Adsorption-controlled growth of $\mathrm{BiMnO_3}$ films by molecular-beam epitaxy

J. H. Lee, X. Ke, R. Misra, J. F. Ihlefeld, X. S. Xu, Z. G. Mei, T. Heeg, M. Roeckerath, J. Schubert, Z. K. Liu, J. L. Musfeldt, P. Schiffer, and D. G. Schlom

Citation: Appl. Phys. Lett. **96**, 262905 (2010); doi: 10.1063/1.3457786
View online: https://doi.org/10.1063/1.3457786
View Table of Contents: http://aip.scitation.org/toc/apl/96/26
Published by the American Institute of Physics

APPLIED PHYSICS LETTERS **96**, 262905 (2010)

Adsorption-controlled growth of $BiMnO_3$ films by molecular-beam epitaxy

J. H. Lee,[1,2] X. Ke,[3] R. Misra,[3] J. F. Ihlefeld,[2] X. S. Xu,[4] Z. G. Mei,[2] T. Heeg,[1]
M. Roeckerath,[5] J. Schubert,[5] Z. K. Liu,[2] J. L. Musfeldt,[4] P. Schiffer,[3] and D. G. Schlom[1,a)]
[1]*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA*
[2]*Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[3]*Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[4]*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA*
[5]*Institute of Bio- and Nano-Systems (IBN1-IT), JARA-Fundamentals of Future Information Technology, Research Centre Jülich, D-52425 Jülich, Germany*

(Received 20 February 2010; accepted 4 June 2010; published online 2 July 2010)

We have developed the means to grow $BiMnO_3$ thin films with unparalleled structural perfection by reactive molecular-beam epitaxy and determined its band gap. Film growth occurs in an adsorption-controlled growth regime. Within this growth window bounded by oxygen pressure and substrate temperature at a fixed bismuth overpressure, single-phase films of the metastable perovskite $BiMnO_3$ may be grown by epitaxial stabilization. X-ray diffraction reveals phase-pure and epitaxial films with ω rocking curve full width at half maximum values as narrow as 11 arc sec (0.003°). Optical absorption measurements reveal that $BiMnO_3$ has a direct band gap of 1.1 ± 0.1 eV. © *2010 American Institute of Physics*. [doi:10.1063/1.3457786]

Multiferroic materials are being studied for their rich properties, fascinating physics, and application potential.[1] Bismuth manganite, $BiMnO_3$, is a well-known, but controversial multiferroic. Early first-principles calculations suggested that $BiMnO_3$ might be simultaneously ferroelectric and ferromagnetic, arising from bismuth 6*s* lone pairs and magnetic ordering of manganese.[2] Subsequent experiments confirmed multiferroism in thin films.[3–5] The prediction of its ferroelectricity was based on the reported noncentrosymmetric *C*2 space group of $BiMnO_3$.[6–8] Recent calculations and experiments, however, find that $BiMnO_3$ belongs to the centrosymmetric *C*2/*c* space group and therefore stoichiometric $BiMnO_3$ may not be a multiferroic at all.[9,10]

To better establish the properties of $BiMnO_3$, we have grown films of it by reactive molecular-beam epitaxy (MBE) using adsorption-controlled growth conditions. Adsorption-controlled growth conditions are the standard way of growing phase-pure compound semiconductors;[11] it has also been applied to the growth of ferroelectric oxide thin films.[12,13] In this letter, we first describe the adsorption-controlled growth of single phase $BiMnO_3$ films by controlling bismuth overpressure, substrate temperature, and oxidant partial pressure. The ferromagnetic properties and optical absorption spectrum of the grown films are then reported.

The pressure-temperature region for the adsorption-controlled growth of $BiMnO_3$ was calculated using the CALPHAD approach.[14] It was empirically established using *in situ* reflection high-energy electron diffraction (RHEED) and confirmed by *ex situ* four circle x-ray diffraction (XRD). Figure 1 shows a calculated Ellingham diagram representing the phase stability regions of (I) $BiMnO_3+Mn_3O_4$, (II) $BiMnO_3$, and (III) $BiMnO_3+Bi_2O_{2.5}$ as a function of substrate temperature and O_2 overpressure. The boundaries between regions I, II, and III were calculated with the Gibbs free energy functions of the gas phase containing various bismuth and Bi–O species and the stable and metastable manganese and bismuth oxides.[15] Unfortunately there is no Gibbs free energy of formation reported for $BiMnO_3$ or $Bi_2O_{2.5}$. First-principles calculations, using the generalized gradient approximation (GGA) and GGA plus Hubbard *U* (GGA+*U*) method, predicted the enthalpy of formation of $BiMnO_3$ to be between +400 J/mol and +4000 J/mol of $BiMnO_3$ with respect to Bi_2O_3 and Mn_2O_3, respectively.[16] Since there is no detailed crystal structure of $Bi_2O_{2.5}$ available for first-principles calculations, we assume its enthalpy of formation to be +100 J/mol or +4500 J/mol with respect to bismuth and Bi_2O_3, as assumed in Ref. 13. The phase stability region was calculated using THERMOCALC[17] with the partial pressure of bismuth fixed at 2.6×10^{-10} atm, which

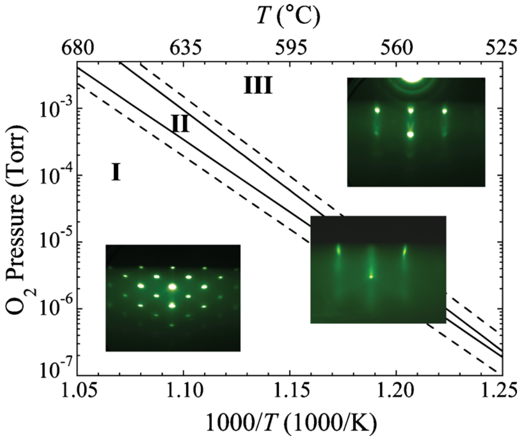

FIG. 1. (Color online) Calculated Ellingham diagram and RHEED patterns collected along the [110] azimuth of $SrTiO_3$ during the deposition of $BiMnO_3$ at different temperatures and oxygen partial pressures. Solid lines represent phase boundaries using +4000 J/mol and +100 J/mol formula unit Gibbs free energies for $BiMnO_3$ and $Bi_2O_{2.5}$, respectively, specifying the narrowest growth window possible. Dashed lines are for +400 J/mol and +4500 J/mol formula unit, indicating the approximate uncertainty in width of the growth window. Phase stability between Bi_xO_y gases and $BiMnO_3+Mn_3O_4$, $BiMnO_3$, and $BiMnO_3+Bi_2O_{2.5}$ condensed phases is represented by regions I, II, and III, respectively.

[a)] Electronic mail: schlom@cornell.edu.

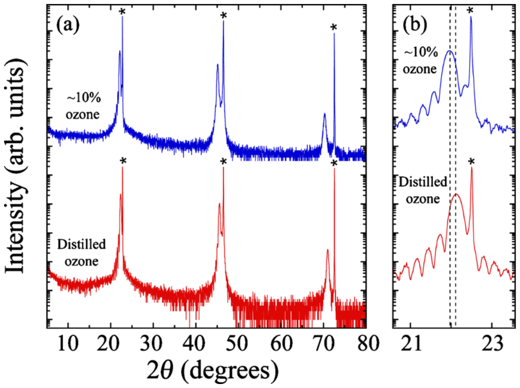

FIG. 2. (Color online) (a) θ-2θ XRD scans of $BiMnO_3$ films grown on (001) $SrTiO_3$ at an oxidant background pressure of 1×10^{-6} Torr and the 3:1 Bi:Mn flux ratio stated above. The difference was that one film was grown in ~10% ozone directly out of an ozone generator at $T_{sub}=590$ °C whereas the other was grown using distilled ozone (~80% ozone) at $T_{sub}=630$ °C. Substrate peaks are marked with an asterisk . (b) A close-up of the 001 peak, showing a clear difference in the out-of-plane lattice constant.

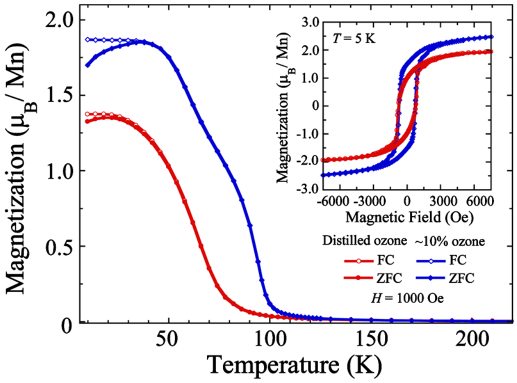

FIG. 3. (Color online) Field-cooled and zero field-cooled magnetization of the same $BiMnO_3$ films as Fig. 2 grown using ~10% ozone and distilled ozone. (Inset) Magnetic hysteresis of these films at 5 K.

corresponds to the pressure at the plane of the substrate for an incident bismuth flux of 5.5×10^{13} atom/(cm^2 s).[18]

$BiMnO_3$ thin films were deposited on buffered-HF treated (001) $SrTiO_3$ (Ref. 19) and (110) $DyScO_3$ substrates in a similar manner to previous adsorption-controlled oxides by MBE.[12,13] The volatile bismuth and oxygen components were supplied continuously and the nonvolatile component (manganese) was supplied in doses corresponding to individual (MnO_2) monolayers making up the $BiO-MnO_2-BiO-MnO_2-\cdots$ stacking sequence along the [001] pseudocubic growth direction of the $BiMnO_3$ perovskite structure. Due to the narrow growth window for phase-pure $BiMnO_3$ growth (region II in Fig. 1), the substrate temperature was monitored *in situ* by measuring the absorption edge of the $SrTiO_3$ substrate.[20] The thermodynamic predictions were verified by investigating a horizontal slice through Fig. 1 at constant bismuth [bismuth flux$=5.5\times10^{13}$ Bi/(cm^2 s)] and oxygen ($O_2+\sim10\%$ O_3 background pressure$=1\times10^{-6}$ Torr) overpressure during the deposition of Bi–Mn–O over a temperature range of 580–690 °C and a fixed Bi:Mn flux ratio of 3:1. The *in situ* RHEED patterns collected along the ⟨110⟩ azimuthal direction of (001)-oriented $SrTiO_3$ delineating the three regions are superimposed in Fig. 1. Above 650 °C (region I), RHEED spots are observed and can be indexed to diffraction from (101)-oriented Mn_3O_4. The presence of this phase was verified by *ex situ* XRD. Between 610 and 640 °C (region II), phase-pure $BiMnO_3$ can be grown. Below 610 °C (region III), additional spots form, which can be indexed by *ex situ* XRD as (001)-and (110)-oriented $Bi_2O_{2.5}$. The occurrence of these spots corresponds to the phase boundary separating region II and III. A change in bismuth flux or oxygen activity results in a shift in the growth window of single-phase $BiMnO_3$ (region II in Fig. 1). The calculated O_2 overpressures compare well with what is expected given the enhanced activity of O_3 and our directed gas inlet that locally increases the oxygen pressure at the substrate surface.[18]

The structure of two 29 nm thick $BiMnO_3$ films deposited on (001) $SrTiO_3$ was characterized. Both films were grown under adsorption-controlled conditions (region II in Fig. 1). θ-2θ XRD scans of both films in Fig. 2(a) reveal them to be phase-pure and epitaxial. The full width at half maximum (FWHM) of the ω rocking curve of the pseudocubic 002 film peaks are equal to 80 arc sec (0.02°) and 36 arc sec (0.01°), which are the same as the underlying $SrTiO_3$ substrates. Both films show clear thickness fringes [Fig. 2(b)], corresponding to a film thickness of 29 ± 2 nm. The out-of-plane lattice constant was calculated to be 4.01 ± 0.01 Å for the $BiMnO_3$ films grown in ~10% ozone and 3.98 ± 0.01 Å for the film grown in distilled ozone. The extended out-of-plane lattice constants result from the lattice mismatch between the $SrTiO_3$ substrate ($a=3.905$ Å) and the $BiMnO_3$ film ($a_{pseudocubic}=3.95$ Å).[10] The ~0.03 Å difference in out-of-lattice constants between the two samples is a result of the different oxidating atmosphere during growth. The films grown in ~10% ozone show a longer lattice constant than the films grown in distilled ozone. Rutherford backscattering spectrometry confirms that the ratio of Bi:Mn of these films is 1:1 within the 5% experimental error of the measurements.

Magnetic measurements on the same two $BiMnO_3$ films are shown in Fig. 3. Both films exhibit clear ferromagnetic hysteresis loops. The oxygen-rich films tend to show lower T_C and saturation magnetization than the oxygen-stoichiometric films. $BiMnO_3$ films grown in ~10% ozone showed a ferromagnetic transition at ~105 K, which is close to T_C of bulk $BiMnO_3$, and a magnetization value of 2.5 μ_B/Mn at 5 K. In contrast, films grown in distilled ozone showed a T_C at ~95 K and a magnetization value of 1.9 μ_B/Mn at 5 K. A depression of T_C has been reported in films grown by pulsed-laser deposition.[3,21] We attribute it to oxygen stoichiometry since the Bi:Mn ratio was observed not to influence the transition temperature. Measurements on bulk $BiMnO_{3+x}$ ($0<x<0.16$) samples also observed this depression of T_C and magnetization in samples with higher oxygen content.[10]

The optical spectra of $BiMnO_3$ films were measured in transmittance using a Perkin–Elmer Lambda-900 spectrometer (3000–190 nm and 0.41–6.53 eV) with bare substrates as references. The film on $DyScO_3$ had a rocking curve FWHM of 11 arc sec (0.003°), comparable to the underlying $DyScO_3$ substrate and over 100× narrower than any reported $BiMnO_3$ film.[3–5] Absorption was calculated as $\alpha(E)=-(1/d)\ln[T(E)]$, where d is the film thickness, T is the measured transmittance, and E is the energy of the light.

Figure 4 displays the absorption spectrum of $BiMnO_3$ at 300 and 4 K. The onset of optical absorption in $BiMnO_3$ is ~0.75 eV (1650 nm),[22] much lower than the ~2.2 eV

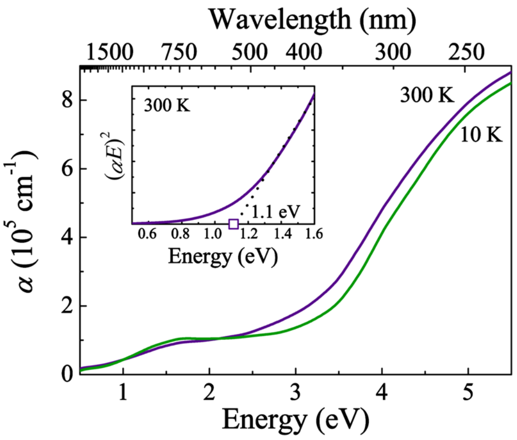

FIG. 4. (Color online) Optical absorption spectrum of 33 nm thick $BiMnO_3$ films grown on (001) $SrTiO_3$ and (110) $DyScO_3$ at $T_{sub}=640$ °C in a background pressure of 1×10^{-6} Torr of distilled ozone were combined to create a composite absorption curve and were identical in the overlap regime. (Inset) Charge gap extraction from 300 K absorption.

(560 nm) onset in $BiFeO_3$ thin films.[13,23,24] Peaks occur at ~1.6 eV (780 nm) and ~5.5 eV (230 nm), with a broad shoulder near 4 eV. The near-infrared feature in perovskite manganites has been studied extensively.[25–28] Relevant predictions from first-principles electronic structure calculations for $BiMnO_3$ include strong Mn–O hybridization, a stereochemically active Bi lone pair that mixes Bi and O states, and insulating behavior in calculations that employ strong exchange correlation.[2,9,29,30] Several very different assignments might reasonably account for the 1.6 eV near infrared excitation in $BiMnO_3$: (i) on-site excitations between crystal field split 3*d* levels, (ii) charge transfer excitations involving strongly hybridized Mn^{3+} and oxygen states, or (iii) transitions between localized Hubbard bands. Based upon comparison with electronic structure calculations,[2,9,23,30] the experimental spectrum of chemically similar materials with Mn^{3+} centers in locally distorted octahedral environments such as $LaMnO_3$,[25–28] and the overall intensity ($\alpha\sim1.05\times10^{-5}$ cm^{-1}), we assign the near infrared peak at ~1.6 eV to charge transfer excitations between mixed O 2*p* and Mn 3*d* states. The limited temperature dependence of the 1.6 eV structure supports this assignment. A plot of $(\alpha E)^2$ versus energy (inset, Fig. 4) places the 300 K charge gap in $BiMnO_3$ at $\sim1.1\pm0.1$ eV.[22] Our fitting indicates that $BiMnO_3$ has a direct band gap. The relatively small direct band gap of $BiMnO_3$ could be relevant to ferroelectric solar cell applications, e.g., creating a solid solution with $BiFeO_3$ with $E_g=2.7$ eV (Refs. 13, 23, and 24) could result in a band gap ideally matched to the solar spectrum.

According to electronic structure calculations,[30] the charge excitations are predicted to be strongly spin polarized. The gap is determined by majority carriers, and minority states are involved only above 3 eV. Higher energy excitations [above 3.7 eV (330 nm)] are assigned as O 2*p* → Mn 3*d* charge transfer, with some mixing of Bi 6*p* levels above 3 eV. The aforementioned electronic excitations sharpen and blueshift slightly with decreasing temperature (Fig. 4). We find no obvious anomalies at the 105 K Curie temperature within our sensitivity, indicative of modest charge-spin interactions.

We gratefully acknowledge the financial support from the National Science Foundation through Grant No. DMR-0507146 and the MRSEC program (Grant No. DMR-0820404) and from the U.S. DOE through Grant No. DE-FG02-01-ER45885(UT).

[1] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[2] N. A. Hill and K. M. Rabe, Phys. Rev. B **59**, 8759 (1999).
[3] A. Moreira dos Santos, A. K. Cheetham, W. Tian, X. Pan, Y. Jia, N. Murphy, J. Lettieri, and D. G. Schlom, Appl. Phys. Lett. **84**, 91 (2004).
[4] A. Sharan, J. Lettieri, Y. Jia, W. Tian, X. Pan, D. G. Schlom, and V. Gopalan, Phys. Rev. B **69**, 214109 (2004).
[5] J. Y. Son and Y.-H. Shin, Appl. Phys. Lett. **93**, 062902 (2008).
[6] T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, and Y. Syono, J. Solid State Chem. **145**, 639 (1999).
[7] A. Moreira dos Santos, A. K. Cheetham, T. Atou, Y. Syono, Y. Yamaguchi, K. Ohoyama, H. Chiba, and C. N. R. Rao, Phys. Rev. B **66**, 064425 (2002).
[8] K. Kodama, S. Iikubo, S. Shamoto, A. A. Belik, and E. Takayama-Muromachi, J. Phys. Soc. Jpn. **76**, 124605 (2007).
[9] P. Baettig, R. Seshadri, and N. A. Spaldin, J. Am. Chem. Soc. **129**, 9854 (2007).
[10] A. A. Belik, T. Kolodiazhnyi, K. Kosuda, and E. Takayama-Muromachi, J. Mater. Chem. **19**, 1593 (2009).
[11] J. Y. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic, Boston, 1993).
[12] D. G. Schlom, J. H. Haeni, J. Lettieri, C. D. Theis, W. Tian, J. C. Jiang, and X. Q. Pan, Mater. Sci. Eng., B **87**, 282 (2001).
[13] J. F. Ihlefeld, N. J. Podraza, Z. K. Liu, R. C. Rai, X. Xu, T. Heeg, Y. B. Chen, J. Li, R. W. Collins, J. L. Musfeldt, X. Q. Pan, J. Schubert, R. Ramesh, and D. G. Schlom, Appl. Phys. Lett. **92**, 142908 (2008).
[14] L. Kaufman, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **25**, 141 (2001).
[15] Scientific Group Thermodata Europe, in *Thermodynamic Properties of Inorganic Materials*, Landolt-Börnstein, New Series, Group IV Vol. 19, edited by Lehrstuhl für Theoretische Hüttenkunde (Springer, Berlin, 1999).
[16] Z. G. Mei, S. Shang, Y. Wang, D. G. Schlom, and Z. K. Liu (unpublished).
[17] J. O. Andersson, T. Helander, L. H. Hoglund, P. F. Shi, and B. Sundman, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **26**, 273 (2002).
[18] D. G. Schlom and J. S. J. Harris, in *Molecular Beam Epitaxy: Applications to Key Materials*, edited by R. F. C. Farrow (Noyes, Park Ridge, NJ, 1995), pp. 505–622.
[19] G. Koster, B. L. Kropman, G. Rijnders, D. H. A. Blank, and H. Rogalla, Appl. Phys. Lett. **73**, 2920 (1998).
[20] kSA BandiT, k-Space Associates, Ann Arbor, MI.
[21] S. Fujino, M. Murakami, S.-H. Lim, L. G. Salamanca-Riba, M. Wuttig, and I. Takeuchi, J. Appl. Phys. **101**, 013903 (2007).
[22] The ±0.1 eV error bars on the gap and the background absorption in $BiMnO_3$ come from the small film thickness (and the associated challenges in growing $BiMnO_3$ films with thicknesses >33 nm). Fortunately, they do not obscure the most important physics.
[23] S. R. Basu, L. W. Martin, Y. H. Chu, M. Gajek, R. Ramesh, R. C. Rai, X. Xu, and J. L. Musfeldt, Appl. Phys. Lett. **92**, 091905 (2008).
[24] A. Kumar, R. C. Rai, N. J. Podraza, S. Denev, M. Ramirez, Y.-H. Chu, L. W. Martin, J. Ihlefeld, T. Heeg, J. Schubert, D. G. Schlom, J. Orenstein, R. Ramesh, R. W. Collins, J. L. Musfeldt, and V. Gopalan, Appl. Phys. Lett. **92**, 121915 (2008).
[25] K. Tobe, T. Kimura, Y. Okimoto, and Y. Tokura, Phys. Rev. B **64**, 184421 (2001).
[26] M. A. Quijada, J. R. Simpson, L. Vasiliu-Doloc, J. W. Lynn, H. D. Drew, Y. M. Mukocskii, and S. G. Karabashev, Phys. Rev. B **64**, 224426 (2001).
[27] M. W. Kim, P. Murugavel, S. Parashar, J. S. Lee, and T. W. Noh, New J. Phys. **6**, 156 (2004).
[28] N. N. Kovaleva, A. V. Boris, C. Bernhard, A. Kulakov, A. Pimenov, A. M. Balbashov, G. Khaliullin, and B. Keimer, Phys. Rev. Lett. **93**, 147204 (2004).
[29] R. Seshadri and N. A. Hill, Chem. Mater. **13**, 2892 (2001).
[30] P. Baettig, R. Seshadri, and N. A. Spaldin, private communication (September 26, 2008).