



## Exploiting kinetics and thermodynamics to grow phase-pure complex oxides by molecular-beam epitaxy under continuous codeposition

Eva H. Smith,<sup>1,\*</sup> Jon F. Ihlefeld,<sup>2</sup> Colin A. Heikes,<sup>1,†</sup> Hanjong Paik,<sup>1</sup> Yuefeng Nie,<sup>1,‡</sup> Carolina Adamo,<sup>3</sup> Tassilo Heeg,<sup>4</sup> Zi-Kui Liu,<sup>5</sup> and Darrell G. Schlom<sup>1,6,§</sup>

<sup>1</sup>*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA*

<sup>2</sup>*Department of Materials Science and Engineering and Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*

<sup>3</sup>*Department of Applied Physics, Stanford University, Stanford, California 94305, USA*

<sup>4</sup>*Heeg Vacuum Engineering, Kerpen, Germany*

<sup>5</sup>*Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*

<sup>6</sup>*Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA*

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We report the growth of PbTiO<sub>3</sub> thin films by molecular-beam epitaxy utilizing continuous codeposition. In addition to the requirements from thermodynamics, whether the resulting film is single-phase PbTiO<sub>3</sub> or not at a particular temperature depends strongly on the film growth rate and the incident fluxes of all species, including titanium. We develop a simple theory for the kinetics of lead oxidation on the growing film surface and find that it qualitatively explains the manner in which the adsorption-controlled growth window of PbTiO<sub>3</sub> depends on lead flux, oxidant flux, and titanium flux. We successfully apply the kinetic theory to the dependence of the growth of BiFeO<sub>3</sub> on oxidant type and surmise that the theory may be generally applicable to the adsorption-controlled growth of complex oxides by MBE.

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### I. INTRODUCTION

Reactive molecular-beam epitaxy (MBE) is unique in its ability to grow high-quality films with atomically sharp interfaces and high crystalline quality, including (and especially) materials that do not exist in nature [1]. Component elements are generally deposited on a substrate starting from single-element sources as low-energy molecular beams; multicomponent materials, including heterostructures, may be deposited layer by layer. The layer-by-layer growth regime gives the grower a high degree of control, with film composition and structure being directed by the user with atomic layer precision. The ability to deposit precise monolayers via shuttering of the molecular beams depends directly on user knowledge of source fluxes, which may vary from day to day or even from hour to hour. Thus the sensitivity of crystal structure and composition to grower input is both a strength and potential challenge of this growth technique; an uncontrolled flexible growth parameter causes chaos.

In contrast to shuttered growth, adsorption-controlled growth leverages thermodynamics to ensure phase purity. Such automatic composition control is key to the growth of compound semiconductors by MBE [2–11]. Within a particular range of temperatures and pressures (the so-called adsorption-controlled growth window), one component of a multicomponent material has a sticking coefficient that

depends strongly on surface composition. Within this growth window, the volatile species will only stick to the growing film surface and be incorporated into the film bulk if the result is the single-phase, multicomponent material of interest; any excess of the volatile material beyond the single-phase region will not stick or enter the film. Complex oxides that have been grown within the adsorption-controlled growth regime by molecular-beam epitaxy include PbTiO<sub>3</sub> [12–15], Bi<sub>2</sub>Sr<sub>2</sub>CuO<sub>y</sub> [16], Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> [17,18], BiFeO<sub>3</sub> [19–22], EuO [23], SrTiO<sub>3</sub> [24], BiMnO<sub>3</sub> [25], LuFe<sub>2</sub>O<sub>4</sub> [26], SrRuO<sub>3</sub> [27,28], GdTlO<sub>3</sub> [29], BiVO<sub>4</sub> [30], Ba<sub>2</sub>IrO<sub>4</sub> [31], BaTiO<sub>3</sub> [32], SrIrO<sub>3</sub> [33], Sr<sub>2</sub>IrO<sub>4</sub> [33,34], LaVO<sub>3</sub> [35], Ba<sub>2</sub>RuO<sub>4</sub> [36,37], Sr<sub>2</sub>RuO<sub>4</sub> [36,37], CaTiO<sub>3</sub> [38], (La,Sr)VO<sub>3</sub> [39], BaSnO<sub>3</sub> [40–42], CaRuO<sub>3</sub> [43], Ca<sub>2</sub>RuO<sub>4</sub> [44], and PbZrO<sub>3</sub> [45].

In contrast to what is suggested by thermodynamic theory, however, a significant number of these multicomponent oxides are not actually grown by continuous codeposition [12–22,25,30]. Rather, in these cases, the nonvolatile species is supplied in monolayer doses, with pauses between the doses in which only the volatile species is supplied. When the materials are continuously codeposited, the complex oxide does not form as a single phase [13–15,17]. The apparent requirement for the supply of the nonvolatile species to be modulated is not explained within the thermodynamic theory, and furthermore confers clear disadvantages, such as substantially increasing growth times (as elements are deposited in series rather than parallel) and requiring calibration of the dose times. Thus the advantages of adsorption-controlled growth are not, in general, fully utilized. The importance of oxidation kinetics has been conjectured for the adsorption-controlled growth of some oxides such as PbTiO<sub>3</sub> [12–15] and MgO [46] but not fully or generally explored. Of the complex oxides that are grown by continuous codeposition, some circumvent possible oxidation challenges by employing oxidized precursors rather than elemental source materials plus an oxidant [29,32,35,38–42].

\*ehs73@cornell.edu

†Current address: NIST Center for Neutron Research, Gaithersburg, Maryland 20899, USA.

‡Current address: National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, P. R. China.

§Corresponding author: schlom@cornell.edu

Using as a model system the growth of  $\text{PbTiO}_3$  by continuous codeposition of lead, titanium, and distilled ozone, we measure the dependence of the adsorption-controlled growth window on flux of both the volatile and nonvolatile species. We establish a simple kinetic model for adsorption-controlled growth that complements the existing thermodynamic theory, and delineate the factors controlling the kinetic growth window. We find that besides qualitatively explaining the dependence of the adsorption-controlled growth window of  $\text{PbTiO}_3$  on the flux of both volatile and nonvolatile species, the kinetic theory also may be used to explain the dependence of the growth window of  $\text{BiFeO}_3$  on the oxidant mixture. We find that oxidation kinetics is critical to growing phase-pure materials by this method.

## II. METHODS

### A. Growth and analysis of $\text{PbTiO}_3$

We grew thin films of  $\text{PbTiO}_3$  by reactive MBE in a Veeco GEN 10 system using distilled ozone (approximately 80 mol%  $\text{O}_3$ ) as an oxidant and elemental lead and titanium as source materials. We used lead fluxes from  $30$  to  $60 \times 10^{13}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$  and titanium fluxes from  $1$  to  $4.5 \times 10^{13}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ , resulting in beam equivalent pressures [47] of  $1$  to  $2 \times 10^{-6}$  Torr and  $5$  to  $20 \times 10^{-8}$  Torr, respectively. Lead was supplied with an effusion cell and titanium was supplied with a Ti-Ball<sup>TM</sup> [48–51]. During all  $\text{PbTiO}_3$  growths, lead, ozone, and titanium were continuously codeposited. Temperature was monitored using an optical pyrometer and the background chamber pressure was monitored with an ion gauge. We found that opening (closing) the titanium shutter to initiate (halt) growth caused the substrate temperature to increase (decrease) by  $20^\circ\text{C}$  and the chamber background pressure to drop (rise) by 10%. We believe this is due to low temperature of the substrate in comparison to that of the titanium source, which is near  $1550^\circ\text{C}$  in the latter case [49–51], and titanium acting as a getter pump with a large radiating area [49]. We report temperatures and pressures during growth, with both lead and titanium shutters open. All  $\text{PbTiO}_3$  films were grown using (001)-oriented  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrates [52] with a miscut of less than  $0.2^\circ$ . The crystalline phases present in the films and their orientations were monitored *in situ* with reflection high-energy electron diffraction (RHEED) along the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  azimuths and *ex situ* with four-circle x-ray diffraction (XRD) on a PANalytical X'Pert PRO using  $\text{Cu } K\alpha_1$  radiation monochromated with a four-bounce Ge 220 monochromator.

### B. Growth and analysis of $\text{BiFeO}_3$

We grew thin films of  $\text{BiFeO}_3$  by reactive MBE in a Veeco 930 system described elsewhere [12] using as an oxidant either 9 mol% ozone directly out of the ozone generator or 90 mol% ozone following distillation, and elemental bismuth and iron as source materials. Both iron and bismuth were supplied with effusion cells.  $\text{BiFeO}_3$  was grown in an adsorption-controlled regime, as described previously [20–22], under a constant bismuth flux of  $1.4 \times 10^{14}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ . Growth was controlled by supplying monolayer doses of iron at a flux of  $2 \times 10^{13}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$  and allowing equivalent bismuth-only time intervals between iron doses. Unlike the

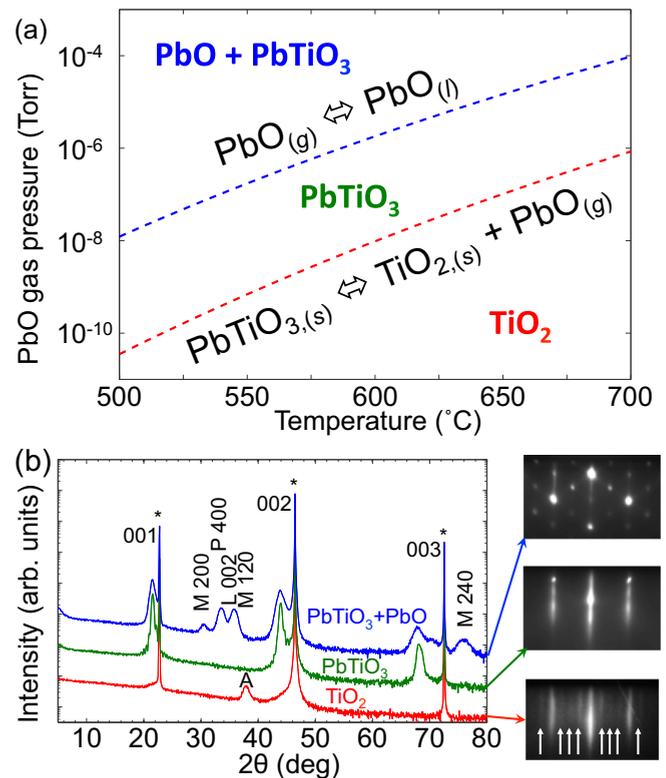


FIG. 1. (a) The adsorption-controlled growth window of  $\text{PbTiO}_3$  as a function of  $\text{PbO}$  gas pressure and substrate temperature, as calculated from thermodynamics [13,55]. (b) Indexed x-ray diffraction patterns and RHEED images taken along the substrate  $\langle 100 \rangle$  azimuth of films grown within each of the three regions of condensed phases: (i)  $\text{PbO} + \text{PbTiO}_3$ ; (ii)  $\text{PbTiO}_3$  only; and (iii)  $\text{TiO}_2$ . Arrows have been added to aid the eye in the  $\text{TiO}_2$ -phase RHEED image. Impurities are labeled as follows: A=anatase  $\text{TiO}_2$ ; M=massicot  $\text{PbO}$ ; L=litharge  $\text{PbO}$ ; P=pyrochlore  $\text{Pb}_2\text{Ti}_2\text{O}_6$ . (See Ref. [56] for a full list of growth conditions and a description of secondary phases appearing in part (b)).

$\text{PbTiO}_3$  thin films, the  $\text{BiFeO}_3$  thin films were not grown by continuous codeposition. The substrate temperature during growth was monitored *in situ* via band edge spectroscopy of the  $\text{SrTiO}_3$  substrate [53,54]. All  $\text{BiFeO}_3$  films were grown on (001)-oriented  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrates [52]. The growth surface and phase assemblage were monitored *in situ* with RHEED along the substrate  $\langle 110 \rangle$  azimuth and verified *ex situ* using XRD.

## III. RESULTS

Figure 1 shows the expected dependence [13,55] of the adsorption-controlled growth window of  $\text{PbTiO}_3$  on temperature and pressure as predicted from thermodynamics. The thermodynamic growth window is a region in gas pressure and substrate temperature; because experimental ozone pressures are many orders of magnitude greater than what is required thermodynamically to oxidize lead, the gas pressure relevant to the thermodynamics of  $\text{PbTiO}_3$  formation is the partial pressure of  $\text{PbO}$  gas. When the gas pressure is too high or the substrate temperature too low, solid  $\text{PbO}$  is expected to

accumulate on the film surface. When the gas pressure is too low or the substrate temperature too high, all PbO is expected to desorb and not be incorporated into the growing film, resulting in the film being just TiO<sub>2</sub>. We note that the width of the window (in temperature) has only a very weak dependence on gas pressure (increasing pressure from  $1 \times 10^{-8}$  to  $1 \times 10^{-7}$  Torr widens the window from 105 °C to 111 °C, a change of only 6%) and that there is no explicit dependence on titanium flux of the growth window at all [13]. Indeed, thermodynamics is all about equilibrium and not about growth.

The RHEED and XRD patterns we observed corresponding to PbO excess, pyrochlore Pb<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub>, and TiO<sub>2</sub> excess, as well as phase-pure PbTiO<sub>3</sub>, are shown in Fig. 1. We discuss the secondary phases we observe in Ref. [56].

Next, we characterized the conditions under which the continuous codeposition of lead, titanium, and ozone will yield each of the three sets of product described in Fig. 1(b). In this way we delineate our experimental (rather than theoretical) growth window. In agreement with previous reports, we observed that when the titanium flux is relatively high in comparison with the lead flux (Pb:Ti=7:1 in this work; between 2:1 and 5:1 in previous reports), phase-pure PbTiO<sub>3</sub> cannot be grown by continuous codeposition of the constituents [13,15,17]. When we increase the Pb:Ti ratio by decreasing the titanium flux, however, we are able to grow PbTiO<sub>3</sub> by continuous codeposition, as shown in Fig. 2(a). This finding—that the adsorption-controlled growth window of PbTiO<sub>3</sub> depends strongly on titanium flux—cannot be explained by the thermodynamic window shown in Fig. 1(a). Because the growth rate of the PbTiO<sub>3</sub> (within the growth window) is controlled by the titanium flux, the dependence on the titanium flux may equivalently be considered a dependence on growth rate.

To further understand the role played by kinetics in the growth of PbTiO<sub>3</sub> by continuous codeposition, we also measure the dependence on the lead flux and oxidant flux of the phases grown. While the width of the thermodynamic growth window shown in Fig. 1(a) is only very weakly dependent upon PbO gas pressure, we observe a significant dependence of the width of the experimental growth window on the lead flux, shown in Fig. 2(b). Furthermore, while we supply many orders of magnitude more ozone than the amount necessary to thermodynamically favor oxidation of lead into PbO at growth temperature [13,55], we see in Fig. 2(c) that the growth window is highly sensitive to chamber background pressure as well.

The dependence of the observed growth window on ozone flux and on the lead flux is the inverse of that observed for the titanium flux: increasing either the ozone flux or the lead flux has the effect of widening the growth window. Based on the thermodynamic theory, changing the lead or ozone flux should shift the growth window to higher or lower temperatures without significantly altering its width. In the next section, we develop a simple theory of the role of kinetics of lead oxidation in the growth of PbTiO<sub>3</sub> and see that it may be used to qualitatively explain these results. We then test this theory on a completely different system: the growth of BiFeO<sub>3</sub> by adsorption-controlled MBE when the iron is supplied in sequential monolayer doses (shuttered) rather than being continuously deposited (as are all sources in our growths

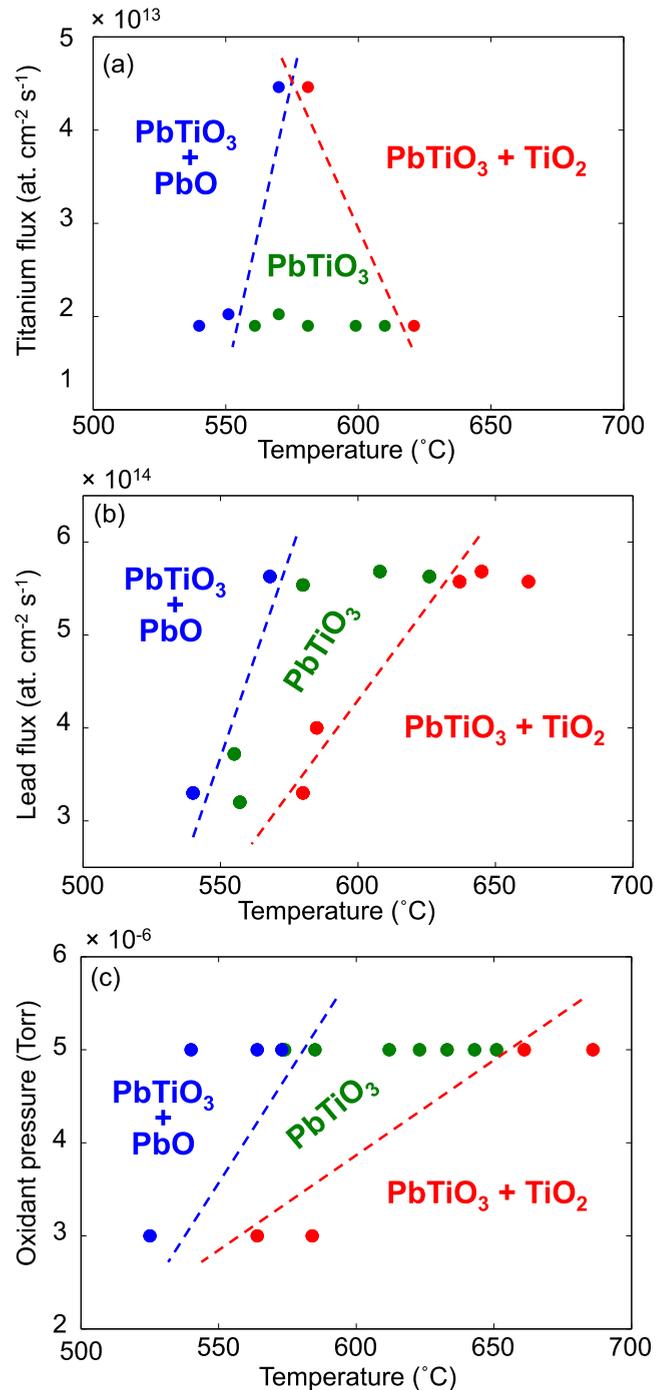


FIG. 2. Dependence of observed film phase as a function of titanium flux, lead flux, or oxidant pressure. Only one variable (source flux or oxidant pressure) was changed in addition to temperature at once. Phases observed when (a) oxidant background pressure and lead flux were fixed, (b) oxidant background pressure and titanium flux were fixed, and (c) titanium and lead fluxes were fixed. (See Ref. [56] for a full list of growth conditions.)

of PbTiO<sub>3</sub>). We find that while thermodynamics cannot explain the dependence of the BiFeO<sub>3</sub> growth window on oxidant type [molecular oxygen (O<sub>2</sub>) versus ozone (O<sub>3</sub>)], the observed dependence is in agreement with the kinetic theory.

#### IV. DISCUSSION: ROLE OF KINETICS IN ADSORPTION-CONTROLLED GROWTH

##### A. Formulation of the kinetic model using PbTiO<sub>3</sub> as an example

We established in the previous section that, in contrast to what is expected from thermodynamic theory, the window in temperature for the adsorption-controlled growth of PbTiO<sub>3</sub> depends strongly on lead flux, titanium flux, and oxidant pressure. During growth of PbTiO<sub>3</sub> by adsorption-controlled MBE, the majority of PbO is formed on the film surface [13]; in this section, we apply the Langmuir-Hinshelwood model [57,58] of bimolecular, surface-catalyzed reactions to the formation of PbO from lead and oxygen adsorbed on the film surface and find that this model suitably explains the dependence of the growth window of PbTiO<sub>3</sub> on lead, oxidant, and titanium flux. The Langmuir-Hinshelwood model, an extension of the Langmuir adsorption isotherm, has been used successfully to explain the rate data of surface-catalyzed reactions such as oxidation of CO by O<sub>2</sub> on Pt(111) and Rh(111); decomposition of ammonia to N<sub>2</sub> and H<sub>2</sub> on Pt(111), Rh(111), or Fe(111); and the water shift reaction on platinum; as well as many others [57].

We consider the formation of PbO on the growing film surface by the reaction of an adsorbed lead atom and an adsorbed oxygen atom:

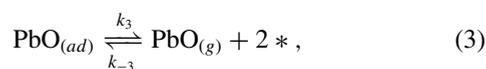


Pb<sub>(ad)</sub> and O<sub>(ad)</sub> are both formed on the surface when gas-phase atoms strike the surface; we assume that the film surface is at steady state during growth by continuous codeposition. We also assume that the adsorption and desorption of lead and oxygen atoms are very rapid in comparison with the reaction in Eq. (1) and that Eq. (1) is thus the rate-limiting step in the formation of PbO on the film surface, though we will return to this latter assumption at the end of this section. Within the Langmuir-Hinshelwood model, the rate of PbO formation will then be [57,58]

$$r_{\text{PbO}} = k_1[\text{Pb}_{(ad)}][\text{O}_{(ad)}], \quad (2)$$

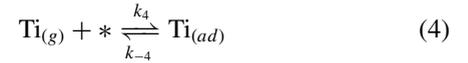
where [Pb<sub>(ad)</sub>] and [O<sub>(ad)</sub>] are the concentrations of the adsorbed species in molecules cm<sup>-2</sup>. Later on we will discuss the factors that determine [Pb<sub>(ad)</sub>] and [O<sub>(ad)</sub>].

After PbO is formed on the surface, it may either remain adsorbed or evaporate. Depending on temperature, PbO<sub>(g)</sub> gas pressure, and surface composition, the following equilibrium will either move towards reactants (high pressure, low temperature) or products (low pressure, high temperature):

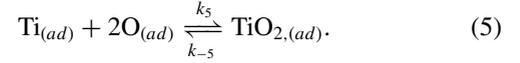


where \* denotes unoccupied surface sites. The particular value of the equilibrium constant  $K_{\text{PbO}} = k_3/k_{-3} = [\text{PbO}_{(g)}]/[\text{PbO}_{(ad)}]$  at a given temperature and pressure may be found with thermodynamics;  $K_{\text{PbO}}$  determines the thermodynamic growth window.

The chemical reactions involving titanium and oxygen atoms are



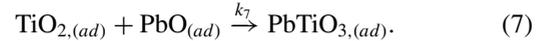
and



Based on the observations that (i) titanium exhibits unity sticking [13], and thus Eq. (4) is zeroth-order in concentration of surface sites [\*], (ii) titanium will be oxidized even with much lower oxidant pressure than is present in our system, and thus Eq. (5) is zeroth-order in oxidant pressure and in [O<sub>(ad)</sub>], and (iii) the above two reactions are irreversible under our growth conditions, we find that the rate of TiO<sub>2</sub> formation is just the titanium flux,  $\Phi_{\text{Ti}}$ :

$$r_{\text{TiO}_2} = k_4[\text{Ti}_{(g)}] = \Phi_{\text{Ti}}. \quad (6)$$

PbTiO<sub>3</sub> formation is given by



For PbTiO<sub>3</sub> to be formed as a single phase without excess TiO<sub>2</sub> accumulation in the film,  $r_{\text{PbO}}$  must equal or exceed  $r_{\text{TiO}_2}$ . When this is true and conditions are within the thermodynamic growth window, the rate of PbTiO<sub>3</sub> formation  $r_{\text{PbTiO}_3} = r_{\text{TiO}_2}$ . On the other hand, if  $r_{\text{PbO}} < r_{\text{TiO}_2}$  then PbTiO<sub>3</sub> will not form as a phase-pure material; rather, deposition of TiO<sub>2</sub> will “outrun” formation of PbO and the excess TiO<sub>2</sub> will accumulate as a secondary phase. It is possible for this to occur within the thermodynamic growth window; we would consider such growth conditions to be within the thermodynamic growth window but outside the *kinetic* growth window.

We delineate the kinetic growth window, within which PbTiO<sub>3</sub> may grow because  $r_{\text{PbO}} \geq r_{\text{TiO}_2}$ , by substituting in the preceding inequality Eqs. (2) and (6):

$$k_1[\text{Pb}_{(ad)}][\text{O}_{ad}] \geq \Phi_{\text{Ti}}. \quad (8)$$

We immediately see that for higher titanium fluxes, more lead and oxygen must be present on the surface in order for PbO formation to keep up with TiO<sub>2</sub> formation. This explains the result in Fig. 2(a), that increasing the titanium flux while holding other conditions constant has the effect of closing the growth window and preventing growth of phase-pure PbTiO<sub>3</sub>.

We describe the relationship between [Pb<sub>(ad)</sub>] and the beam equivalent gas pressure [Pb<sub>(g)</sub>] using thermodynamics [55] and the relationship between the lead flux  $\Phi_{\text{Pb}}$  and [Pb<sub>(g)</sub>] using the kinetic theory of gases [47]. Combining these relationships, [Pb<sub>(ad)</sub>] relates to the lead flux as

$$[\text{Pb}_{(ad)}] \propto \Phi_{\text{Pb}} e^{-\Delta H_{\text{Pb}(g) \rightarrow \text{Pb}(l)}/k_B T}. \quad (9)$$

At MBE-amenable chamber pressures and substrate temperatures, the concentration of adsorbed, possibly activated oxygen atoms available for oxidizing the film appears to be a linear function of ozone flux [59–63]. See Ref. [56] for a fuller discussion of these relationships.

Substituting into Eq. (8) the relationship between lead flux  $\Phi_{\text{Pb}}$  and [Pb<sub>(ad)</sub>] described in Eq. (9) and assuming a linear

relationship between ozone flux  $\Phi_{O_3}$  and  $[O_{(ad)}]$ , we may summarize the kinetic growth window as

$$k\Phi_{Pb}e^{-\Delta H_{Pb(g)\rightarrow Pb(l)}/k_B T}\Phi_{O_3} \geq \Phi_{Ti}, \quad (10)$$

for  $k$  a proportionality constant; or, in terms of a flux ratio,

$$\frac{\Phi_{Pb}\Phi_{O_3}}{\Phi_{Ti}} \geq \kappa e^{+\Delta H_{Pb(g)\rightarrow Pb(l)}/k_B T}. \quad (11)$$

The term on the right side of Eq. (11) will *increase* exponentially with increasing temperature: at higher substrate temperatures larger flux ratios will be required to grow  $PbTiO_3$  by continuous codeposition. At constant temperature, this flux ratio describes the effect on the kinetic growth window of changing the lead flux, ozone flux, or titanium flux observed experimentally in Fig. 2: increasing titanium flux closes the growth window, while increasing the lead or ozone flux opens it.

This kinetic growth window theory complements, rather than replaces, the thermodynamic growth window theory. Growth conditions must be within both windows for  $PbTiO_3$  to be grown as a single phase by continuous codeposition. At high titanium flux, it is possible to be within the thermodynamic growth window (any  $PbO$  that forms is incorporated into the film at no more than a 1:1 ratio with  $TiO_2$ ) but outside the kinetic growth window ( $PbO$  formation cannot keep up with  $TiO_2$  formation, and excess  $TiO_2$  accumulates as a secondary phase). As noted in the previous paragraph, at larger flux ratios  $\Phi_{Pb}\Phi_{O_3}/\Phi_{Ti}$  the temperature at which  $TiO_2$  formation outruns  $PbO$  formation is higher; given the independence of the thermodynamic growth window on titanium flux, increasing the flux ratio has the effect of widening the overall growth window. Increasing the lead flux and titanium flux by equal measure, on the other hand, which does not alter the flux ratio, has the effect of shifting the growth window to higher temperatures while leaving its width unchanged.

The fact that increasing ozone flux is observed experimentally in Fig. 2 to have a larger effect on the width of the growth window than does increasing the lead flux brings into question our earlier approximation that the rate-limiting step in the formation of  $PbO$  is the collision of an adsorbed lead atom and an adsorbed oxygen atom, Eq. (1). If  $[Pb_{(ad)}] \gg [O_{(ad)}]$ , then the rate of  $PbO$  formation on the surface may be less than first order in  $[Pb_{(ad)}]$ , and  $\Phi_{Pb}$  in Eqs. (10) and (11) could be replaced by  $\Phi_{Pb}^x$  for  $0 < x < 1$ . Such a factor could help explain why such extraordinary excesses of lead relative to titanium are required. Further increases to ozone flux at the film surface might permit reduction of the Pb:Ti flux ratio.

That the kinetic growth window of  $PbTiO_3$  may be more dependent upon the ozone flux than the lead flux might explain our success in growing  $PbTiO_3$  by continuously codeposited MBE. In addition to our use of distilled ozone as an oxidant, our ozone delivery tube is rather close to the 10 mm  $\times$  10 mm substrate (5.1 cm from the end of the ozone delivery tube to the substrate center at a 40° angle of incidence). If ozone flux were more rate-limiting to the kinetics of lead oxidation than lead flux, it would follow that maximizing ozone flux at the substrate would be key to the growth of  $PbTiO_3$  by continuous codeposition at reasonable growth rates. In addition to  $PbTiO_3$ , another complex oxide,  $CaRuO_3$ , has been grown for the first time by continuous codeposition of source elements in our modified chamber [43], and we have grown  $BiFeO_3$  by

continuous codeposition [64,65] in a chamber with a similar ozone delivery tube geometry, though in the next section we employ shuttering in our growth of  $BiFeO_3$ .

### B. Application of model to growth of $BiFeO_3$

To test the generality of the importance of oxidation kinetics to adsorption-controlled growth, we turn our consideration to another system: the adsorption-controlled growth of  $BiFeO_3$  by reactive MBE from metallic bismuth, iron, and oxidant [molecular oxygen ( $O_2$ ) and ozone ( $O_3$ )]. For this portion of our experiments, we continuously supplied bismuth and oxidant, while supplying monolayer doses of iron interspersed with pauses. This “shuttered” growth technique is how many complex oxides are grown by adsorption-controlled MBE [12–22,25,30].

$BiFeO_3$  may be grown by MBE using a relatively low quantity of ozone in comparison to that required to grow

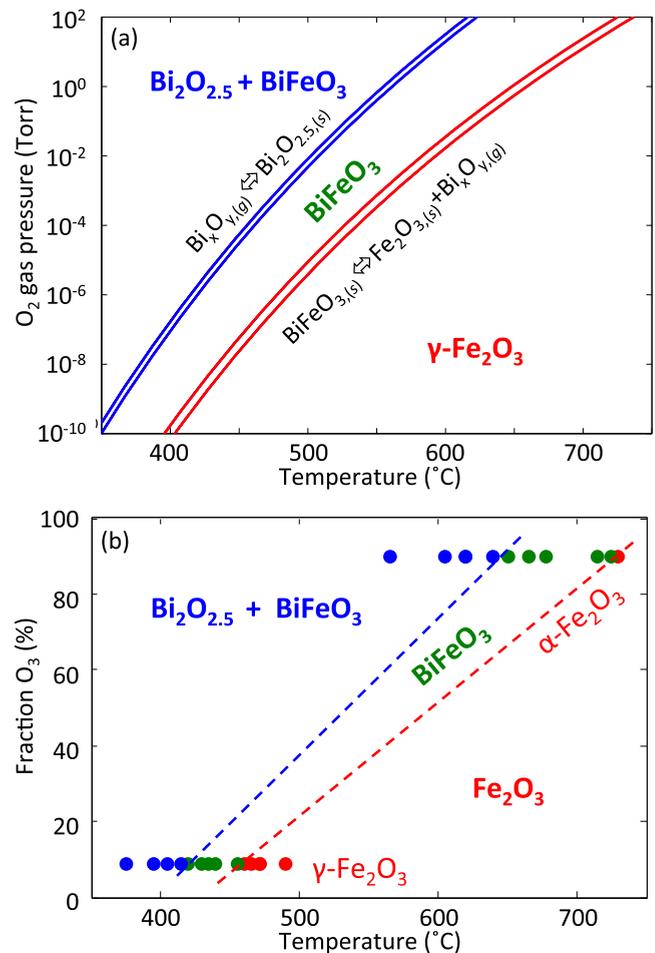


FIG. 3. (a) Adsorption-controlled growth window of  $BiFeO_3$  as a function of molecular oxygen pressure as calculated from thermodynamics, after Ihlefeld and co-workers [21]. (b) Dependence of observed film phase as a function of fraction ozone in the oxidant blend. We note that different phases of  $Fe_2O_3$  appear as secondary phases outside the growth window at the two different oxidant mixtures. Ozone is 250 $\times$  more active in oxidizing bismuth than diatomic oxygen in the process chamber in which we grew  $BiFeO_3$ . (See Ref. [56] for a full list of growth conditions and for our measurements of ozone activity.)

PbTiO<sub>3</sub>. At a 5:1 Pb:Ti ratio, distilled ozone at a background pressure of  $1 \times 10^{-5}$  Torr is necessary to oxidize lead even when the titanium is shuttered [13]; however, at a 7:1 Bi:Fe ratio, we find that BiFeO<sub>3</sub> may be grown when the iron is shuttered at  $1 \times 10^{-6}$  Torr of oxidant using either distilled ozone (90% in this study) or ozone at the concentration produced by the ozone generator, i.e., 9% O<sub>3</sub> + 91% O<sub>2</sub>. Thus, consideration of BiFeO<sub>3</sub> allows us to study the effect of different oxidant mixtures. Similar to PbTiO<sub>3</sub>, however, the width of the thermodynamic adsorption-controlled growth window of BiFeO<sub>3</sub> (shown in Fig. 3(a), after Ihlefeld and co-workers [21]) only shows a very weak dependence on gas pressure. Increasing the oxygen pressure by an order of magnitude, from  $1 \times 10^{-7}$  to  $1 \times 10^{-6}$  Torr, increases the width of the thermodynamic window by only 4 °C, an increase of less than 10%. In our chamber, ozone has about 250 times the activity of molecular oxygen for the oxidation of bismuth. Similar activity enhancement for ozone over molecular oxygen has been observed for the oxidation of copper as well [63]. Replacing oxygen with ozone in Fig. 3(a) would be expected to shift the growth window to lower pressures without otherwise changing its form. (See Ref. [56] for our measurements of ozone activity.)

We present in Fig. 3(b) the observed dependence of the growth window of BiFeO<sub>3</sub> on ozone concentration. Using 9% ozone, Bi<sub>2</sub>O<sub>2.5</sub> appears in the RHEED up to 415 °C, and Fe<sub>2</sub>O<sub>3</sub> appears at 460 °C, giving a window for the growth of BiFeO<sub>3</sub> 45 °C wide. Using 90% ozone both moves the growth window up by roughly 200 °C in substrate temperature, and doubles its width: Bi<sub>2</sub>O<sub>2.5</sub> appears in the RHEED up to 640 °C, and Fe<sub>2</sub>O<sub>3</sub> appears at 725 °C, giving a window for growth of BiFeO<sub>3</sub> of 90 °C. The shift in the growth window to higher oxygen pressure at higher temperature is expected from thermodynamics, but the increase in the width of the growth window can only be explained by our kinetic model. The change in phase of Fe<sub>2</sub>O<sub>3</sub> that appears as an impurity outside the BiFeO<sub>3</sub> growth window, from  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at low

ozone fraction to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at high ozone fraction, may be attributable to the effect of epitaxial strain combined with thermodynamics (see Ref. [56]).

## V. CONCLUSIONS

We have grown PbTiO<sub>3</sub> by MBE using continuous codeposition of all source elements for the first time. We find the successful growth of phase-pure PbTiO<sub>3</sub> by this method depends on achieving a sufficient ratio of fluxes  $\Phi_{\text{Pb}}\Phi_{\text{O}_3}/\Phi_{\text{Ti}}$ , with increasing lead or oxidant flux favoring PbTiO<sub>3</sub> growth and increasing titanium flux disfavoring PbTiO<sub>3</sub> growth. The thermodynamics of PbTiO<sub>3</sub> growth within the adsorption-controlled regime depends on the equilibrium between adsorption and desorption of PbO; we argue that the kinetics of PbO formation on the growing film surface is also of high importance, and present a simple theory that describes it. In conjunction with the existing thermodynamic theory, our kinetic theory qualitatively explains our observed dependence of the growth window on the flux ratio  $\Phi_{\text{Pb}}\Phi_{\text{O}_3}/\Phi_{\text{Ti}}$ , as well as substrate temperature. We find that this model may also be used to qualitatively explain the dependence of the growth window of BiFeO<sub>3</sub> on oxidant mixture.

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