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Adsorption-controlled growth of BiMnO₃ films by molecular-beam epitaxy

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We have developed the means to grow BiMnO₃ 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 BiMnO₃ 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 BiMnO₃ 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, BiMnO₃, is a well-known, but controversial multiferroic. Early first-principles calculations suggested that BiMnO₃ might be simultaneously ferroelectric and ferromagnetic, arising from bismuth 6s 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 C2 space group of BiMnO₃.^{6–8} Recent calculations and experiments, however, find that BiMnO₃ belongs to the centrosymmetric C2/c space group and therefore stoichiometric BiMnO₃ may not be a multiferroic at all.^{9,10}

To better establish the properties of BiMnO₃, 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 BiMnO₃ 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 BiMnO₃ 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) BiMnO₃+Mn₂O₃, (II) BiMnO₃, and (III) BiMnO₃+Bi₂O_{2.5} as a function of substrate temperature and O₂ 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 BiMnO₃ or Bi₂O_{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 BiMnO₃ to be between +400 J/mol and +4000 J/mol of BiMnO₃ with respect to Bi₂O₃ and Mn₂O₃, respectively.¹⁶ Since there is no detailed crystal structure of Bi₂O_{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 Bi₂O₃, as assumed in Ref. 13. The phase stability region was calculated using THERMOCALC¹⁷ with the partial pressure of bismuth fixed at 2.6×10^{-10} atm, which

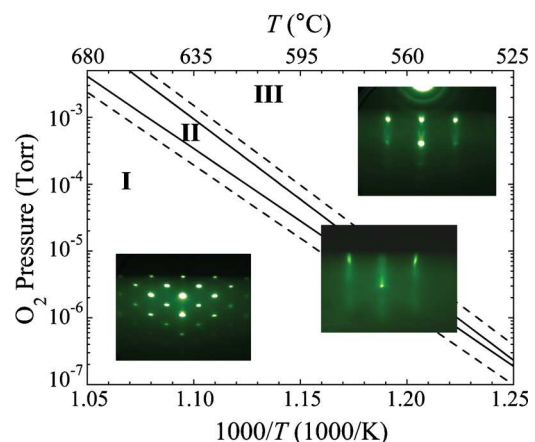


FIG. 1. (Color online) Calculated Ellingham diagram and RHEED patterns collected along the [110] azimuth of SrTiO₃ during the deposition of BiMnO₃ at different temperatures and oxygen partial pressures. Solid lines represent phase boundaries using +4000 J/mol and +100 J/mol formula unit Gibbs free energies for BiMnO₃ and Bi₂O_{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 BiMnO₃+Mn₂O₃, BiMnO₃, and BiMnO₃+Bi₂O_{2.5} condensed phases is represented by regions I, II, and III, respectively.

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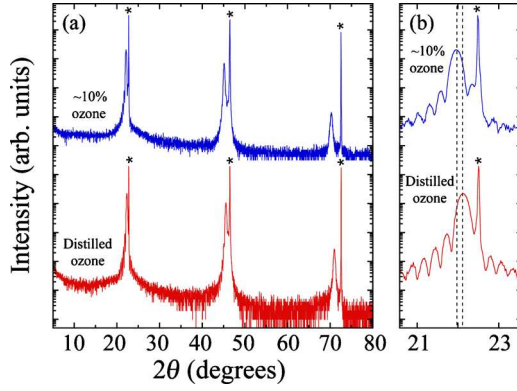


FIG. 2. (Color online) (a) θ - 2θ XRD scans of BiMnO₃ films grown on (001) SrTiO₃ at an oxidant background pressure of 1×10^{-6} Torr and the 3:1 Bi:Mn flux ratio stated above. The difference was that one film was grown in $\sim 10\%$ ozone directly out of an ozone generator at $T_{\text{sub}} = 590^\circ\text{C}$ whereas the other was grown using distilled ozone ($\sim 80\%$ ozone) at $T_{\text{sub}} = 630^\circ\text{C}$. 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.

corresponds to the pressure at the plane of the substrate for an incident bismuth flux of 5.5×10^{13} atom/(cm² s).¹⁸

BiMnO₃ thin films were deposited on buffered-HF treated (001) SrTiO₃ (Ref. 19) and (110) DyScO₃ 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 (MnO₂) monolayers making up the BiO–MnO₂–BiO–MnO₂–... stacking sequence along the [001] pseudocubic growth direction of the BiMnO₃ perovskite structure. Due to the narrow growth window for phase-pure BiMnO₃ growth (region II in Fig. 1), the substrate temperature was monitored *in situ* by measuring the absorption edge of the SrTiO₃ substrate.²⁰ The thermodynamic predictions were verified by investigating a horizontal slice through Fig. 1 at constant bismuth [bismuth flux = 5.5×10^{13} Bi/(cm² s)] and oxygen (O₂ + $\sim 10\%$ O₃ background pressure = 1×10^{-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 $\langle 110 \rangle$ azimuthal direction of (001)-oriented SrTiO₃ 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 Mn₃O₄. The presence of this phase was verified by *ex situ* XRD. Between 610 and 640 °C (region II), phase-pure BiMnO₃ can be grown. Below 610 °C (region III), additional spots form, which can be indexed by *ex situ* XRD as (001)- and (110)-oriented Bi₂O_{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 BiMnO₃ (region II in Fig. 1). The calculated O₂ overpressures compare well with what is expected given the enhanced activity of O₃ and our directed gas inlet that locally increases the oxygen pressure at the substrate surface.¹⁸

The structure of two 29 nm thick BiMnO₃ films deposited on (001) SrTiO₃ 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

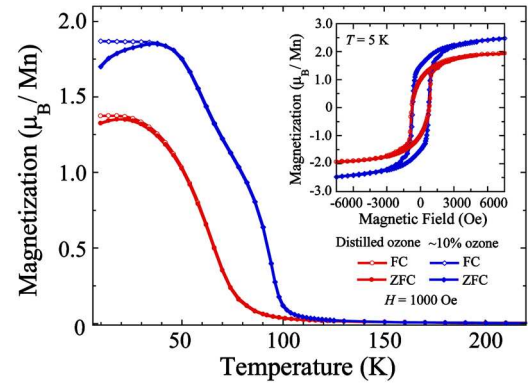


FIG. 3. (Color online) Field-cooled and zero field-cooled magnetization of the same BiMnO₃ films as Fig. 2 grown using $\sim 10\%$ ozone and distilled ozone. (Inset) Magnetic hysteresis of these films at 5 K.

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 SrTiO₃ 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 BiMnO₃ films grown in $\sim 10\%$ 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 SrTiO₃ substrate ($a = 3.905$ Å) and the BiMnO₃ film ($a_{\text{pseudocubic}} = 3.95$ Å).¹⁰ The ~ 0.03 Å difference in out-of-lattice constants between the two samples is a result of the different oxidizing atmosphere during growth. The films grown in $\sim 10\%$ 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 BiMnO₃ 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. BiMnO₃ films grown in $\sim 10\%$ ozone showed a ferromagnetic transition at ~ 105 K, which is close to T_C of bulk BiMnO₃, and a magnetization value of $2.5 \mu_B/\text{Mn}$ at 5 K. In contrast, films grown in distilled ozone showed a T_C at ~ 95 K and a magnetization value of $1.9 \mu_B/\text{Mn}$ 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 BiMnO₃ 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 DyScO₃ had a rocking curve FWHM of 11 arc sec (0.003°), comparable to the underlying DyScO₃ substrate and over $100\times$ narrower than any reported BiMnO₃ 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 BiMnO₃ at 300 and 4 K. The onset of optical absorption in BiMnO₃ is ~ 0.75 eV (1650 nm),²² much lower than the ~ 2.2 eV

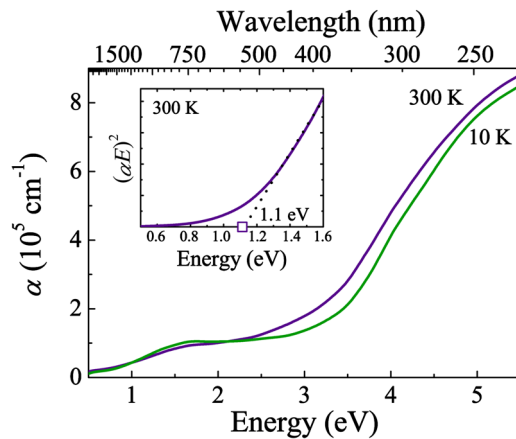


FIG. 4. (Color online) Optical absorption spectrum of 33 nm thick BiMnO₃ films grown on (001) SrTiO₃ and (110) DyScO₃ at $T_{\text{sub}}=640^\circ\text{C}$ in a background pressure of 1×10^{-6} Torr of distilled ozone were combined to create a composite absorption curve and were identical in the overlap regime. (Inset) Charge gap extraction from 300 K absorption.

(560 nm) onset in BiFeO₃ 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 BiMnO₃ 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 BiMnO₃: (i) on-site excitations between crystal field split 3d levels, (ii) charge transfer excitations involving strongly hybridized Mn³⁺ 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 Mn³⁺ centers in locally distorted octahedral environments such as LaMnO₃,^{25–28} and the overall intensity ($\alpha \sim 1.05 \times 10^{-5} \text{ cm}^{-1}$), we assign the near infrared peak at ~ 1.6 eV to charge transfer excitations between mixed O 2p and Mn 3d 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 BiMnO₃ at $\sim 1.1 \pm 0.1$ eV.²² Our fitting indicates that BiMnO₃ has a direct band gap. The relatively small direct band gap of BiMnO₃ could be relevant to ferroelectric solar cell applications, e.g., creating a solid solution with BiFeO₃ 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 2p $\rightarrow$ Mn 3d charge transfer, with some mixing of Bi 6p 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.

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