

# Superconducting Phase of $\text{Ti}_x\text{O}_y$ Thin Films Grown by Molecular Beam Epitaxy

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We investigate the complex relationship between the growth conditions and the structural and transport properties of  $\text{Ti}_x\text{O}_y$  thin films grown by molecular beam epitaxy. Transport properties ranging from metallicity to superconductivity and insulating states are stabilized by effectively tuning the O/Ti ratio via the Ti flux rate and the O partial pressure,  $P_{O_x}$ , for films grown on (0001)- $\text{Al}_2\text{O}_3$  substrates at 850° C. A cubic  $c$  -  $\text{TiO}_{1+\delta}$  buffer layer is formed for low O/Ti ratios while a corundum cr- $\text{Ti}_2\text{O}_3$  layer is formed under higher oxidizing conditions. Metallicity is observed for  $c$ - $\text{TiO}_{1-\delta}$  buffer layers. The superconducting  $\gamma$  -  $\text{Ti}_3\text{O}_5$  Magnéli phase is found to nucleate on a  $c$ - $\text{TiO}_{1-\delta}$  buffer for intermediate  $P_{O_x}$  conditions and an insulator-superconducting transition is observed at 4.5 K ( $T_C^{onset} = 6\text{K}$ ) for 85 nm thick films. Strain relaxation of the  $\gamma$  -  $\text{Ti}_3\text{O}_5$  occurs with increasing film thickness and correlates with a thickness-dependent increase in  $T_C$  observed for  $\text{Ti}_x\text{O}_y$  thin films.

## I. INTRODUCTION

The simple binary oxide, titanium oxide,  $\text{Ti}_x\text{O}_y$ , forms a wide range of polymorphs and Magnéli ( $\text{Ti}_n\text{O}_{n-1}$ ) phases with properties ranging from insulating rutile and anatase  $\text{TiO}_2$ , to corundum cr -  $\text{Ti}_2\text{O}_3$  which undergoes a metal-insulator transition at 450 K, to superconducting cubic NaCl-type  $c$ - $\text{TiO}$  (bulk  $T_C = 1\text{-}2\text{ K}$ ).<sup>[1-5]</sup> The ability to utilize the epitaxial stabilization of a given phase in thin films synthesised with atomic-layer control provides a route to tune the electronic properties of  $\text{Ti}_x\text{O}_y$ .<sup>[6-12]</sup> Recent reports of superconductivity in  $\text{Ti}_x\text{O}_y$  thin films as high as 11 K has sparked renewed interest in superconducting binary oxides.<sup>[13]</sup> The transition temperature,  $T_c$  has been reported to depend on the film thickness,<sup>[14, 15]</sup> oxygen stoichiometry<sup>[16, 17]</sup> and growth temperature<sup>[15]</sup>. The enhanced  $T_C$  in thin films was attributed to the formation of a high growth-temperature orthorhombic o -  $\text{Ti}_2\text{O}_3$  phase<sup>[15]</sup> ( $T_C = 8\text{ K}$ ), excess oxygen in  $c$ - $\text{TiO}_{1+\delta}$  films ( $T_C = 7.4\text{ K}$ ),<sup>[6, 16]</sup> interfacial superconductivity at stoichiometric  $c$ - $\text{TiO}$ /non-stoichiometric  $\text{TiO}_{1+\delta}$  interfaces in core-shell structures ( $T_C = 11\text{ K}$ ),<sup>[13]</sup> and the epitaxial stabilization of the  $\gamma$  -  $\text{Ti}_3\text{O}_5$  ( $T_C = 7\text{ K}$ )<sup>[18]</sup> Magnéli phase. Studies of mixed eutectic phases indicated a correlation between the coexistence of  $c$ - $\text{TiO}_{1+\delta}$ , cr- $\text{Ti}_2\text{O}_3$  and  $\gamma$  -  $\text{Ti}_3\text{O}_5$  phases with enhanced  $T_C$  hinting at the non-trivial role of interactions at interfaces between  $\text{Ti}_x\text{O}_y$  phases in enhancing  $T_C$ .<sup>[19]</sup> Thus, a critical step in understanding the enhanced transition temperature,  $T_c$ , in  $\text{Ti}_x\text{O}_y$  thin films involves elucidating the atomic-scale structure and composition of the system as a function of growth conditions (growth temperature, oxygen pressure, film thickness) using synthesis techniques which allow for the control of the film stoichiometry.

The relation between the transport properties and structural phases of  $\text{Ti}_x\text{O}_y$  was previously investigated for thin films grown by pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) on (0001)-oriented  $\alpha$  -  $\text{Al}_2\text{O}_3$ .<sup>[6, 11, 16, 18-22]</sup> Figure 1 shows the lattice structures of the lattice planes of  $\text{Ti}_x\text{O}_y$  phases grown epitaxially on (0001)-oriented  $\alpha$  -  $\text{Al}_2\text{O}_3$ . A summary of reported phases and their superconducting  $T_{CS}$ s is given in Table I. Li *et. al.* reported an orthorhombic o- $\text{Ti}_2\text{O}_3$  phase for films grown by PLD above 650°C as evidenced by high-resolution transmission electron microscopy (TEM), Raman spectroscopy and specular X-ray diffraction measurements (XRD).<sup>[11, 15]</sup> They observed a dependence of  $T_c$  on the film thickness of the o -  $\text{Ti}_2\text{O}_3$  phase with a maximum  $T_c$  of 8 K for 168 nm thick films.<sup>[15]</sup> Low temperature growth (below 650 °C) led to the stabilization of the insulating bulk trigonal cr -  $\text{Ti}_2\text{O}_3$  phase. Fan *et. al.* investigated the growth oxygen pressure dependence between  $4.5 \times 10^{-6}$  to  $6.7 \times 10^{-6}$  Torr for 80 nm thick films and found a suppression of superconductivity at high oxygen growth pressures.<sup>[16]</sup> The conclusion of a  $c$ - $\text{TiO}$  structure was based on the analysis of the film layers close to the substrate by TEM and XRD measurements.<sup>[6]</sup> It is important to note that while multiple structures have been proposed/observed, the  $T_{CS}$ s are consistent with the reported thickness-dependence.<sup>[14, 15]</sup> Additionally, local TEM measurements indicated a

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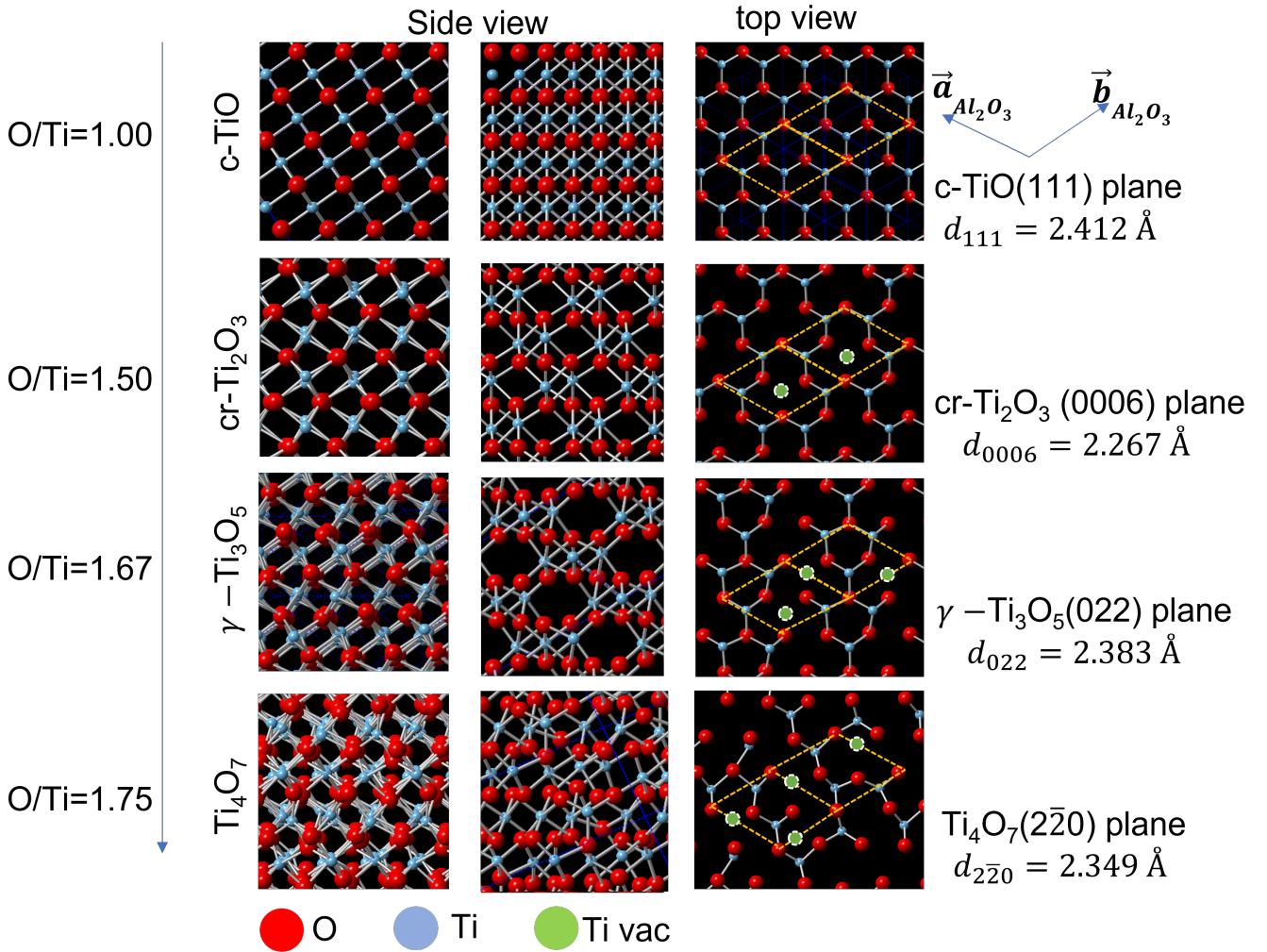


FIG. 1. Atomic structure of cubic c-TiO, corundum  $\text{cr}-\text{Ti}_2\text{O}_3$ ,  $\gamma-\text{Ti}_3\text{O}_5$  and  $\text{Ti}_4\text{O}_7$  along projections in the  $\alpha-\text{Al}_2\text{O}_3$  [10\bar{1}0] direction (left panel), [11\bar{2}0] direction (middle panel) and the [0001] direction (right panel).

transitional c-TiO interface layer for o-Ti<sub>2</sub>O<sub>3</sub>.[15] A study of eutectic  $\text{Ti}_x\text{O}_y$  prepared by varying the growth and post-growth Ar annealing conditions showed a variation of  $T_C$  with the relative fractions of c-TiO,  $\gamma-\text{Ti}_3\text{O}_5$  and  $\text{cr}-\text{Ti}_2\text{O}_3$ . Thus, the complexity of the system requires a systematic investigation of how specific growth conditions influence the relative fractions of the phases of  $\text{Ti}_x\text{O}_y$  and the resulting effect on the transport properties.

In this letter, we investigate the transport and structural properties of  $\text{Ti}_x\text{O}_y$  films grown by MBE to elucidate the effect of tuning the film stoichiometry and thickness on the superconducting properties of  $\text{Ti}_x\text{O}_y$  thin films. Here, we perform high-resolution synchrotron X-ray diffraction measurements on  $\text{Ti}_x\text{O}_y$  films grown on (0001)-oriented  $\alpha-\text{Al}_2\text{O}_3$  at 850 °C. The film stoichiometry is tuned by controlling the growth oxygen pressure,  $P_{O_x}$ , Ti flux rate, and film thickness.  $P_{O_x}$  is varied from  $4 \times 10^{-8}$  Torr to  $1 \times 10^{-6}$  Torr. Films grown at low oxygen partial pressures ( $P_{O_x} \leq 1 \times 10^{-7}$  Torr) are found to be metallic with carrier concentrations ranging from  $3 \times 10^{22} \text{ cm}^{-3}$  at 300 K to  $6 \times 10^{21} \text{ cm}^{-3}$  at 10 K. Metallicity is correlated with the formation of oxygen-deficient  $\text{c-TiO}_{1-\delta}$ . By tuning the  $P_{O_x}$ , the Ti flux rate and the film thickness, an insulating-superconducting transition is observed in 85 nm thick films which are characterized by a thin  $\text{c-TiO}_{1\pm\delta}$  interfacial buffer layer and the formation of the  $\gamma-\text{Ti}_3\text{O}_5$  phase. Strain relaxation is observed in  $\gamma-\text{Ti}_3\text{O}_5$  with increasing film thickness and correlates with a thickness-tuned  $T_C$  observed in  $\text{Ti}_x\text{O}_y$  films.[14, 15]

Substrate (Method)	Thickness	Structure	T <sub>c</sub>
Al <sub>2</sub> O <sub>3</sub> (PLD)	80 nm	TiO <sub>1±δ</sub>	7.4 K [6]
(Sintering)	bulk	TiO <sub>1±δ</sub>	5.5 K [22]
Al <sub>2</sub> O <sub>3</sub> (PLD)	168 nm	o-Ti <sub>2</sub> O <sub>3</sub>	8 K [15]
Al <sub>2</sub> O <sub>3</sub> (PLD)	120 nm	o-Ti <sub>2</sub> O <sub>3</sub>	I (no T <sub>c</sub> ) [11]
Al <sub>2</sub> O <sub>3</sub> (PLD)	120 nm	γ - Ti <sub>3</sub> O <sub>5</sub>	7.1 [18]
LSAT, MgAl <sub>2</sub> O <sub>4</sub> (PLD)	120 nm	Ti <sub>4</sub> O <sub>7</sub>	3.0 [18]
Al <sub>2</sub> O <sub>3</sub> (PLD)	80 nm	TiO <sub>1±δ</sub>	1.4-6 K [16]
Al <sub>2</sub> O <sub>3</sub> (PLD)	150 nm	cr-Ti <sub>2</sub> O <sub>3</sub>	I (no T <sub>c</sub> ) [20]

TABLE I. Summary of reported Ti<sub>x</sub>O<sub>y</sub> structures and superconducting transition temperatures, T<sub>c</sub>. I refers to insulating phase.

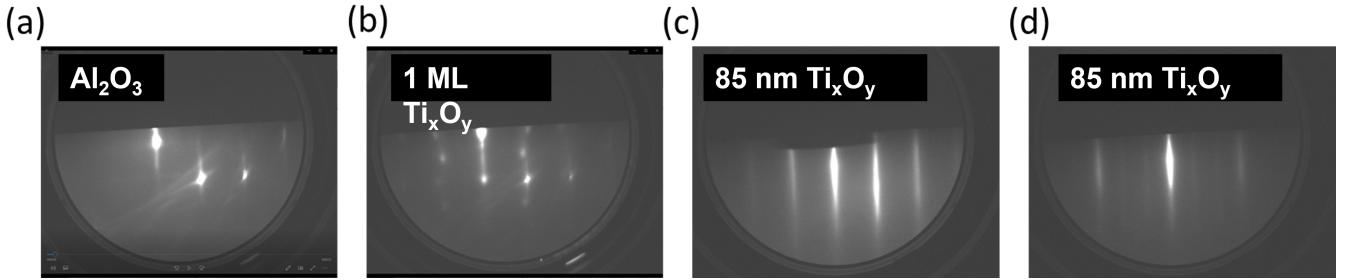


FIG. 2. Evolution of the surface RHEED pattern for the growth of 85 nm thick Ti<sub>x</sub>O<sub>y</sub> film on (0001)-oriented  $\alpha$  - Al<sub>2</sub>O<sub>3</sub> at  $P_{O_2} = 2 \times 10^{-7}$  Torr and a growth rate of 2.5 Å/min (Sample E). (a) Diffraction pattern of the initial Al<sub>2</sub>O<sub>3</sub> surface (b) after 1 ML Ti<sub>x</sub>O<sub>y</sub> along the [1120] azimuth, (c) after 85 nm along the [1120] and (d)[1010] directions.

## II. RESULTS AND DISCUSSION

Ti<sub>x</sub>O<sub>y</sub> films with thicknesses 25-85 nm were grown by oxide MBE. Prior to growth, the Al<sub>2</sub>O<sub>3</sub> substrates were annealed at 1100 °C in a tube furnace tube for 12 hours. Atomic force microscope images show smooth surfaces with atomic steps. The films were grown by deposition of Ti from an effusion cell under partial pressures of molecular oxygen ranging from  $4 \times 10^{-8}$  to  $1 \times 10^{-6}$  Torr at a substrate temperature of 850 °C. The growth rates were determined from the Ti fluxes measured by a quartz crystal monitor and X-ray reflectivity measurements to be 1.3-2.5 Å/min. The sample growth conditions are summarized in Table II. After growth, the films were cooled down at a rate of 25 °C/min from the deposition temperature to room temperature in vacuum.

Sample	Thickness	Ti flux rate (atoms/cm <sup>2</sup> s)	P <sub>O<sub>x</sub></sub> (Torr)	Normalized P <sub>O<sub>x</sub></sub> /Ti <sub>rate</sub>	Phase	Transport
A	25 nm	$1.2 \times 10^{13}$	$3 \times 10^{-7}$	2.9	cr - Ti <sub>2</sub> O <sub>3</sub>	I
B	25 nm	$1.2 \times 10^{13}$	$4 \times 10^{-8}$	0.4	c-TiO <sub>1-δ</sub> , γ - Ti <sub>3</sub> O <sub>5</sub>	M
C	25 nm	$1.2 \times 10^{13}$	$8 \times 10^{-8}$	0.8	c-TiO <sub>1-δ</sub> , γ - Ti <sub>3</sub> O <sub>5</sub>	M
D	45 nm	$2.4 \times 10^{13}$	$2 \times 10^{-7}$	1.0	c-TiO <sub>1-δ</sub> , γ - Ti <sub>3</sub> O <sub>5</sub>	M,SC
E	85 nm	$2.4 \times 10^{13}$	$2 \times 10^{-7}$	1.0	c-TiO, γ - Ti <sub>3</sub> O <sub>5</sub>	I,SC
F	80 nm	$1.7 \times 10^{13}$	$2 \times 10^{-7}$	1.4	c-TiO/γ - Ti <sub>3</sub> O <sub>5</sub> , cr - Ti <sub>2</sub> O <sub>3</sub> , Ti <sub>4</sub> O <sub>7</sub>	I, SC

TABLE II. Summary of growth conditions, film thickness and measured phases and transport properties of MBE-grown Ti<sub>x</sub>O<sub>y</sub> films on (0001)-oriented  $\alpha$  - Al<sub>2</sub>O<sub>3</sub>. I, M and SC refer to the insulating, metallic and superconducting phases, respectively. The  $P_{O_x}/Ti_{rate}$  are normalized to the values for the superconducting Sample E.

Figure 2(a) shows an *in-situ* reflection high energy electron diffraction (RHEED) image of the initial Al<sub>2</sub>O<sub>3</sub> substrate surface prior to deposition of the Ti<sub>x</sub>O<sub>y</sub> films at  $P_{O_x} = 2 \times 10^{-7}$  Torr. Figure 2(b) shows the RHEED pattern after the deposition of 1 ML of Ti<sub>x</sub>O<sub>y</sub>. Roughening and relaxation are evident from the spotty nature of the RHEED pattern and the development of streaks with a closer spacing than the diffraction from the substrate. A streaky 2D pattern

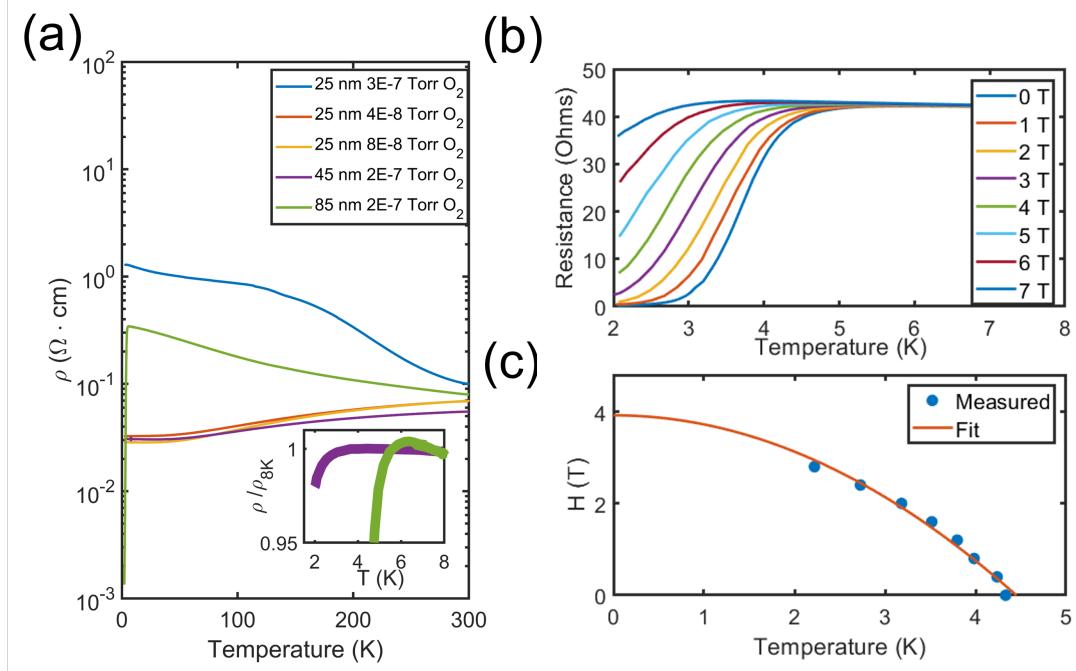


FIG. 3. (a) Comparison of sheet resistance for MBE-grown  $\text{Ti}_x\text{O}_y$  films as a function of growth oxygen pressure and film thickness. The inset shows the drop in resistivity at low temperatures for the superconducting samples (Samples D and E). (b) Resistivity as a function of magnetic field applied in-plane for 85 nm thick  $\text{Ti}_x\text{O}_y$  film (Sample E) grown at  $P_{\text{O}_x} = 2 \times 10^{-7}$  Torr. (c) Relationship between critical magnetic field and  $T_C$  and the corresponding Werthamer-Helfand-Hohenberg (WHH) fit.

emerges after the 2nd ML and remains for the entire film growth. Figure 2(c) and 2(d) show the RHEED patterns after the growth of an 85 nm thick film along the  $[11\bar{2}0]$  and  $[10\bar{1}0]$  directions respectively. The narrow streaks are indicative of a smooth 2D surface. Along the  $[10\bar{1}0]$  direction, a 3x reconstruction is observed. A comparison of the final RHEED patterns of Samples A-F is shown in Figure S1 of the supplemental materials.[23] Atomic force microscope images of the as-grown films (See Figure S2 of supplemental materials)[23] show atomically flat layers with step-like features identical to the substrate.

### A. Transport Properties

The dependence of the transport properties on the film thickness and growth conditions is determined by comparing the resistivities of a series of  $\text{Ti}_x\text{O}_y$  films with thicknesses between 25 nm and 85 nm for  $4 \times 10^{-8} \leq P_{\text{O}_x} \leq 3 \times 10^{-7}$  Torr in Figure 3(a). The transport measurements are performed in the Van der Pauw configuration using Au contacts deposited on the corners of 5mm  $\times$  5 mm samples. Films grown with  $P_{\text{O}_x} \leq 1 \times 10^{-7}$  Torr are metallic for thicknesses less than 45 nm. Growth at higher oxygen pressures ( $P_{\text{O}_x} \geq 3 \times 10^{-7}$  Torr) results in insulating transport properties.

At the intermediate growth pressure of  $P_{\text{O}_x} = 2 \times 10^{-7}$  Torr, the transport properties depend on the film thickness and the Ti flux rate. The 45 nm film grown at  $P_{\text{O}_x} = 2 \times 10^{-7}$  Torr (Sample D) is metallic and undergoes a metal-superconducting transition at  $\sim 3.7$  K. The thicker 85 nm film (Sample E) is insulating below 300 K and transitions to a superconducting state at 4.5 K. The absence of superconductivity above 2 K for the 25 nm thick films, for the Ti flux rates investigated, is consistent with the thickness dependence of  $T_C$  observed for PLD grown films.[15] Films grown with  $P_{\text{O}_x} > 8 \times 10^{-7}$  Torr are insulating due to the formation of  $\text{TiO}_2$  as evidenced by X-ray diffraction measurements.

Superconductivity in the 85 nm film (Sample E) is confirmed by measuring the resistance as a function of a magnetic field,  $H$  applied parallel to the sample surface. Figure 3(b) shows the suppression of  $T_C$  for  $0 \text{ T} < H < 7 \text{ T}$ . The upper critical field  $H_{C2}(T)$  is defined by a 90% drop in the normal state resistance. Figure 3(c) shows a plot of  $H_{C2}$  as a function of temperature. The results are fit to the Werthamer-Helfand-Hohenberg (WHH) equation  $H_{C2}(T) = H_{C2}(0)[1 - (\frac{T}{T_C})^2]$ .[24] From the fit, the upper critical field at 0 K,  $H_{C2}(0)$  is determined to be 9.8 T. The coherence length,  $\xi$ , is determined to be 5.7 nm from the the Ginzburg-Landau superconducting coherence length

relation,  $\xi = [(\hbar/2e)/(H_{c2}(0))]^{1/2}$ . The measured coherence length is comparable to previous reports. [6, 16]

The insulating-superconducting transition has been previously observed in  $\text{Ti}_x\text{O}_y$  films[3, 14] and another 3D superconductor,  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  which also exhibits a strong dependence of  $T_C$  on the film thickness and the presence of multiple polymorphs (tetragonal and orthorhombic fractions of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ).[25] Thus, structural disorder arising from local fluctuations in oxygen content may enhance disorder leading to the insulator-superconductor transition.

## B. XRD Structure

The relationship between the synthesis conditions, crystal structure, and the transport properties is determined by synchrotron XRD measurements at the 33ID beamline at the Advanced Photon Source. Figure 4(a) shows a specular scan around the substrate (0006) Bragg peak measured with an X-ray energy of 16 KeV ( $\lambda = 0.774 \text{ \AA}$ ) for a series of  $\text{Ti}_x\text{O}_y$  samples. For Sample A grown with the highest  $P_{O_x}/T_{rate}$  ratio, the main Bragg peak corresponds to the cr- $\text{Ti}_2\text{O}_3$  phase. A second peak is observed corresponding to a slightly O-rich c-TiO layer.

The diffraction intensities for the 25 nm metallic  $\text{Ti}_x\text{O}_y$  film (Sample B) comprise of a broad shoulder with lattice spacing  $d=2.423 \text{ \AA}$  and a main peak with  $d=2.375 \text{ \AA}$ . The shoulder and main peaks correspond, respectively, to the (111) Bragg reflection of oxygen-deficient c- $\text{TiO}_{1-\delta}$  and the (022) Bragg peak of  $\gamma - \text{Ti}_3\text{O}_5$  compressively strained to the buffer layer.

While weak insulating behavior has been reported for c- $\text{TiO}_{1+\delta}$ , the observation of metallicity in Samples B and C arises from the stabilization of Ti-rich/oxygen poor c- $\text{TiO}_{1-\delta}$  due to the low growth oxygen pressures. For  $0.05 \leq \delta \leq 0.2$ , Hulm *et. al.* show metallicity for as-cast single-phase c- $\text{TiO}_{1-\delta}$  samples.[3] An expansion in the lattice parameter is expected for the oxygen deficient c- $\text{TiO}_{1-\delta}$ ,[3] hence, from fits to the 00L data, the broad shoulder at low  $L$  ( $c_{measured}=4.19 \text{ \AA}$ ) is assigned to a  $\sim 15 \text{ \AA}$  thick metallic c- $\text{TiO}_{1-\delta}$  layer which dominates the resistivity measurements in Figure 3(a). Annealing Sample B in flowing  $\text{O}_2$  for 3 hours at  $600 \text{ }^\circ\text{C}$  leads to the oxidation of both layers and a shift in the Bragg peaks to  $d=2.324 \text{ \AA}$  corresponding to the formation of cr- $\text{Ti}_2\text{O}_3$  and a metal-insulator transition.

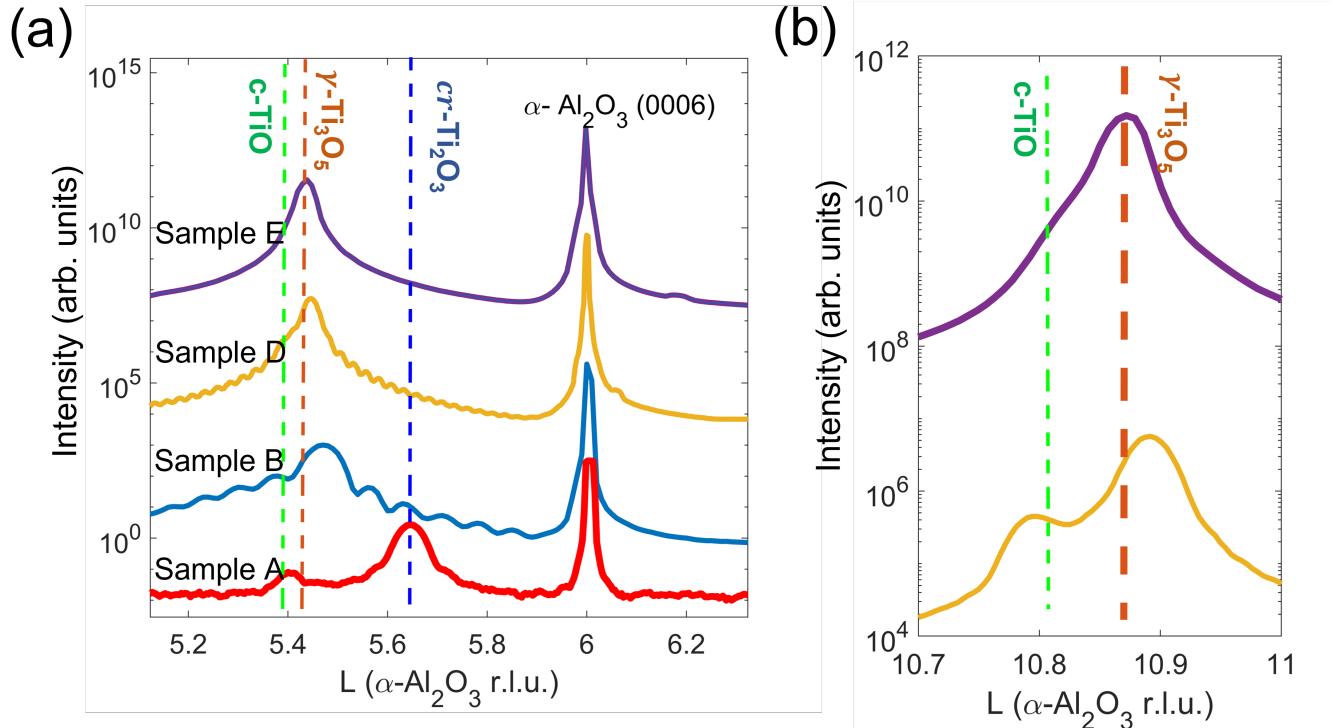


FIG. 4. (a) Comparison of specular X-ray diffraction around the  $\alpha - \text{Al}_2\text{O}_3$  (0006) Bragg peak for Samples A (25 nm,  $P_{O_x} = 3 \times 10^{-7} \text{ Torr}$ ), B (25 nm,  $P_{O_x} = 4 \times 10^{-8} \text{ Torr}$ ), D (45 nm,  $P_{O_x} = 2 \times 10^{-7} \text{ Torr}$ ) and E (85 nm,  $P_{O_x} = 2 \times 10^{-7} \text{ Torr}$ )  $\text{Ti}_x\text{O}_y$  films grown by MBE. (b) Corresponding reflections for Sample D and E at higher  $q$ .

The 45 nm metallic Sample D also has a main peak at  $d=2.385 \text{ \AA}$  corresponding to the (022) peak of  $\gamma - \text{Ti}_3\text{O}_5$

and a shoulder with  $d=2.4171$  Å corresponding to slightly oxygen-deficient  $c\text{-TiO}_{1-\delta}$ . The metallicity observed for this sample is again, due to the metallic oxygen-deficient  $c\text{-TiO}_{1-\delta}$  layer. Around 3.7 K, a decrease in the resistivity is observed (Figure 3(a) inset) due to the superconducting transition in the  $\gamma\text{-Ti}_3\text{O}_5$  layer.[18]

The superconducting Sample E has a main Bragg peak at  $d=2.388$  Å corresponding to the (022) peak of relaxed  $\gamma\text{-Ti}_3\text{O}_5$ . Close to the (044)  $\gamma\text{-Ti}_3\text{O}_5$  in Figure 4(b), we observe a shoulder at lower  $q$  which corresponds to the (222) reflection of cubic stoichiometric  $\text{TiO}$  ( $c_{\text{measured}} = 4.167$  Å). The metallic phase is strongly suppressed, possibly, due to the longer deposition time which allows for complete oxidation of the  $c\text{-TiO}$  buffer layer. The transport properties of the Sample E in Figure 3(a) are dominated by the superconducting relaxed  $\gamma\text{-Ti}_3\text{O}_5$  phase.[17]

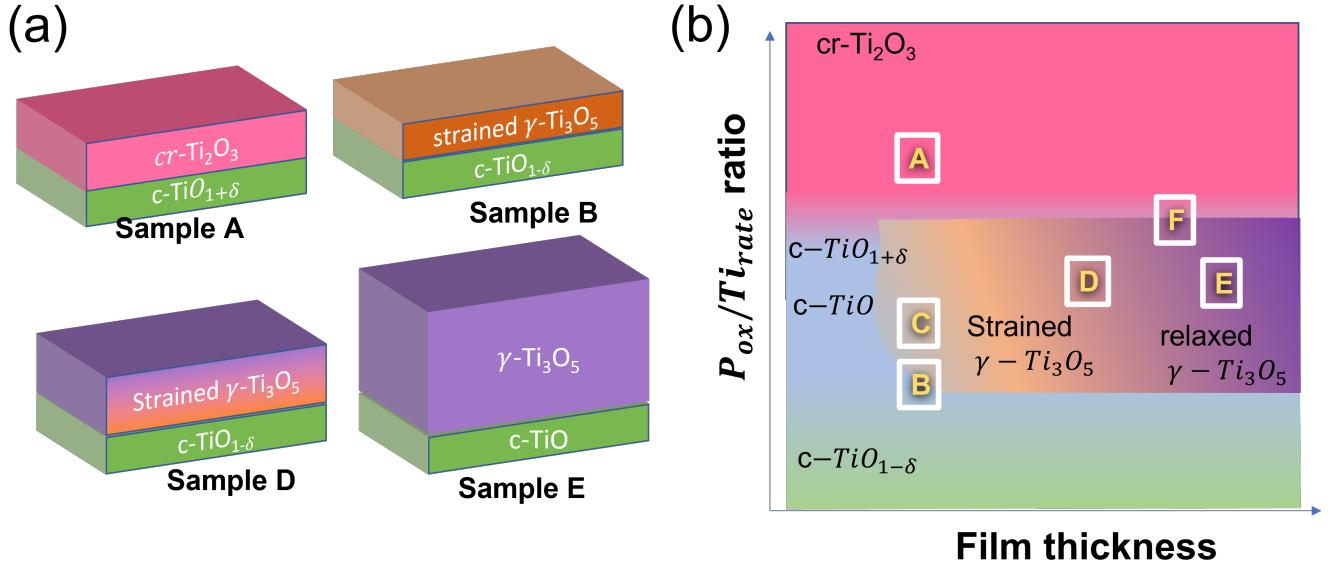


FIG. 5. (a) Schematic structures of samples A,B,D and E determined from X-ray diffraction measurements and (b) the corresponding phase diagram showing the relationship between the ratio of the growth oxygen pressure  $P_{ox}$  to the Ti flux rate and the film thickness.

Based on the X-ray diffraction measurements, the emergent picture of the structural profiles of the films under different growth conditions is summarized in Figure 5. Oxygen-poor growth of  $\text{Ti}_x\text{O}_y$  on (0001)-oriented  $\alpha\text{-Al}_2\text{O}_3$  at high growth temperatures leads to the formation of a thin (111)-oriented cubic  $\text{TiO}_{1-\delta}$  metallic buffer layer. As the film thickness increases, if the oxygen pressure is sufficiently high, the structure transforms into the Magnéli  $\gamma\text{-Ti}_3\text{O}_5$  phase. The  $\gamma\text{-Ti}_3\text{O}_5$  is initially strained to the buffer layer and the strain is relaxed as the film thickness is increased. Since pressure is known to suppress superconductivity in  $\text{Ti}_x\text{O}_y$ ,[6] this picture is consistent with the observed increase in  $T_C$  with increasing film thickness.[15, 17]

### C. Phase segregation in $\text{Ti}_x\text{O}_y$

The transport and structural results indicate a strong correlation between the growth conditions and film thickness on the physical and structural properties of the  $\text{Ti}_x\text{O}_y$  films. Stoichiometric  $c\text{-TiO}$  has an NaCl structure with lattice constant  $c=4.177$  Å. The NaCl structure is stable for oxygen concentrations ranging from 0.8 to 1.3 with  $T_C$  increasing from 0.5 K to 1 K for bulk  $c\text{-TiO}_x$ .[3, 5, 8, 26] The tendency of  $\text{Ti}_x\text{O}_y$  to form Magnéli phases and related polymorphs of the form  $\text{Ti}_n\text{O}_{2n-1}$  suggests that the oxygen stoichiometry and the growth conditions strongly influence the structure and physical properties of the thin films.

To further investigate the delicate balance between film stoichiometry and the transport properties of the  $\text{Ti}_x\text{O}_y$  system, we consider the structural properties of an eutectic film formed by growing at a reduced Ti rate with the oxygen pressure of  $2 \times 10^{-7}$  Torr. The slight increase in the O/Ti ratio is expected to allow for the thermodynamic stabilization of oxygen-rich  $\text{Ti}_x\text{O}_y$  phases such as  $\text{cr}\text{-Ti}_2\text{O}_3$ .

The initial RHEED images for the sample grown at the lower Ti rate shows diffraction spots indicative of surface roughening, however, the final RHEED image in Figure 6(a) shows well defined 2D streaks after the growth of 80 nm. Figure 6(b) shows an optical image of the as-grown film. Clear dark and bright regions are observed indicating

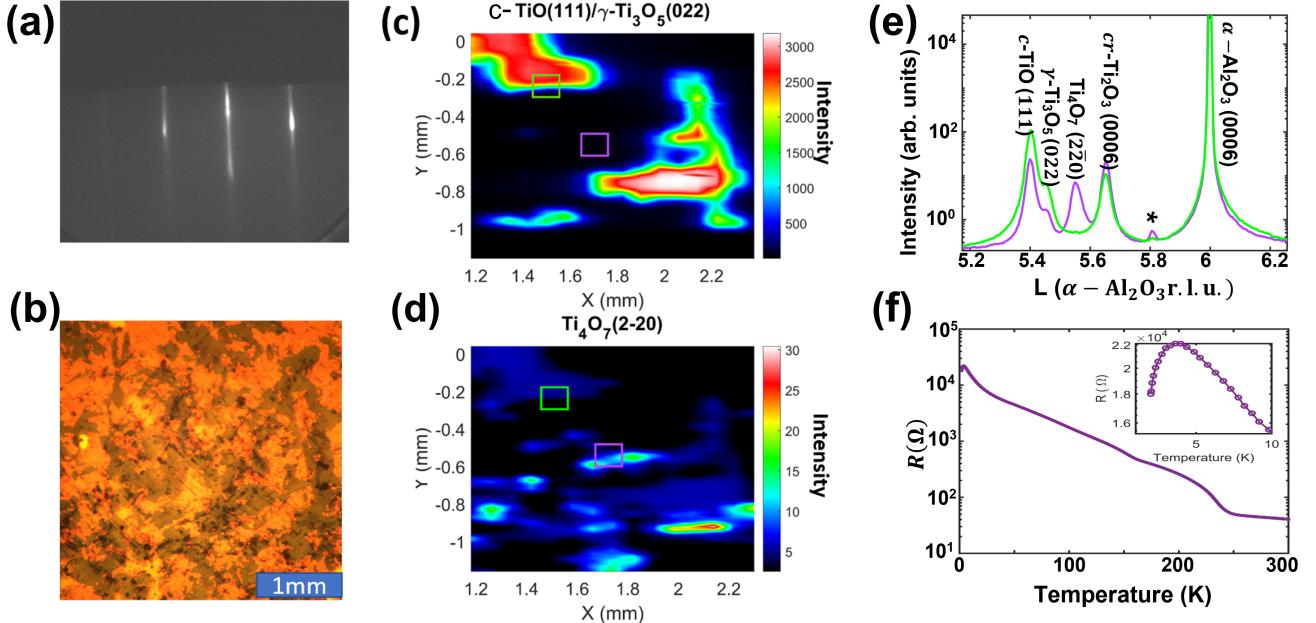


FIG. 6. Structural and transport properties of a 80 nm thick  $\text{Ti}_x\text{O}_y$  film grown at Ti flux rate of  $1.8 \text{ \AA/min}$  in  $P_{\text{O}_2} = 2 \times 10^{-7}$  Torr (Sample F). (a) Reflection high energy diffraction for 80 nm  $\text{Ti}_x\text{O}_y$  on (0001)-oriented  $\text{Al}_2\text{O}_3$ . (b) Optical micrograph of film indicating structural domains. High-resolution synchrotron X-ray diffraction raster maps around Bragg peaks observed at diffraction conditions fixed for (c) c-TiO (111) Bragg peak and (d)  $\text{Ti}_4\text{O}_7$  (2-20) Bragg peak indicating structural phase separation. (e) Specular diffraction along the substrate 00L direction at different points on the sample. (f) Resistance versus temperature. The inset shows the superconducting transition at low temperature.

macroscopic phase separation. These variations are not observed for the uniform films previously discussed (Figure S3 of supplemental materials)[23]. To determine the differences in the structure of the observed phases, we perform micro-diffraction experiments at the Advanced Photon source where the X-ray beam is focused to a  $20\mu\text{m} \times 40\mu\text{m}$  spot size using a KirkpatrickBaez mirror. Figure 6(c) and 6(d) shows diffraction intensity maps with the diffraction conditions fixed at the c-TiO (111) Bragg reflection and the  $\text{Ti}_4\text{O}_7$  (2-20) reflection. The maps show that the two phases are not uniformly distributed throughout the sample. Figure 6(e) shows (00L) scans at locations close to the c-TiO phase and the  $\gamma - \text{Ti}_3\text{O}_5$  phase. The scans show that the intensity of the  $\text{Ti}_4\text{O}_7$  is suppressed in regions of the film with increased fractions of the c-TiO and  $\gamma - \text{Ti}_3\text{O}_5$  phase. At both locations surveyed in Figure 6(e), a cr- $\text{Ti}_2\text{O}_3$  peak is present indicating that the c-TiO/ $\gamma - \text{Ti}_3\text{O}_5$  and  $\text{Ti}_4\text{O}_7$  grains are located in a matrix of the insulating cr- $\text{Ti}_2\text{O}_3$  phase (The regions with 0 intensity in Figure 6(c) and (d)). The  $\text{Ti}_4\text{O}_7$  grains have lateral dimensions on the order of  $100 \mu\text{m}$  while the c-TiO/ $\gamma - \text{Ti}_3\text{O}_5$  grains are an order of magnitude larger in dimensions. An additional peak indicated by the asterisk (\*) at  $L \approx 5.8 \text{ r.l.u.}$  ( $d = 2.18 \text{ \AA}$ ) suggests the presence of a small fraction of rutile  $\text{TiO}_2$ .

The transport properties of the eutectic sample is shown in Figure 6(f). The multiple electronic transitions are consistent with the coexistence of multiple structural phases. Transitions in the resistivity are observed at 250 K and 150 K which are consistent with reported transitions for cr- $\text{Ti}_2\text{O}_3$  [19] and  $\text{Ti}_4\text{O}_7$  [18]. The resistivity drops at 3 K is indicative of a superconducting transition expected for either  $\text{Ti}_4\text{O}_7$  or  $\gamma - \text{Ti}_3\text{O}_5$ , however, no zero-resistant state is observed at the instruments minimum temperature of 2 K.

### III. CONCLUSION

In conclusion, we have used a combination of high-resolution synchrotron X-ray diffraction mapping and temperature-dependent transport to investigate the correlation between film thickness, phase separation and superconductivity in  $\text{Ti}_x\text{O}_y$  films grown on (0001)-oriented  $\alpha - \text{Al}_2\text{O}_3$ . The films with thicknesses ranging from 25 to 85 nm are grown by MBE where the oxygen stoichiometry of the films is tuned by the oxygen partial pressure and the Ti flux rate during growth. The transport properties are correlated with the  $P_{\text{ox}}/\text{Ti}_{\text{rate}}$  ratio and thickness-dependent strain relaxation. A metallic c-TiO<sub>1- $\delta$</sub>  buffer layer is formed for films grown under oxygen-poor conditions. A superconducting Magnélli

$\gamma$  –  $Ti_3O_5$  layer nucleates on the buffer layer. Strain-relaxation occurs as the film thickness increases and correlates with a thickness-dependent increase in  $T_C$ . As the  $P_{ox}/Ti$  flux ratio increases, the buffer composition transitions to an insulating cr- $Ti_2O_3$  phase. A mixed-phase structure is formed for  $P_{ox}/Ti$  flux ratios close to the c- $TiO$ /cr- $Ti_2O_3$  phase boundary. These results suggest that the thickness-dependence of  $T_C$  in  $Ti_xO_y$  is related to a complex interplay between, strain and the nucleation kinetics of  $Ti_xO_y$  phases and polymorphs. Thus, a complete elucidation of phase formation and phase separation and the electronic and structural interactions at inter-phase boundaries will allow for understanding and enhancing  $T_C$  in atomically-thin  $Ti_xO_y$  layers.

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## IV. DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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