Superconductivity in Ti$_4$O$_7$ and γ-Ti$_3$O$_5$ films

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Titanium dioxide is one of the most popular compounds among simple oxides. Except for the fully oxidized titanate, titanium oxides have partially filled d states and their exotic properties have captured attention. Here, we report on the discovery of superconductivity in Ti$_4$O$_7$ and γ-Ti$_3$O$_5$ in a thin film form. The epitaxial Ti$_4$O$_7$ and γ-Ti$_3$O$_5$ thin films were grown using pulsed-laser deposition on (LaAlO$_3$)$_{2/3}$SrAlO$_2$$_{2/3}$O$_{1.7}$ and α-Al$_2$O$_3$ substrates, respectively. The highest superconducting transition temperatures are 3.0 K and 7.1 K for Ti$_4$O$_7$ and γ-Ti$_3$O$_5$, respectively. The mechanism behind the superconductivity is discussed on the basis of electrical measurements and previous theoretical predictions. We conclude that the superconductivity arises from unstabilized bipolaronic insulating states with the assistance of oxygen non-stoichiometry and epitaxial stabilization.

In the periodic table, titanates are the first group of simple oxides, which are defined as oxides consisted of a kind of the cation and oxygen ion(s), indicating metallicity, and all the simple oxides of scandium or much lighter elements are insulating. Therefore, the choice of titanates is favourable for large electron–phonon coupling. In the periodic table, titanates are the first group of simple oxides, which are defined as oxides consisted of a kind of the cation and oxygen ion(s), indicating metallicity, and all the simple oxides of scandium or much lighter elements are insulating. Therefore, the choice of titanates is favourable for large electron–phonon coupling.

We find that Ti$_4$O$_7$ and γ-Ti$_3$O$_5$ films synthesized using epitaxial growth are superconductors with $T_c$ of 3.0 K and 7.1 K, respectively. The temperature dependence of resistivity strongly depended on the growth atmosphere. The Ti$_4$O$_7$ film grown under a less oxidative condition of Ar atmosphere, and the superconducting phase appeared at low temperatures. These results and the previous theoretical prediction suggest that epitaxial stabilization and oxygen non-stoichiometry play key roles in the realization of superconductivity in these titanates.

Results

Structural characterization. The formation of the Ti$_4$O$_7$ and γ-Ti$_3$O$_5$ phases was verified using x-ray diffraction (XRD). The out-of-plane XRD patterns showed intense reflections from the Ti$_4$O$_7$ films grown on (LaAlO$_3$)$_{2/3}$SrAlO$_2$$_{2/3}$O$_{1.7}$ (100) substrates and the γ-Ti$_3$O$_5$ film grown on α-Al$_2$O$_3$ (0001) substrates [Fig. 2(a) and (b), respectively]. These substrates are insulating, non-magnetic, and exhibit high resistance, providing advantages in the growth and search of a superconducting sample. Irrespective of the growth condition, Ti$_4$O$_7$ 202 reflection was detected at $2\theta = 42.38^\circ$, corresponding to $d_{202} = 2.13 \text{ Å}$. No other film reflections except for the 404 reflection at $2\theta = 92.60^\circ$ was detected in wide-range XRD patterns. The γ-Ti$_3$O$_5$ 022 reflection...
was detected at $2\theta = 37.83^\circ$, corresponding to $d_{022} = 2.38$ Å. The out-of-plane single orientation was verified using wide-range XRD patterns (not shown). Surface morphology of the films are shown in the inset of Fig. 2. The small grains were observed and the root mean square roughness was about 1 nm for both films. Their surface morphology was different from that of TiO and Ti$_2$O$_3$ (see Fig. S1 in Supplementary information)

Because of various polymorphisms with different ratios of oxygen to titanium, their crystal structures must be carefully distinguished. Then, we used the tilt angle $\chi$-dependence of $2\theta-\theta$ XRD profiles to survey the asymmetric film reflections (see Figs S2 and S6 in Supplementary Information). Reflections coming from the substrate and film were found at characteristic $\chi$ angles. Since the intensities of the film reflections were too weak to determine the $d$ values of interplanar spacing precisely, synchrotron radiation XRD measurements were also performed (see Figs S3–S5, S7 and S8 in Supplementary Information). From the $d$ values and $\chi$ angles, we identified the Miller indices as those listed in Tables S2 and S3. In comparison to the previous structural analyses of titanates

Figure 1. Crystal structures of titanates. Schematics of the crystal structures for (a) the first member of Magnéli-phase Ti$_4$O$_7$ and (b) $\gamma$-Ti$_3$O$_5$.

Figure 2. Structural characterization of titanate films. (a) Out-of-plane XRD patterns for Ti$_4$O$_7$ films grown on LSAT (100) substrates under Ar gas at $1 \times 10^{-3}$ Torr (top) and under oxygen gas at $1 \times 10^{-7}$ Torr (bottom). (b) Out-of-plane XRD pattern for the $\gamma$-Ti$_3$O$_5$ film grown on $\alpha$-Al$_2$O$_3$ (0001) substrates under oxygen gas at $1 \times 10^{-7}$ Torr. The insets show AFM images (5 $\mu$m x 5 $\mu$m) taken for the same films. Colour codes are 13 nm and 8 nm in height for (a) and (b), respectively.
At 300 K (10 K), the inverse titanate films and bulk are listed in Tables S2 and S4 for comparison. The resistivity curves strongly depended on the growth atmosphere for Ti4O7 films [Fig. 3(a)]. For the film grown under \( P_{O_2} = 1 \times 10^{-7} \text{ Torr} \), the a-axis lattice constant of both TiO7 films is smaller than that of bulk. In contrast, b- and c-axes lattice constants of the former TiO7 films were in agreement with those of bulk. The b- (c-) axis lattice constant of the latter TiO7 film was smaller (larger) than that of bulk. We note that the c-axis length directly corresponds to the Ti–Ti bond length in the TiO6 tetramer [see Fig. 1(a)] and c-axis lattice constant of the former TiO7 film is larger than that of the latter TiO7 film. For the Ti4O7 film, all of the lattice constants were smaller than those of bulk. The lattice parameters of the titanate films and bulk are listed in Tables S2 and S4 for comparison.

The resistivity upturn was much weaker, suggesting the suppression of the insulating Ti4O7 film at low temperatures. In contrast, the inverse H at 10 K was four orders of magnitude smaller than that of bulk Ti4O7. The variation in the Hall coefficient (\( R_H \)) during warming exhibited a tendency similar to that of resistivity. At 300 K (10 K), the inverse \( R_H \) was \( 3.6 \times 10^{-4} \) (1.5) \( \mu \Omega \text{cm} \) \( \Omega^{-1} \) \( \text{cm} \) \( \Omega^{-1} \) \( \text{cm} \) \( \text{cm} \) for films grown under \( P_{O_2} = 1 \times 10^{-7} \text{ Torr} \) and \( P_{O_2} = 1 \times 10^{-3} \text{ Torr} \), respectively. For the insulating Ti4O7 film, the temperature dependence of the inverse \( R_H \) [inset of Fig. 3(a)] suddenly decreased at around 150 K, suggesting that the MIT was induced by the depletion of hole carriers. The inverse \( R_H \) at 10 K was four orders of magnitude smaller than that at 300 K. The MIT in the bulk is associated with the formation of bipolarons9–11, which remains robust in the insulating Ti4O7 film at low temperatures. In contrast, the inverse \( R_H \) for the superconducting Ti4O7 film was almost independent of temperatures, and even the value at 10 K was comparable to that at 300 K, suggesting the suppression of a bipolaronic insulating state.

The temperature dependence of the resistivity for the Ti4O7 film exhibited a complex curve along three electronic phase transitions: MIT around 350 K, insulator–insulator transition around 100 K, and superconducting transition [Fig. 3(b)]. The intermediate transition would be related to the MIT of Ti4O7 due to their similar transition temperatures. Nevertheless, the resistivity upturn was much weaker, suggesting the suppression of the insulating states, as with the case of the superconducting Ti4O7 film. The inverse \( R_H \) almost [inset of Fig. 3(b)] remained the same (\( 3 \times 10^{-3} \text{ cm}^2 \text{C}^{-1} \)) over the entire temperature range. The sign and magnitude of the \( R_H \) also reflected this correspondence.

**Figure 3.** Temperature dependence of resistivity of titanate films. (a) Temperature dependence of resistivity for Ti4O7 films grown under three different conditions. The inset shows the temperature dependence of the Hall measurement. (b) Temperature dependence of resistivity for the Ti4O7 film. The inset shows the temperature dependence of the Hall measurement.

\[ \beta = 57.3^\circ, \gamma = 108.8^\circ \], TiO7 film grown under \( P_{O_2} = 1 \times 10^{-7} \text{ Torr} \) (\( a = 5.52 \text{ Å}, b = 7.11 \text{ Å}, c = 20.46 \text{ Å}, \alpha = 67.5^\circ, \beta = 57.2^\circ, \gamma = 108.8^\circ \)), and TiO7 film (\( a = 4.99 \text{ Å}, b = 8.90 \text{ Å}, c = 7.06 \text{ Å}, \alpha = 110.3^\circ \)). The a-axis lattice constant of both Ti4O7 films is smaller than that of bulk. In contrast, b- and c-axes lattice constants of the former Ti4O7 films were in agreement with those of bulk. The b- (c-) axis lattice constant of the latter Ti4O7 film was smaller (larger) than that of bulk. We note that the c-axis length directly corresponds to the Ti–Ti bond length in the TiO6 tetramer [see Fig. 1(a)] and c-axis lattice constant of the former TiO7 film is larger than that of the latter TiO7 film. For the Ti4O7 film, all of the lattice constants were smaller than those of bulk. The lattice parameters of the titanate films and bulk are listed in Tables S2 and S4 for comparison.

Formation of the different titanate phases under the identical growth condition suggests that epitaxial effects play an important role for stabilizing the TiO7 and Ti4O7 films on each substrate (see Fig. S9 in Supplementary Information). In fact, we have grown neither Ti4O7 films on LSAT (100) substrates nor TiO7 films on TiO7 (000) substrates. The in-plane epitaxial relationship between the substrates and films were also investigated and described in Supplementary Information.

**Temperature dependence of resistivity.** The electrical properties of the films were investigated using the temperature dependence of resistivity (Fig. 3). The resistivity curves strongly depended on the growth atmosphere for Ti4O7 films [Fig. 3(a)]. For the film grown under \( P_{O_2} = 1 \times 10^{-7} \text{ Torr} \), MIT accompanied by clear hysteresis was found at around 150 K, which is in agreement with the behaviour of a bipolaron insulator of bulk Ti4O79–11. In contrast, the insulating behaviours were strongly suppressed for the film grown under \( P_{O_2} = 1 \times 10^{-3} \text{ Torr} \); the upturn in resistivity was weak. The different behaviour across MIT was in agreement with the difference in c-axis lattice constants of the Ti4O7 films: the larger c-axis length weakened the Ti4+–Ti4+ bond in the TiO6 tetramers for the Ti4O7 films grown under \( P_{O_2} = 1 \times 10^{-3} \text{ Torr} \). Weaker resistivity upturn was also reported on V-doped bulk Ti4O7. When V content exceeds 0.35 at%, the disordered bipolarons dominate the electronic properties in the insulating phase. If we account for the lower degree of oxidation at \( P_{O_2} = 1 \times 10^{-3} \text{ Torr} \), oxygen deficiency would play a similar role to substitution of the Ti site with V and be responsible for the suppression of the insulating states.

Superconductivity was observed at low temperatures. The Ti4O7 film grown under an intermediate condition (\( P_{O_2} = 1 \times 10^{-7} \text{ Torr} \)) exhibited both hysteresis and superconducting characteristics in the resistivity curve (also see Fig. S10 in Supplementary Information). We will refer to the Ti4O7 films grown under \( P_{O_2} = 1 \times 10^{-7} \text{ Torr} \) (\( P_{O_2} = 1 \times 10^{-3} \text{ Torr} \)) as insulating (superconducting) ones in the following discussion.

The variation in the Hall coefficient (\( R_H \)) during warming exhibited a tendency similar to that of resistivity. At 300 K (10 K), the inverse \( R_H \) was \( 3.6 \times 10^{-4} \) (1.5) \( \mu \Omega \text{cm} \) \( \Omega^{-1} \) \( \text{cm} \) \( \Omega^{-1} \) \( \text{cm} \) \( \text{cm} \) for films grown under \( P_{O_2} = 1 \times 10^{-7} \text{ Torr} \) and \( P_{O_2} = 1 \times 10^{-3} \text{ Torr} \), respectively. For the insulating Ti4O7 film, the temperature dependence of the inverse \( R_H \) [inset of Fig. 3(a)] suddenly decreased at around 150 K, suggesting that the MIT was induced by the depletion of hole carriers. The inverse \( R_H \) at 10 K was four orders of magnitude smaller than that at 300 K. The MIT in the bulk is associated with the formation of bipolarons9–11, which remains robust in the insulating Ti4O7 film at low temperatures. In contrast, the inverse \( R_H \) for the superconducting Ti4O7 film was almost independent of temperatures, and even the value at 10 K was comparable to that at 300 K, suggesting the suppression of a bipolaronic insulating state.
Superconducting properties. The temperature dependence of resistivity around the temperature of liquid helium indicates further similarity between the superconducting TiO$_2$ and γ-TiO$_2$ films [Fig. 4(a) and (b), respectively]. The $T_C$ of TiO$_2$ and γ-TiO$_2$ were 3.0 K and 7.1 K for $T_{C_{\text{Ge}}}$ 2.7 K and 6.6 K for $T_{C_{\text{Ge}}}$ and 5.8 K and 2.5 K for $T_{C_{\text{Ge}}}$, respectively. Note that the $T_c$ of both films exceeded that of other simple-oxide superconductors in bulk [TiO ($T_c = 2.3$ K), NbO ($T_c = 1.4$ K), and SnO ($T_c = 1.4$ K under 9.3 GPa)]$^{[13-16]}$. We also note that enhancement of $T_c = ~7$ K in TiO films has been reported in recent$^{[17]}$. The superconducting states were gradually degraded under applied magnetic fields. Here, the magnetic fields were applied perpendicular to the film surface. $T_c$ shifted toward a lower temperature under a higher magnetic field, and the superconducting phase finally disappeared for the TiO$_2$ film at above 2 K. As for the γ-TiO$_2$ films, superconductivity remained robust even under 9 T. In addition, from the temperature dependence of magnetization measurements, where magnetic field was applied parallel to the film surface, clear diamagnetic signals were observed [insets of Fig. 4(a) and (b)]. The observation of diamagnetic signals in field-cooling curves indicates the Meissner effect of bulk superconductivity in TiO$_2$ and γ-TiO$_2$ films, and roles out major influences arising from impurity, filament, and/or surface states.

Discussion
Chakraverty et al. proposed a theory to predict Superconductivity in TiO$_2$ with the largest $\lambda_{\text{ep}}$ value$^{[18-20]}$. Therefore, experimental verifications for superconductivity in bulk TiO$_2$ were attempted by applying high pressures. However, no superconducting transition was observed under a hydrostatic pressure of up to 5.0 GPa, although the high-temperature metallic phase was extended down to 3 K$^{[9,10]}$. Our first observation of superconductivity in a TiO$_2$ film demonstrates the importance of the epitaxial thin film. Titanium-based simple oxides with various chemical formulae and polymorphisms easily transform from one to another, and subtle tuning of oxygen stoichiometry causes modulation of carrier density.Epitaxial growth on LSAT substrates enables us to stabilize the Magnéli phase. In fact, the γ-TiO$_2$ and TiO$_2$ films can also be grown on different substrates under the same growth conditions ($T_R$ = 900 °C and $P_{O_2}$ = 1 × $10^{-7}$ Torr) (see Fig. S9 in Supplementary Information). The lack of these advantages would be inevitable for hidden superconducting phases in bulk specimens. The MIT of the stoichiometric TiO$_2$ bulk is premised on the bipolaronic interaction$^{[9-11]}$. Sharp increase in resistivity and the lack of these advantages would be inevitable for hidden superconducting phases in bulk specimens. The MIT of TiO$_2$ films grown on MgAl$_2$O$_4$ (100) substrates also exhibited superconductivity (see Figs S11 and S12 in Supplementary Information). Thus, the observed superconductivity is intrinsic to the TiO$_2$ phase. Furthermore, superconductors composed of Mg, Al, Ti, and O with $T_c$ of more than 3 K are not yet known, indicating that any elements from the substrates cannot induce the superconductivity in our samples.

For bulk γ-TiO$_2$, the MIT occurs with the structural phase transition at ~240 K$^{[7]}$. There was no sign of such a structural phase transition at the temperature in the resistivity curve of the γ-TiO$_2$ film [Fig. 3(b)], suggesting that the metallic γ-phase was stabilized in an epitaxial thin film. The first-principle calculations revealed a one-dimensional conducting pathway along the c-axis arising from the density of states at the Fermi level$^{[7]}$. The low-dimensional electronic structure would lead to the pairing of electrons at ~100 K where MIT occurred in γ-TiO$_2$. On the other hand, the small number of studies on γ-TiO$_2$ makes it difficult to discuss the strength of the electron–phonon interaction, the formation of bipolarons, and the density of states at the Fermi level. Further investigation will be necessary to reveal the origin of superconductivity as well as several electronic phase transitions.

Figure 4. Superconducting properties of titane films. (a) Temperature dependence of resistivity of the TiO$_2$ film grown under $P_{O_2} = 1 \times 10^{-7}$ Torr at low temperatures. (b) Temperature dependence of resistivity of the γ-TiO$_2$ film at low temperatures. The insets of (a) and (b) show temperature dependence of magnetization for (a) the superconducting TiO$_2$ and (b) γ-TiO$_2$ films at low temperatures, respectively. FC and ZFC denote field-cooling and zero-field cooling curves, respectively.
In summary, we study new superconductors produced from Ti$_2$O$_3$ and γ-Ti$_3$O$_5$ films whose $T_c$ are 3.0 and 7.1 K, respectively. The latter is one of the highest known values among simple oxides. Our investigations on the electronic properties and the previous theoretical prediction suggest that epitaxial stabilization and oxygen non-stoichiometry play key roles in the realization of superconductivity in the titanates.

**Methods**

**Thin-Film Preparation.** A TiO$_2$ ceramic tablet was prepared using a conventional solid-state reaction method. Ti (3 N) and TiO$_2$ (4 N) powders with a molar ratio of 1:3 were mixed and pressed into a pellet. This was sintered at 1000 °C for 12 h in vacuum. Prior to the film growth, LSAT and α-Al$_2$O$_3$ substrates were annealed in air to obtain a step-and-terrace surface. The annealing conditions were 1200 °C for 3 h for (LaAlO$_3$)$_{0.3}$–(SrAl$_{0.1}$Ti$_{0.9}$O$_{3.9}$)$_{0.7}$ (LSAT), and 1100 °C for 3 h for α-Al$_2$O$_3$. The films were grown using PLD in an ultra-high-vacuum chamber. KrF excimer laser pulses (5 Hz, 2.0 J/cm$^2$) were focused on the TiO$_2$ ceramics tablets. The growth temperature was set at 900 °C. The chamber pressure was controlled with the continuous flow of oxygen or Ar gas (6 N purity for both). Ar atoms in the chamber tend to scatter with the lighter oxygen, especially when mean free path of the gaseous species exceeds the target-substrate distance$^{21,22}$. Therefore, introduction of Ar (oxygen) gas during the growth corresponds to reduction (oxidation) of the films. In fact, we have also grown TiO and Ti$_2$O$_3$ films using PLD in Ar atmosphere (see Fig. S1 in Supplementary Information)$^9$. After the growth, the gas flow was stopped immediately, and the samples were quenched to room temperature.

**Characterization of the thin films.** Thickness of all the films was ~120 nm, as measured by a stylus profiler. The crystal structures of the films were characterized using XRD with Cu Kα$_1$ radiation ( Rigaku, SmartLab) and synchrotron radiation at BL15XU in SPring-8. The photon energy of the synchrotron radiation was set at 15 keV ($\lambda = 0.826$ Å). The temperature dependence of resistivity was measured using a standard four-probe method with a physical properties measurement system (Quantum Design, PPMS). The temperature dependence of the Hall measurements was also measured using PPMS in a standard six-terminal geometry. The temperature dependence of magnetization was measured using magnetic properties measurement system (Quantum Design, MPMS).

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Author Contributions
K.Y. performed the experiments and analysed experimental data. O.S. supervised the synchrotron X-ray diffraction measurements. All authors discussed the results and wrote the manuscript. A.O. supervised the project.

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