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Phys. Rev. Materials **1**, 023403 — Published 12 July 2017

DOI: [10.1103/PhysRevMaterials.1.023403](https://doi.org/10.1103/PhysRevMaterials.1.023403)

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

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(Dated: May 15, 2017)

Abstract

We report the growth of PbTiO_3 thin films by molecular-beam epitaxy utilizing continuous codeposition. Contrary to what would be expected from thermodynamics, whether the resulting film is single-phase PbTiO_3 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_3 depends on lead flux, oxidant flux, and titanium flux. We successfully apply the kinetic theory to the dependence of the growth of BiFeO_3 on oxidant type and surmise that the theory may be generally applicable to the adsorption-controlled growth of complex oxides by MBE.

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 nature¹. 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 MBE²⁻¹¹. 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_3 ¹²⁻¹⁵, $\text{Bi}_2\text{Sr}_2\text{CuO}_y$ ¹⁶, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ^{17,18}, BiFeO_3 ¹⁹⁻²², EuO ²³, SrTiO_3 ²⁴, BiMnO_3 ²⁵, LuFe_2O_4 ²⁶, SrRuO_3 ^{27,28}, GdTiO_3 ²⁹, BiVO_4 ³⁰, Ba_2IrO_4 ³¹, BaTiO_3 ³², SrIrO_3 ³³, Sr_2IrO_4 ^{33,34}, LaVO_3 ³⁵, Ba_2RuO_4 ^{36,37}, Sr_2RuO_4 ^{36,37}, CaTiO_3 ³⁸, $(\text{La,Sr})\text{VO}_3$ ³⁹, BaSnO_3 ⁴⁰⁻⁴², CaRuO_3 ⁴³, Ca_2RuO_4 ⁴⁴, and PbZrO_3 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 non-volatile 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 non-volatile 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_3 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^{29,32,35,38-41,47}.

Using as a model system the growth of 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 non-volatile 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 PbTiO_3 on flux of both volatile and non-volatile species, the kinetic theory also may be used to explain the dependence of the growth window of BiFeO_3 on oxidant mixture. We find that oxidation kinetics are critical to growing phase-pure materials by this method.

II. METHODS

A. Growth and analysis of PbTiO_3

We grew thin films of PbTiO_3 by reactive MBE in a Veeco GEN 10 system using distilled ozone (approximately 80 mol% O_3) as an oxidant and elemental lead and titanium as source materials. We used lead fluxes from 30 to 60×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$ and titanium fluxes from 1 to 4.5×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$, resulting in beam equivalent pressures⁴⁸ of 1 to 2×10^{-6} Torr and 5 to 20×10^{-8} Torr, respectively. Lead was supplied with an effusion cell and titanium was supplied with a Ti-Ball^{TM49-52}. During all 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°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°C in the latter case⁵⁰⁻⁵², and titanium acting as a getter pump with a large radiating area⁵⁰. We report temperatures and pressures during growth, with both lead and titanium shutters open. All PbTiO₃ films were grown using (001)-oriented TiO₂-terminated SrTiO₃ substrates⁵³ with a miscut of less than 0.2°.

The crystalline phases present in the films and their orientations were monitored *in situ* with reflection high-energy electron diffraction (RHEED) along the <100> and <110> azimuths and *ex situ* with four-circle X-ray diffraction (XRD) on a PANalytical X'Pert PRO using Cu K α ₁ radiation monochromated with a four-bounce Ge 220 monochromator.

B. Growth and analysis of BiFeO₃

We grew thin films of BiFeO₃ by reactive MBE in a Veeco 930 system described elsewhere¹² 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. BiFeO₃ was grown in an adsorption-controlled regime, as described previously²⁰⁻²², under a constant bismuth flux of 1.4×10^{14} atoms cm⁻² s⁻¹. Growth was controlled by supplying monolayer doses of iron at a flux of 2×10^{13} atoms cm⁻² s⁻¹ and allowing equivalent bismuth-only time intervals between iron doses. Unlike the PbTiO₃ thin films, the BiFeO₃ thin films were not grown by continuous codeposition. The substrate temperature during growth was monitored *in situ* via band edge spectroscopy of the SrTiO₃ substrate^{54,55}. All BiFeO₃ films were grown on (001)-oriented TiO₂-terminated SrTiO₃ substrates⁵³.

The growth surface and phase assemblage were monitored *in situ* with RHEED along the substrate <110> azimuth and verified *ex situ* using XRD.

III. RESULTS

Figure 1 shows the expected dependence^{13,56} of the adsorption-controlled growth window of PbTiO₃ 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 PbTiO_3 formation is the partial pressure of PbO gas. When the gas pressure is too high or the substrate temperature too low, solid 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_2 . We note that the width of the window (in temperature) has only a very weak dependence on gas pressure (increasing pressure from 1×10^{-8} Torr to 1×10^{-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 all¹³. Indeed, thermodynamics is all about equilibrium and not about growth.

The RHEED and XRD patterns we observed corresponding to PbO excess, pyrochlore $\text{Pb}_2\text{Ti}_2\text{O}_6$, and TiO_2 excess, as well as phase-pure PbTiO_3 , are shown in Fig. 1. We discuss the secondary phases we observe in the Supplementary Information.

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 ($\text{Pb}:\text{Ti}=7:1$ in this work; between 2:1 and 5:1 in previous reports), phase-pure PbTiO_3 cannot be grown by continuous codeposition of the constituents^{13,15,17}. When we increase the $\text{Pb}:\text{Ti}$ ratio by decreasing the titanium flux, however, we are able to grow PbTiO_3 by continuous codeposition, as shown in Fig. 2(a). This finding – that the adsorption-controlled growth window of PbTiO_3 depends strongly on titanium flux – cannot be explained by the thermodynamic window shown in Fig. 1(a). Because the growth rate of the PbTiO_3 (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_3 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^{13,56}, 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 PbTiO₃ 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 BiFeO₃ 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 of PbTiO₃). We find that while thermodynamics cannot explain the dependence of the BiFeO₃ growth window on oxidant type [molecular oxygen (O₂) versus ozone (O₃)], 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 PbTiO₃ 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 PbTiO₃ depends strongly on lead flux, titanium flux, and oxidant pressure. During growth of PbTiO₃ by adsorption-controlled MBE the majority of PbO is formed on the film surface¹³; 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 PbTiO₃ 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 O₂ on Pt(111) and Rh(111); decomposition of ammonia to N₂ and H₂ on Pt(111), Rh(111), or Fe(111); and the water shift reaction on platinum; as well as many others⁵⁷.

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



$\text{Pb}_{(ad)}$ and $\text{O}_{(ad)}$ 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 $[\text{Pb}_{(ad)}]$ and $[\text{O}_{(ad)}]$ are the concentrations of the adsorbed species in molecules cm^{-2} . Later on we will discuss the factors that determine $[\text{Pb}_{(ad)}]$ and $[\text{O}_{(ad)}]$.

After PbO is formed on the surface, it may either remain adsorbed or evaporate. Depending on temperature, $\text{PbO}_{(g)}$ gas pressure, and surface composition, the following equilibrium will either move towards reactants (high pressure, low temperature) or products (low pressure, high temperature):

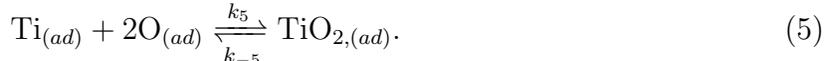


where * denotes unoccupied surface sites. The particular value of the equilibrium constant $K_{\text{PbO}} = k_3/k_{-3} = [\text{PbO}_{(g)}]/[\text{PbO}_{(ad)}]$ at a given temperature and pressure may be found with thermodynamics; K_{PbO} determines the thermodynamic growth window.

The chemical reactions involving titanium and oxygen atoms are:



and

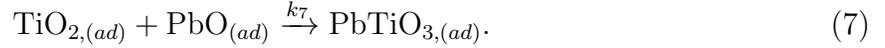


Based on the observations that (i) titanium exhibits unity sticking¹³, and thus Eq. (4) is zeroth-order in concentration of surface sites [*]; (ii) titanium will be oxidized even with much lower oxidant pressure than is present in our system, and thus Eq. (5) is zeroth-order

in oxidant pressure and in $[O_{(ad)}]$; and (iii) the above two reactions are irreversible under our growth conditions; we find that the rate of TiO_2 formation is just the titanium flux, Φ_{Ti} :

$$r_{TiO_2} = k_4[Ti_{(g)}] = \Phi_{Ti}. \quad (6)$$

$PbTiO_3$ formation is given by



For $PbTiO_3$ to be formed as a single phase without excess TiO_2 accumulation in the film, r_{PbO} must equal or exceed r_{TiO_2} . When this is true and conditions are within the thermodynamic growth window, the rate of $PbTiO_3$ formation $r_{PbTiO_3} = r_{TiO_2}$. On the other hand, if $r_{PbO} < r_{TiO_2}$ then $PbTiO_3$ will not form as a phase-pure material; rather, deposition of TiO_2 will “outrun” formation of PbO and the excess TiO_2 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 $PbTiO_3$ may grow because $r_{PbO} \geq r_{TiO_2}$, by substituting in the preceding inequality Eqs. (2) and (6):

$$k_1[Pb_{(ad)}][O_{ad}] \geq \Phi_{Ti}. \quad (8)$$

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_2 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 $PbTiO_3$.

We describe the relationship between $[Pb_{(ad)}]$ and the beam equivalent gas pressure $[Pb_{(g)}]$ using thermodynamics⁵⁶ and the relationship between the lead flux Φ_{Pb} and $[Pb_{(g)}]$ using the kinetic theory of gases⁴⁸. Combining these relationships, $[Pb_{(ad)}]$ relates to the lead flux as

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

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 the Supplementary Information for a fuller discussion of these relationships.

Substituting in to Eq. (8) the relationship between lead flux Φ_{Pb} and $[\text{Pb}_{(ad)}]$ described in Eq. (9) and assuming a linear relationship between ozone flux Φ_{O_3} and $[\text{O}_{(ad)}]$, we may summarize the kinetic growth window as

$$k\Phi_{\text{Pb}}e^{-\Delta H_{\text{Pb}(g)\rightarrow\text{Pb}(l)}/k_B T}\Phi_{\text{O}_3} \geq \Phi_{\text{Ti}}, \quad (10)$$

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

$$\frac{\Phi_{\text{Pb}}\Phi_{\text{O}_3}}{\Phi_{\text{Ti}}} \geq \kappa e^{+\Delta H_{\text{Pb}(g)\rightarrow\text{Pb}(l)}/k_B T}. \quad (11)$$

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 $\Phi_{\text{Pb}}\Phi_{\text{O}_3}/\Phi_{\text{Ti}}$ 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.

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 $[\text{Pb}_{(ad)}] \gg [\text{O}_{(ad)}]$, then the rate of PbO formation on the surface may be less than first order in $[\text{Pb}_{(ad)}]$, and Φ_{Pb} in Eqs. (10) and (11) could be replaced by Φ_{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 $10 \text{ mm} \times 10 \text{ mm}$ 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 chamber⁴³, 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 PbTiO_3 . At a 5:1 Pb:Ti ratio, distilled ozone at a background pressure of 1×10^{-5} Torr is necessary to oxidize lead even when the titanium is shuttered¹³; however, at a 7:1 Bi:Fe ratio, we find that BiFeO_3 may be grown when the iron is shuttered at 1×10^{-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_3 + 91% O_2 . Thus, consideration of BiFeO_3 allows us to study the effect of different oxidant mixtures. Similar to PbTiO_3 , however, the width of the thermodynamic adsorption-controlled growth window of BiFeO_3 (shown in Fig. 3(a), after Ihlefeld and co-workers²¹) only shows a very weak dependence on gas pressure. Increasing the oxygen pressure by an order of magnitude, from 1×10^{-7} Torr to

1×10^{-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 well⁶³. 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 Supplementary Information for our measurements of ozone activity.

We present in Fig. 3(b) the observed dependence of the growth window of BiFeO_3 on ozone concentration. Using 9% ozone, $\text{Bi}_2\text{O}_{2.5}$ appears in the RHEED up to 415°C , and Fe_2O_3 appears at 460°C , giving a window for the growth of BiFeO_3 45°C wide. Using 90% ozone both moves the growth window up by roughly 200°C in substrate temperature, and doubles its width: $\text{Bi}_2\text{O}_{2.5}$ appears in the RHEED up to 640°C , and Fe_2O_3 appears at 725°C , giving a window for growth of BiFeO_3 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_2O_3 that appears as an impurity outside the BiFeO_3 growth window, from $\gamma\text{-Fe}_2\text{O}_3$ at low ozone fraction to $\alpha\text{-Fe}_2\text{O}_3$ at high ozone fraction, may be attributable to the effect of epitaxial strain combined with thermodynamics. See Supplementary Information.

V. CONCLUSIONS

We have grown PbTiO_3 by MBE using continuous codeposition of all source elements for the first time. We find the successful growth of phase-pure PbTiO_3 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_3 growth and increasing titanium flux disfavoring PbTiO_3 growth. The thermodynamics of PbTiO_3 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 are 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_3 on oxidant mixture.

VI. ACKNOWLEDGEMENTS

E.H.S. and D.G.S. acknowledge support by the Center for Nanoscale Science, with funding from the NSF MRSEC program (DMR-1420620). This work made use of the Cornell Center for Materials Research (CCMR) Shared Facilities, which are supported through the NSF MRSEC program (DMR-1120296). Substrate preparation was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (Grant ECCS-15420819). J.F.I. acknowledges funding from the Office of Naval Research Grant No. N00014-04-1-0426.

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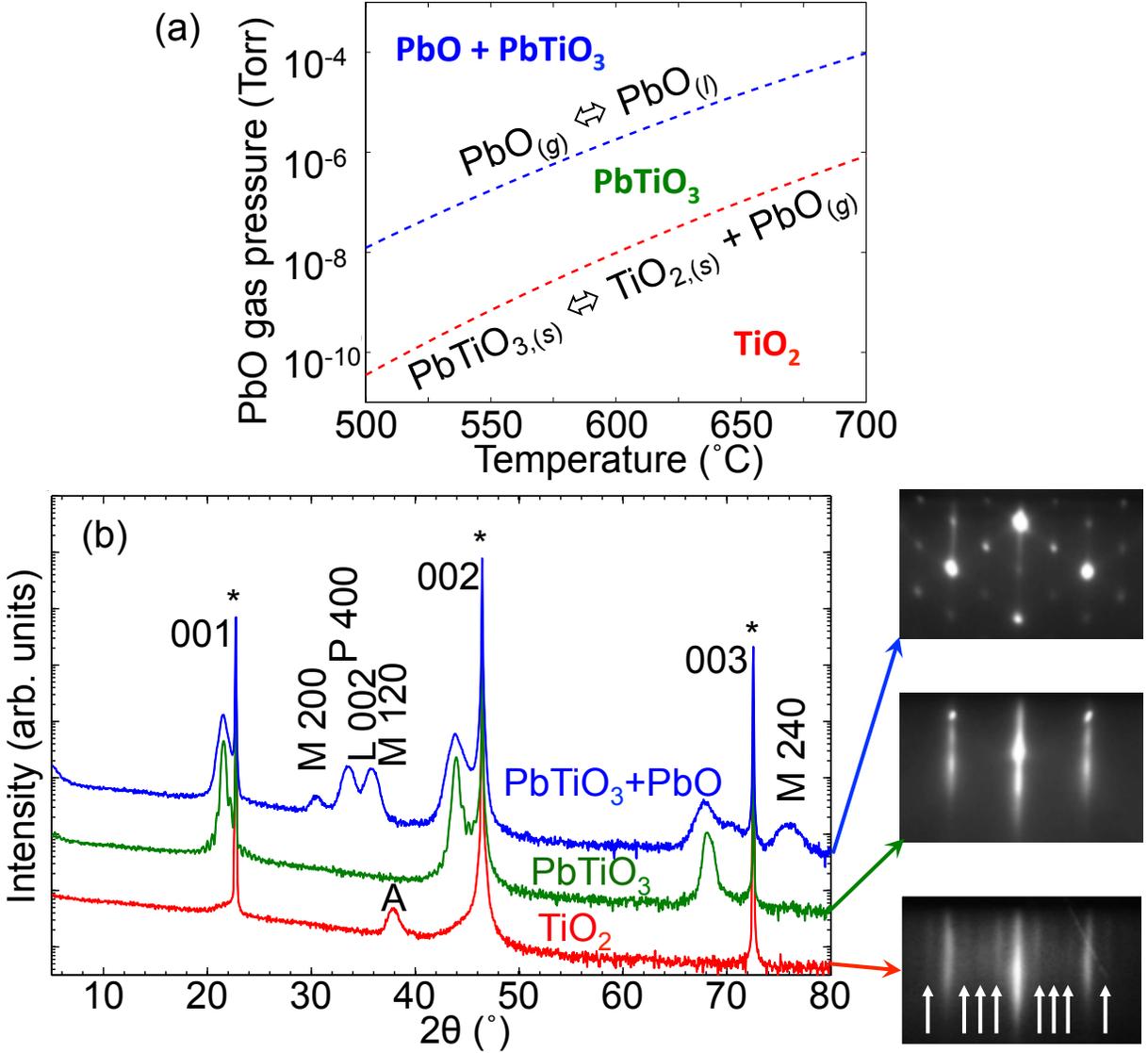


FIG. 1. (Color online) (a) The adsorption-controlled growth window of PbTiO_3 as a function of PbO gas pressure and substrate temperature, as calculated from thermodynamics^{13,56}. (b) Indexed x-ray diffraction patterns and RHEED images taken along the substrate $\langle 100 \rangle$ azimuth of films grown within each of the three regions of condensed phases: (i) $\text{PbO} + \text{PbTiO}_3$; (ii) PbTiO_3 only; and (iii) TiO_2 . Arrows have been added to aid the eye in the TiO_2 -phase RHEED image. Impurities are labeled as follows: A=anatase TiO_2 ; M=massicot PbO ; L=litharge PbO ; P=pyrochlore $\text{Pb}_2\text{Ti}_2\text{O}_6$. See Supplementary Information for a full list of growth conditions and a description of secondary phases appearing in part (b).

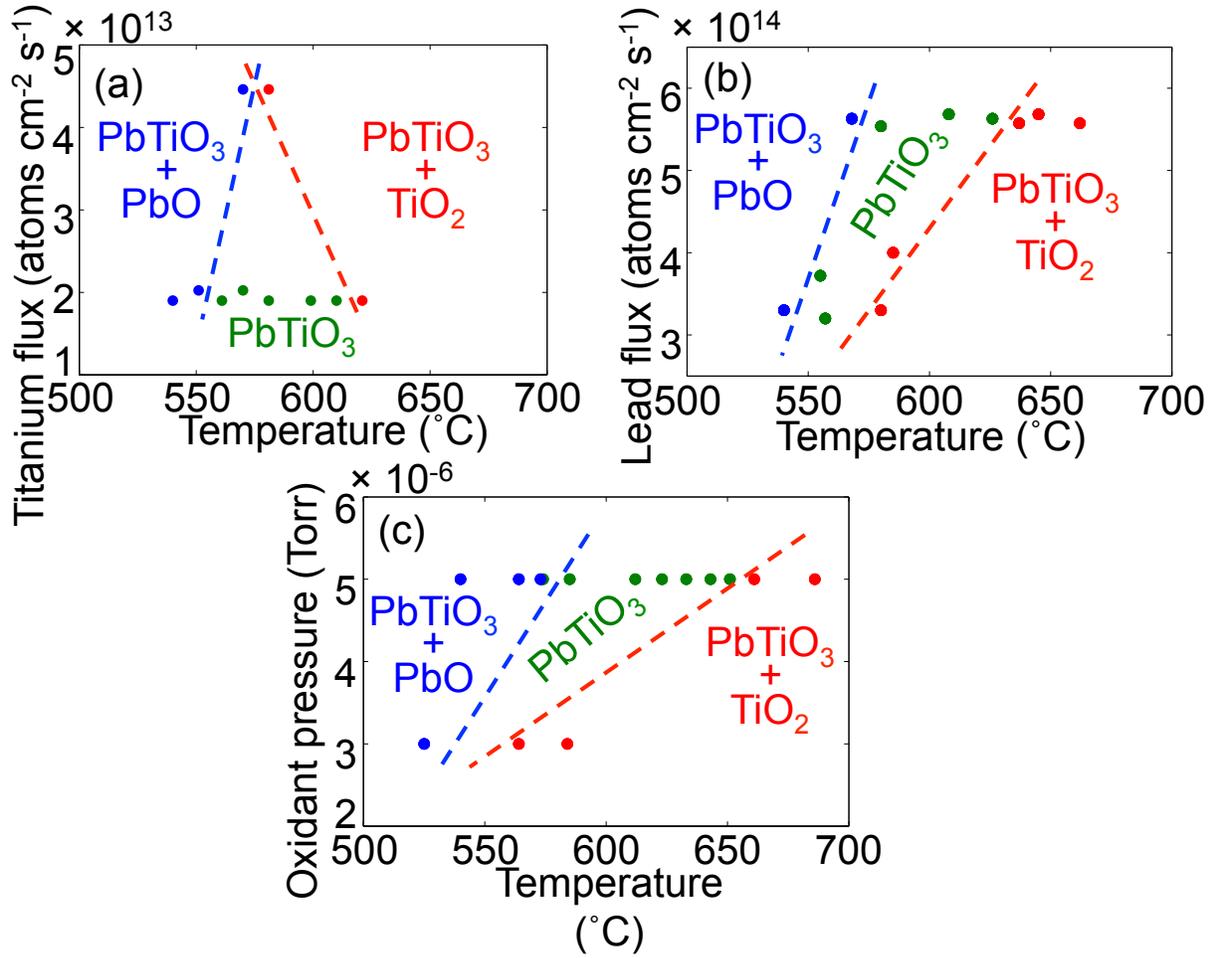


FIG. 2. (Color online) Dependence of observed film phase as a function of titanium flux, lead flux, or oxidant pressure. Only one variable (source flux or oxidant pressure) was changed, in addition to temperature, at once. Phases observed when (a) oxidant background pressure and lead flux were fixed;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

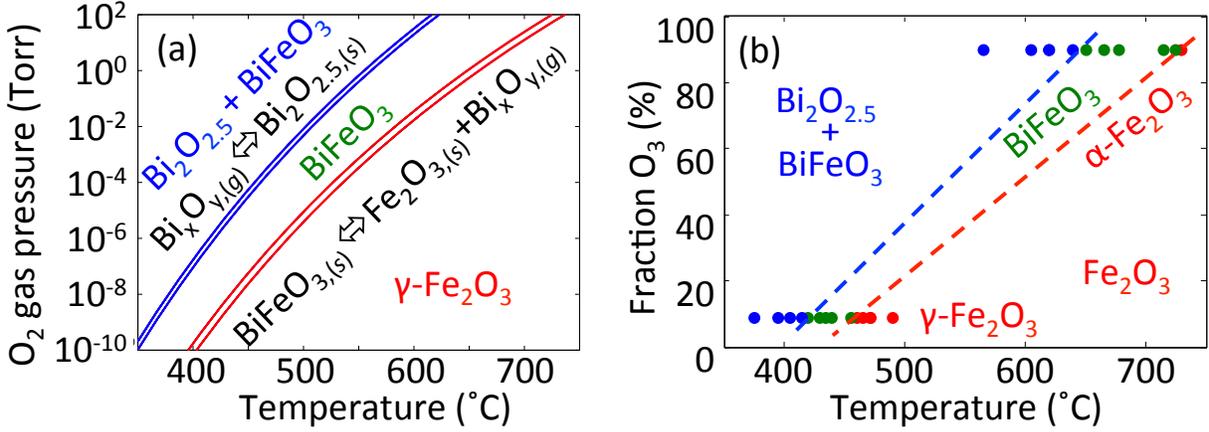


FIG. 3. (Color online) (a) Adsorption-controlled growth window of BiFeO₃ as a function of molecular oxygen pressure as calculated from thermodynamics, after Ihlefeld and co-workers²¹. (b) Dependence of observed film phase as a function of fraction ozone in the oxidant blend. Ozone We note that different phases of Fe₂O₃ appear as secondary phases outside the growth window at the two different oxidant mixtures. Ozone is 250× more active in oxidizing bismuth than diatomic oxygen in the process chamber in which we grew BiFeO₃. See Supplementary Information for a full list of growth conditions and for our measurements of ozone activity.