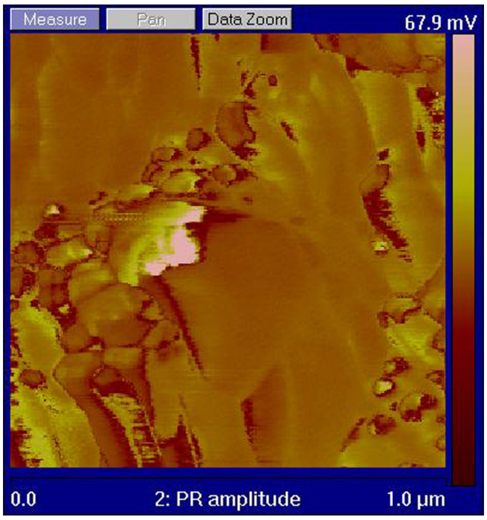

Fig. 3. Piezoelectric Responsive Microscope image of the ferroelectric $BaTiO_3$ thin films on Ni tape with orientation preferred structure.

parameters and conditions, which is of importance both scientifically and technologically. Successful fabrication of orientation-preferred structures of ferroelectric and ferromagnetic oxides on metallic substrates will open ways for the development of new applications by integrating the ceramic oxide devices for promising applications for health monitoring of structural materials. The orientation-preferred structures in ferroelectric BTO thin films have been successfully fabricated on Ni substrates using pulsed laser ablation. The BTO films have nanopillar, crystalline tetragonal structures with a good interface with respect to the substrate. More than 60% BTO grains share a common orientation with their ***a***-axis in the film plane and the [011] direction parallel to the growth direction of the films. Such orientation-preferred nanopillar structures were grown on a layer of nanocrystalline Ni. Successful fabrication of these films on metallic substrates is expected to have significant importance for the development of new applications by integrating the oxides with various promising properties to the structural materials.

Acknowledgement

This work was supported by the National Science Foundation under Award Number NSF/CMS-0528873.

References

[1] K. Iijima, T. Terashima, K. Yamamoto, K. Hirata, Y. Bando, Preparation of ferroelectric $BaTiO_3$ thin films by activated reactive evaporation, Appl. Phys. Lett. 56 (1990) 527-529.

[2] D. Roy, S. B. Krupanidhi, Pulsed excimer laser ablated barium titanate thin films, Appl. Phys. Lett. 61 (1992) 2057-2059.

[3] K. Nashimoto, D.K. Fork, F.A. Ponce, J.C. Tramontana, Epitaxial $BaTiO_3$ MgO structure grown on GaAs(100) by pulsed-laser deposition, Jpn. J. Appl. Phys. 32 (1992) 4099-4102.

[4] H.A. Lu, L.A. Wills, B.W. Wessels, Electrical properties and poling of $BaTiO_3$ thin films, Appl. Phys. Lett. 64 (1994) 2973-2975.

[5] T.M. Shaw, S. Trolier-McKinstry, P.C. McIntyre, The properties of ferroelectric films at small dimensions, Annu. Rev. Mater. Sci. 30 (2000) 263-298.

[6] D.L. Polla, L.F. Francis, Processing and characterization of piezoelectric materials and integration into microelectromechanical systems, Annu. Rev. Mater. Sci. 28 (1998) 563-597.

[7] L.R. Dalton, optical-materials - fresh start for photonics, Nature 359 (1992) 269-270.

[8] P. Muralt, Ferroelectric thin films for micro-sensors and actuators: a review, J. Micromech. Microeng. 10 (2000) 136-146.

[9] B. Fan, G. Song, F. Hussain, Simulation of a piezoelectrically actuated valveless micropump, Smart Materials & Structures 14 (2005) 400-405.

[10] V. Sethi, G. Song, Optimal vibration control of a model frame structure using piezoceramic sensors and actuators, J. Vibration and Control 11 (2005) 671-684.

[11] W. Tian, J.C. Jiang, X.Q. Pan, J.H. Haeni, D.G. Schlom, J.B. Neaton, K.M. Rabe, Structural evidence for enhanced polarization in a commensurate short-period $BaTiO_3/SrTiO_3$ superlattice, Appl. Phys. Lett. 89 (2006) Art. No. 092905.

[12] R. Ramesh, K. Luther, B. Wilkins, D.L. Hart, E. Wang, J. M.Tarascon, A. Inam, X. D. Wu, T. Venkatesan, Epitaxial growth of ferroelectric bismuth titanate thin films by pulsed laser deposition,Appl. Phys. Lett. 57 (1990) 1505-1508.

[13] M. de Keijser, G. J. Dormans, J.F. Cillessen, D.M. de Leeuw, H.W. Zandbergen, Epitaxial $PbTiO_3$ thin films grown by organometallic chemical vapor deposition, Appl. Phys. Lett. 58 (1991) 2636-2638.

[14] G. M. Davis, M.C. Gower, Epitaxial growth of thin films of $BaTiO_3$ using excimer laser ablationAppl. Phys. Lett. 55 (1989) 112-114.

[15] K. Kajiyoshi, N. Ishizawa, M. Yoshimura, Heteroepitaxial growth of $BaTiO_3$ thin-films on $SrTiO_3$ substrates under hydrothermal conditions, Jpn. J. Appl. Phys. 30 (1991) L120-L123.

[16] Z. Yuan, J. Liu, J. Weaver, C. L. Chen, J. C. Jiang, B. Lin, V. Giurgiutiu, A. Bhalla, R. Y. Guo, Ferroelectric $BaTiO_3$ thin films on Ni metal tapes using NiO as buffer layer, Appl. Phys. Lett. 90 (2007) Art. No.202901.

[17] H.A. Lu, L.A. Wills, B.W. Wessels, W.P. Lin, G.K. Wong, Electronic beam induced poling of $BaTiO_3$ thin films, Appl. Phys. Lett. 63 (1993) 874-876.