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# In Situ Observation of Two-Dimensional Electron Gas Creation at the Interface of an Atomic Layer-Deposited Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Thin-Film Heterostructure

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generate free electrons at the interface of the ultrathin  $Al_2O_3/TiO_2$  heterostructure. The activation energy of the electron donor states to move to the Ti 3d conduction band plays an essential role in the electrical characteristics of the 2DEG. Interestingly, the donor state level can be tailored by the control of TiO<sub>2</sub> crystallinity, which eventually adjusts the electron density. The activation energy was decreased to less than 20 meV to generate ultrashallow donor states while improving the TiO<sub>2</sub> crystallinity, such that the 2D electrons become readily delocalized, even at room temperature, to create a 2DEG.

# INTRODUCTION

Two-dimensional electron gases (2DEGs) that form at the interface of a heterojunction have attracted particular attention because of their distinctive electronic properties and physical structure. The electrons occupy a defined energy level and are strictly confined at the interface of the heterojunction, yet move freely along the interface direction.<sup>1</sup> The discovery of a 2DEG at complex oxide interfaces, such as LaAlO<sub>3</sub>/SrTiO<sub>3</sub> (LAO/STO) heterostructures, has drawn vast interest because of the potential application for nanoscale devices.<sup>2-8</sup> The 2DEG at the interface of the LAO/STO heterostructure has achieved fascinating electrical properties, with an electron density of  $10^{13}$  to  $10^{14}$  cm<sup>-2</sup>, which is higher than that of conventional III-V semiconductor interfaces.<sup>1-5</sup> Furthermore, the LAO/STO heterostructures exhibited a tunable metalinsulator ground state and magnetic ground state, making it possible for devices in all-oxide field-effect transistors.<sup>2-</sup> However, 2DEG at the epitaxial interface of the LAO/STO heterostructure was attained only when the LAO layers were grown on Ti-terminated STO single-crystalline substrates by pulsed laser deposition or molecular beam epitaxy at a high temperature (>600 °C). Therefore, these fabrication conditions pose challenges for use in the semiconductor <sup>-7</sup> Recently, it was reported that a 2DEG was industry.1successfully formed using amorphous layers (i.e., LAO and  $Al_2O_3$ ) on a single-crystalline STO substrate.<sup>9–12</sup> Thus, an argument arose over the mechanisms of 2DEG formation at the interface of the oxide heterostructure. A conventional mechanism is based on a polarity discontinuity because of the different charges of the atomic layers, that is, a polar catastrophe, which can be simply described as half an electron charge being transferred to the interface to avoid a potential divergence.<sup>13</sup> Another mechanism is associated with the generation of oxygen vacancies (V<sub>O</sub>) on the surface of the STO layer during LAO or  $Al_2O_3$  layer deposition, acting as n-type dopants for the 2DEG formation.<sup>11,14–16</sup> This mechanism provides an opportunity for 2DEG realization for various oxide heterostructures and fabrication processes.

In this work, the 2DEG was formed at the interface of ultrathin  $\rm Al_2O_3/TiO_2$  heterostructures grown using atomic

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**Figure 1.** (a) Sheet resistance of the  $Al_2O_3/TiO_2$  heterostructure as a function of  $Al_2O_3$  overlayer thickness, which was obtained by ex situ Hall measurements at room temperature with the Van der Pauw configuration. The sheet resistance of the  $Al_2O_3/TiO_2$  heterostructure decreased abruptly beyond the critical thickness (~2 nm) of the  $Al_2O_3$  overlayer, indicating a typical metal–insulator transition to create 2DEGs in oxide heterostructures. The error bars indicate the standard deviation of 100 measurements. The lines are a guide for the eye. (b) Pictures of a specially designed in situ ALD reactor with integrated probes for an in situ resistance measurement and a schematic of the in situ resistance measurement. (c) Sheet resistance of the  $Al_2O_3/TiO_2$  heterostructure measured in the in situ ALD reactor as a function of the ALD cycle number of  $Al_2O_3$  overlayers, which abruptly decreased by only a single ALD cycle of  $Al_2O_3$ . The lines are a guide for the eye.

layer deposition (ALD) at a low temperature (<300 °C), which is compatible with batch-type large-scale production in the semiconductor industry. The origin of the 2DEG formation was systematically revealed by various analytical approaches. Especially, the creation of a 2DEG at the interface of the heterostructure was directly observed using a specially designed in situ resistance measurement system. Further, it was revealed that both the  $V_O$  density at the interface of the  $Al_2O_3/TiO_2$  heterostructure and the activation energy for releasing electrons from the  $V_O$  to the conduction band are the two determinative factors to create a 2DEG, both of which are closely related to the crystallinity of the bottom TiO<sub>2</sub> layer.

# RESULTS AND DISCUSSION

Figure 1a shows the sheet resistance of the  $Al_2O_3/TiO_2$ heterostructures with various thicknesses of TiO<sub>2</sub> layers as a function of Al<sub>2</sub>O<sub>3</sub> thickness. The sheet resistance depends on the thickness of the Al<sub>2</sub>O<sub>3</sub> overlayer on a TiO<sub>2</sub> layer of a given thickness. The Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure appeared to exhibit an insulating behavior with an Al<sub>2</sub>O<sub>3</sub> layer thinner than 2 nm. The resistance of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure drops abruptly across the critical thickness of the  $Al_2O_3$  layer, ~2 nm, and remained a constant value with increasing Al<sub>2</sub>O<sub>3</sub> thickness. Obviously, the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure transitioned from an insulator to a conductor with the Al<sub>2</sub>O<sub>3</sub> overlayer, indicating that the low resistivity of the Al<sub>2</sub>O<sub>3</sub>/ TiO<sub>2</sub> heterostructure originated from the interface of Al<sub>2</sub>O<sub>3</sub>/ TiO<sub>2</sub> instead of the bulk TiO<sub>2</sub>. This is a typical metalinsulator transition characteristics observed in the 2DEG at oxide heterostructures;<sup>3,5</sup> the Al<sub>2</sub>O<sub>3</sub> layer above the critical thickness of 2 nm induced the generation of the 2DEG at the interface of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure.<sup>9</sup> It was expected that the surface of the TiO<sub>2</sub> bottom layer was reduced to generate V<sub>0</sub> by trimethylaluminum (TMA, Al precursor), a

strong reducing agent during the ALD of the  $Al_2O_3$  overlayer, which created the 2DEG at the interface of the  $Al_2O_3/TiO_2$  heterostructure.<sup>16</sup>

However, the surface reduction process of the TiO<sub>2</sub> layer is hard to directly observe because it occurs in the ALD reactor during Al<sub>2</sub>O<sub>3</sub> overlayer deposition. Therefore, we designed a special in situ ALD reactor with integrated probes for in situ electrical (resistance) measurements, as shown in Figure 1b. A TiN/Ti electrode was deposited with a shadow mask (Van der Pauw configuration) on the ALD TiO<sub>2</sub> bottom layer on the  $SiO_2/Si$  substrate, which was loaded in the in situ ALD reactor. The ALD Al<sub>2</sub>O<sub>3</sub> layer was grown at 300 °C, and the sheet resistance was measured at 37 °C without a vacuum break after the 1st, 2nd, 4th, 8th, and 10th ALD cycle of the Al<sub>2</sub>O<sub>3</sub> layer, as shown in Figure 1c. The sheet resistance of the  $Al_2O_3/TiO_2$ heterostructure abruptly decreased to less than  $1 \times 10^4 \Omega/\Box$ after only one ALD cycle of the Al2O3 layer and was maintained with increasing ALD cycle number, which means the 2DEG creation at the  $Al_2O_3/TiO_2$  heterostructure was almost entirely completed by one ALD cycle of the Al<sub>2</sub>O<sub>3</sub> layer. To be more precise, the sheet resistance was measured immediately after the first TMA pulse, which decreased to  $\sim 1$  $\times 10^3 \Omega/\Box$ , less than the resistance measured after a complete ALD cycle (TMA +  $H_2O$ ), and it slightly increased after the following H<sub>2</sub>O pulse. This strongly suggests that the TMA pulse reduced the surface of TiO<sub>2</sub> to create a 2DEG at the interface of the  $Al_2O_3/TiO_2$  heterostructure, which is confirmed by the fact that the following O<sub>3</sub> pulse, a stronger oxygen source than  $H_2O$  for  $Al_2O_3$ , greatly increased the sheet resistance beyond the detection limit.

This in situ resistance measurement is different from the ex situ measurement results given in Figure 1a, showing that the critical thickness of the  $Al_2O_3$  layer for 2DEG formation was over 2 nm. However, the sheet resistance of the hetero-

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**Figure 2.** (a) Sheet resistance, sheet carrier density, and mobility of the  $Al_2O_3/TiO_2$  heterostructure as a function of  $TiO_2$  bottom layer thickness, which was obtained by Hall measurements at room temperature with a Van der Pauw configuration for the  $Al_2O_3/TiO_2$  heterostructures. (b) Sheet carrier density and mobility of the  $Al_2O_3/TiO_2$  heterostructure as a function of  $Al_2O_3$  overlayer thickness. (c–e) Cross-sectional HRTEM images and corresponding SAED patterns (inset) of the  $Al_2O_3/TiO_2$  heterostructures with 5, 10, and 20 nm thick  $TiO_2$  layers, respectively. (f) GIXRD patterns in glancing incidence mode with a 1° incidence angle for the  $Al_2O_3$  (5 nm)/TiO<sub>2</sub> heterostructures with various  $TiO_2$  layer thicknesses (5–13 nm) with a JCPDS of 84-1286. (g,h) Ti  $L_{2,3}$ -edge and O K-edge XAS results of the  $Al_2O_3/TiO_2$  heterostructures with 4, 7, and 10 nm thick  $TiO_2$  layers, respectively. This strongly suggests that the degree of crystallinity increased with the thickness of the  $TiO_2$  bottom layer, and thus, the electronic structure was changed. (i) Sheet resistance of the  $Al_2O_3/a$ -grown or annealed  $TiO_2$  (5 and 10 nm) heterostructures with the as-grown  $TiO_2$  layers. (j) GIXRD patterns for 5 nm thick  $Al_2O_3$  (5 nm)/annealed  $TiO_2$  (5 and 10 nm) heterostructures with a JCPDS of 84-1286. The lines of (a,b,i) are a guide for the eye.

structure (with two ALD cycles of the Al<sub>2</sub>O<sub>3</sub> layer) greatly increased beyond the detection limit when measured after a vacuum break, as indicated by the red open circle, which is similar to the ex situ measurement result (Figure 1c). The increase in sheet resistance after a vacuum break was significantly suppressed with an increasing ALD cycle number of the  $Al_2O_2$  layer in Figure 1c. Therefore, it can be concluded that the 2DEG at the interface of heterostructure was created by only one ALD cycle of the Al<sub>2</sub>O<sub>3</sub> layer (TMA pulse) generating a sufficient concentration of V<sub>0</sub>.<sup>17</sup> However, it vanished with the oxidation of V<sub>O</sub> by air exposure, unless the thickness of the Al<sub>2</sub>O<sub>3</sub> overlayer exceeds the critical thickness,  $\sim$ 2 nm. As a result of analyzing the surface morphology of TiO<sub>2</sub>, the Al<sub>2</sub>O<sub>3</sub> overlayer is expected to have a layer-by-layer growth mode because of the smooth surface of the nanocrystalline TiO<sub>2</sub> underlayer. Generally, the Al<sub>2</sub>O<sub>3</sub> layer with the layer-by-layer growth mode has a surface coverage of 25-33% per each ALD cycle,<sup>18</sup> thus showing full surface coverage in three to four cycles. This coincides with the tendency of the saturation of sheet resistance after four Al<sub>2</sub>O<sub>3</sub> ALD cycles in the results of in situ sheet resistance (Figure 1c). It should be noted that the  $Al_2O_3$  overlayer thicker than  $\sim 2$  nm is necessary to maintain the 2DEG; otherwise, Vo at the interface of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure is eliminated by an air exposure even after deposition of the Al<sub>2</sub>O<sub>3</sub> overlayer.

Meanwhile, note that for a certain thickness of the  $Al_2O_3$  layer above the critical thickness of 2 nm (under the condition of concrete 2DEG formation), the resistance of the  $Al_2O_3/$ 

TiO<sub>2</sub> heterostructure decreased with increasing TiO<sub>2</sub> layer thickness in Figure 1a, which is summarized by the sheet carrier density and carrier mobility as a function of the TiO<sub>2</sub> layer thickness in Figure 2a. Herein, the sheet resistance was obtained by averaging each value above the critical Al<sub>2</sub>O<sub>2</sub> thickness of  $\sim 2$  nm for a given thickness of a TiO<sub>2</sub> layer. The sheet resistance decreased gradually from  $\sim 8 \times 10^7$  to  $\sim 8 \times$  $10^3 \Omega / \Box$  with an increasing TiO<sub>2</sub> layer thickness from 5 to 20 nm. The sheet carrier densities of heterostructures with 13 and 20 nm thick TiO<sub>2</sub> layers were obtained as  $\sim 1 \times 10^{14}$  and  $\sim 5 \times$  $10^{14}$  cm<sup>-2</sup>, respectively, and their mobilities were similar, ~4  $cm^2 V^{-1} s^{-1}$ , which are similar to those of the epitaxial LAO/ STO heterostructures.<sup>1,3</sup> Here, we note that the decrease in the sheet resistance of the 2DEG in Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures with increasing TiO<sub>2</sub> layer thickness is due to an increase in the carrier density rather than carrier mobility. The estimation of the carrier density and mobility using our Hall measurement system was unreliable in the case with a thinner TiO<sub>2</sub> layer (less than 13 nm) because the sheet resistance values were higher than the  $10^6 \Omega/\Box$  measurement limits. The sufficient electrical conduction of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure was achieved only when the  $\rm TiO_2$  layer was thick enough,  ${\sim}13$  and 20 nm. The sheet carrier density and carrier mobility of the 13 and 20 nm thick TiO<sub>2</sub> heterostructures as a function of Al<sub>2</sub>O<sub>3</sub> thickness are shown in Figure 2b.

Figure 2c–e shows the high-resolution transmission electron microscopy (HRTEM) images of the  $Al_2O_3/TiO_2$  hetero-structures with 5, 10, and 20 nm thick TiO<sub>2</sub> layers, respectively.



Figure 3. (a,b) Normalized Ti 2p core-level XPS spectra of the 5 and 10 nm thick as-grown TiO<sub>2</sub> layer with and without the  $Al_2O_3$  overlayer, respectively. (c) Normalized Ti 2p core-level XPS spectra of the 5 nm thick annealed TiO<sub>2</sub> layer with and without the  $Al_2O_3$  overlayer. A TiO<sub>2</sub> layer with an  $Al_2O_3$  overlayer exhibited a shoulder peak corresponding to Ti<sup>3+</sup>, indicating oxygen vacancies, which decreased with the increasing crystallinity of the TiO<sub>2</sub> bottom layer. (d) Temperature-dependent Hall measurement results at the temperature range of -93 to 175 °C; logarithmic conductance of various  $Al_2O_3/TiO_2$  heterostructures as a function of reciprocal temperature. The lines are a guide for the eye. (e) PL spectra of various  $Al_2O_3/TiO_2$  heterostructures. The activation energy releasing the electrons from V<sub>O</sub> (donor level) decreased with increasing crystallinity of the TiO<sub>2</sub> bottom layer.

It is clearly observed that the Al<sub>2</sub>O<sub>3</sub> overlayers exist as the amorphous phase in all Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures, and this amorphous nature excludes the "polar catastrophe" as the origin of the 2DEG.<sup>9,19</sup> This confirms that the 2DEG in this work originated from the oxygen vacancy  $(V_0)$  generated at the interface of the  $Al_2O_3/TiO_2$  heterostructure by a TMA pulse.<sup>16</sup> Meanwhile, it is obvious that the TiO<sub>2</sub> layer thickness crucially affected the generation of Vo acting as n-type dopants for the formation of the 2DEG. In general, the crystallinity of the film has a strong dependence on the film thickness. Thus, in our  $Al_2O_3/TiO_2$  heterostructure, the bottom  $TiO_2$  film thickness determined the crystallinity of the film, which can affect the interface structure of Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>. Figure 2f is grazing incidence X-ray diffraction (GIXRD) spectra of asgrown TiO<sub>2</sub> layer with various thicknesses. No peak was observed for the 5 and 10 nm thick TiO<sub>2</sub> layer because of their amorphous nature. However, the 13 nm thick TiO<sub>2</sub> layer exhibited peaks corresponding to anatase (101) and (200) planes of TiO<sub>2</sub> at 25.1 and 48°, respectively, indicating that the crystallinity of the TiO<sub>2</sub> layer increased with the film thickness. However, the ultrathin polycrystalline nature of the TiO<sub>2</sub> layer may hinder the accurate analysis using GIXRD, and other analytical methods were introduced to further analyze the properties of the  $TiO_2$  layer. Figure 2c-e shows the HRTEM image and the corresponding selective area electron diffraction (SAED) patterns (insets). The 5 nm thick amorphous TiO<sub>2</sub> layer is observed in Figure 2c, where the SAED pattern (inset) shows no Debye-Scherrer rings, corresponding to the lattice disorder of amorphous TiO<sub>2</sub>. However, the TiO<sub>2</sub> layer was partially crystallized at the thickness above 10 nm (Figure 2d,e), and bright spots in the SAED pattern (inset) indicate the existence of the anatase phase. The electron beam-induced

phase transformation in the TEM sample can be found by the excess electron beam dose causing the radiolysis damage to the TEM sample.<sup>20,21</sup> However, we have done TEM experiments under adequate conditions for this kind of amorphous thin film.<sup>16</sup> The phase transformation of the amorphous TiO<sub>2</sub> by electron beam was hardly observed during TEM experiments. Consequently, the degree of crystallinity of the TiO<sub>2</sub> layer increased with the thickness. Furthermore, the X-ray absorption spectroscopy (XAS) technique was adopted to precisely determine the electronic states of the ultrathin TiO<sub>2</sub> layer (<10 nm). Figure 2g,h shows the Ti L<sub>2.3</sub>-edge and O Kedge XAS results of the 4 nm-Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures with various TiO<sub>2</sub> thicknesses (4, 7, and 10 nm), respectively. The heterostructure with a 10 nm thick TiO<sub>2</sub> layer exhibits typical anatase features, showing an eg doublet at 460 eV with a higher intensity and at 461 eV with a lower intensity.<sup>22,23</sup> In cases with 4 and 7 nm thick TiO<sub>2</sub> layers, the features become broader overall; the pre-edge peaks at 456.5 and 457.5 eV are very small, and the intensities of the Ti  $t_{\rm 2g}$  and Ti  $e_{\rm g}$  peaks were lower compared with the case of 10 nm thick  $\mathrm{TiO}_2$  layer, as shown in Figure 2g. This may be interpreted as a higher portion of amorphous TiO<sub>2</sub> phases in the above samples. The increased incidence of structural disorders with decreasing TiO<sub>2</sub> thickness is consistent with the XRD and HRTEM results. In the O K-edge XAS spectra (Figure 2h), the peaks located at around 531 and 533 eV represent the Ti  $t_{2g}$  and Ti  $e_g$  electron states that are hybridized with the O 2p states,<sup>24,25</sup> respectively. The high-energy background slopes are from the  $Al_2O_3$  overlayers. The  $t_{2g}$  and  $e_g$  peak intensities increase in accordance with the increase in the TiO2 layer thickness, reflecting the increase in the TiO<sub>2</sub> concentration relative to  $Al_2O_3$ . The  $t_{2g}$  and  $e_g$  peak features become much sharper with



Figure 4. Schematic of the proposed model for 2DEG formation at the interface of  $Al_2O_3/TiO_2$  heterostructures, including the electronic band structures. (a) Thin  $TiO_2$  layer with an amorphous structure resulted in a high concentration of  $V_O$  at the interface, but most of the electrons are trapped in deep electronic defect levels at ~189 meV from the CBM. (b)  $V_O$  generated at the surface of the crystalline  $TiO_2$  layer induced an ultrashallow donor level ~18 meV from the CBM, despite the lower concentration of  $V_O$ , resulting in a 2DEG formation at the interface.

increasing TiO<sub>2</sub> thickness, strongly suggesting that the electronic structure indeed changed because of the structural order. As a result, 2DEG formation at the interface of Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure may be affected by TiO<sub>2</sub> crystallinity (structural order) and thus the electronic structure of the TiO<sub>2</sub> film.

However, factors other than the crystallinity of the layer that depend on the film thickness may affect the interface structure. Therefore, in turn, we confirmed the 2DEG formation dependence on the crystallinity of the TiO<sub>2</sub> layer by examining the  $Al_2O_3/TiO_2$  heterostructures with annealed TiO<sub>2</sub> layers (5 and 10 nm). A significantly lower sheet resistance was observed for the annealed heterostructures (Figure 2i) in contrast to the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures with the as-grown  $TiO_2$  layers (Figure 1a). The sheet resistance decreased by 3 orders of magnitude with the annealing of the TiO<sub>2</sub> layer. Similarly, the sheet resistance decreased from  $\sim 8 \times 10^5$  to  $\sim 1$  $\times$  10<sup>5</sup>  $\Omega/\Box$  by the adoption of annealed 10 nm thick TiO<sub>2</sub> layers instead of the as-grown TiO<sub>2</sub> layers. Figure 2j shows that the annealed 5 nm thick TiO<sub>2</sub> layer was partially crystallized because of the existence of the anatase phase, which was also confirmed by HRTEM and the corresponding SAED pattern (Figure S2, Supporting Information). This result implies that the thickness of the TiO<sub>2</sub> layer is not essential, but the crystallinity of the TiO<sub>2</sub> layer is positively vital and beneficial to the 2DEG formation at the interface of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure. For a deep understanding of the dependence of 2DEG formation on the crystallinity of the TiO<sub>2</sub> layer, the influence of the crystallinity of the TiO<sub>2</sub> layer on V<sub>O</sub> formation at the interface of the  $Al_2O_3/TiO_2$  heterostructure should be verified. Thus, the chemical structure, in particular, the oxidation state of the TiO<sub>2</sub> layer surface, was examined using X-ray photoelectron spectroscopy (XPS). Figure 3a,b shows the normalized Ti 2p core-level XPS spectra for 5 and 10 nm

thick as-grown TiO<sub>2</sub> with and without the Al<sub>2</sub>O<sub>3</sub> overlayer (~3 nm), respectively. The main peak positioned at a binding energy of ~458.5 eV was observed in all cases, which corresponds to Ti<sup>4+</sup> from stoichiometric TiO<sub>2</sub>. The spectra for the 5 and 10 nm thick TiO<sub>2</sub> layers without the Al<sub>2</sub>O<sub>3</sub> overlayer in Figure 3a,b, respectively, are identical irrespective of the TiO<sub>2</sub> layer thickness, which suggests that the oxidation state of TiO<sub>2</sub> was maintained with increasing thickness. When the Al<sub>2</sub>O<sub>3</sub> overlayer was adopted, the shoulder peak was observed at the binding energy of ~457 eV, which corresponds to the defect state of Ti<sup>3+</sup>. This implies the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> during the ALD of Al<sub>2</sub>O<sub>3</sub> and thus implies the generation of V<sub>O</sub> at the surface of the TiO<sub>2</sub> layer.<sup>9,16,17,19,26,27</sup>

Contrary to our expectation that enhanced crystallinity would have a positive effect on Vo concentration, interestingly, the intensity of the shoulder peak (Ti<sup>3+</sup>) decreased with increasing TiO<sub>2</sub> thickness, as shown in Figure 3a,b. Furthermore, the shoulder peak intensity  $(Ti^{3+})$  of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure using an annealed 5 nm thick TiO<sub>2</sub> layer is lower than that of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure using the as-grown 5 nm thick TiO<sub>2</sub> layer, as shown in Figure 3c. The same tendency was observed in the case of 10 nm thick TiO<sub>2</sub> layer (Figure S3, Supporting Information). This suggests that the enhanced crystallinity of TiO<sub>2</sub> mitigated the formation of  $Ti^{3+}$ , which resulted in the suppression of  $V_{O}$ generation at the interface of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure (the TiO<sub>2</sub> layer surface). This is reasonable considering the general fact that Vo generation is based on the microstructural disorder. Consequently, the concentration of Vo decreased with increasing crystallinity of TiO<sub>2</sub> thin films; this importantly suggests that the carrier density at the interface for the 2DEG was not in proportion to the Vo concentration, even though the origin of the 2DEG is based on Vo generation at the interface. Here, importantly, we recall that the activation energy for releasing electrons from Vo at the interface, the donor state level, is also an important factor other than the  $V_{0}$ concentration for determining the electron density of the 2DEG. Therefore, the donor level was estimated based on the temperature dependence of the conductivity of the  $Al_2O_3/$ TiO<sub>2</sub> heterostructures with Arrhenius behavior, as shown in Figure 3d. The activation energy for the  $Al_2O_3/as$ -grown TiO<sub>2</sub> heterostructures significantly decreased from ~189 to ~27 and ~18 meV to form an ultrashallow donor level with increasing thickness of the TiO<sub>2</sub> layer from 5 to 10 and 13 nm, respectively. In addition, with an annealed 5 nm thick TiO<sub>2</sub> layer, the activation energy decreased to 99 meV compared to 189 meV for the as-grown 5 nm thick TiO<sub>2</sub> layer. Therefore, we can state that the donor state level and Vo concentration have an opposite dependence on the crystallinity of the TiO<sub>2</sub> layer for 2DEG formation and that the electron density of the 2DEG in the  $Al_2O_3/TiO_2$  heterostructures is mainly determined by the donor state level formed by V<sub>0</sub>, rather than the concentration of Vo. The donor level was also analyzed by photoluminescence (PL). Figure 3e shows the PL spectra of  $Al_2O_3$  (3 nm)/TiO<sub>2</sub> heterostructures with as-grown 5, 10, and 13 nm thick TiO<sub>2</sub> layers and the annealed 5 nm thick TiO<sub>2</sub> layer. The band-to-band transition of anatase TiO<sub>2</sub> is difficult to observe in all cases, which is supposed to appear around the wavelength of  $\sim$ 375 nm ( $\sim$ 3.3 eV), indicated by the red dashed line. Because TiO<sub>2</sub> has a wide indirect band gap, the electron excitation via defect levels in an energy band gap is more probable than a one-step band-to-band transition process that requires excess energy.<sup>28,29</sup> The transition via shallow donor states located within 100 meV from the conduction band minimum (CBM) results in the PL emission peak at wavelengths ranging from ~375 to ~388 nm corresponding to the energy ranging from ~3.3 to ~3.2 eV, which originated from the self-trapped emission occurring via V<sub>O</sub> at a shallow donor state.<sup>30,31</sup> The peak intensity in this range increased with the TiO<sub>2</sub> layer thickness, and the peak intensity is higher for the  $Al_2O_3/TiO_2$  heterostructure with the annealed TiO<sub>2</sub> layers compared to that of the as-grown TiO<sub>2</sub> layer.<sup>32,33</sup> Correspondingly, the wavelength at the peak center decreased with increasing TiO<sub>2</sub> layer thickness. This confirms that improved crystallinity of the TiO<sub>2</sub> layer increased the concentration of ultrashallow donor states (generated by  $V_{0}$ ) in the  $Al_2O_3/TiO_2$  heterostructure by decreasing the activation energy, even though it decreased the total  $V_0$  concentration.

The origin of the 2DEG for the conduction mechanism is summarized in Figure 4, which shows the schematic electronic band structures of the TiO<sub>2</sub> layer surface in Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures with various TiO<sub>2</sub> layers. For a thin TiO<sub>2</sub> layer with amorphous structure, the oxygen sublattice is not well defined because the long-range order could not be preserved, but only short-range order is conserved. Therefore, many oxygen atoms were missed in the nearest-neighbor Ti-O units, resulting in a high concentration of V<sub>O</sub> at the interface with  $Al_2O_3$  (surface of TiO<sub>2</sub>). However, this induces a deep electronic defect level at ~189 meV from the CBM, as shown in Figure 4a, where most of the electrons are trapped so that the electron density is too low to form the 2DEG, resulting in a high sheet resistance of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure.<sup>9,34,35</sup> On the other hand, the V<sub>o</sub> generated at the surface of the crystalline (thick or annealed) TiO<sub>2</sub> layer has an ultrashallow donor state level ~18 meV from the CBM, as shown in Figure 4b, which is less than the donor levels in typical extrinsic (As or B-doped) Si (~30-50 meV) and comparable to those of single-crystalline STO or TiO<sub>2</sub> (~10–25 eV), resulting in a provision of many electrons to the CB at room temperature.<sup>15,36–38</sup> Eventually, the increased crystallinity of the TiO<sub>2</sub> layer enables the achievement of a high electron density of ~10<sup>14</sup> cm<sup>-2</sup>, which is adequate to form a 2DEG at the interface of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure.

Meanwhile, the 2DEG device proposed in this work can be a good candidate for transparent thin-film transistors for which a sufficient transmittance of the devices is required because the heterostructure consists of ultrathin oxides with a wide energy band gap, that is,  $Al_2O_3$  (>~7 eV) and TiO<sub>2</sub> (~3.3 eV). The transmittance spectra of the  $Al_2O_3/TiO_2$  heterostructures fabricated on a quartz substrate with various TiO<sub>2</sub> layers were obtained (Figure S4, Supporting Information). In the visible light region, wavelengths ranging from ~390 to ~780 nm, the average transmittance was similar in the range of ~87–90% for the 5–20 nm TiO<sub>2</sub> layers with a 4.5 nm thick  $Al_2O_3$  layer, which is sufficient for transparent thin-film transistor applications.

### CONCLUSIONS

We demonstrated the creation of a 2DEG at the interface of an ultrathin Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure fabricated using ALD. In situ resistance measurements provided an insight into the origin of the 2DEG, explaining that electron donor oxygen vacancies were generated at the surface of the TiO<sub>2</sub> layer during the ALD of  $Al_2O_3$ . Their activation energy for releasing electrons plays an important role in the 2DEG formation. The activation energy exhibited a crucial dependence on the crystallinity of the bottom TiO<sub>2</sub> layer; even though the density of oxygen vacancies decreased with increasing crystallinity of the bottom TiO<sub>2</sub> layer, the activation energy decreased to  $\sim 18$ meV, which resulted in ultrashallow donor states, providing a high density of conduction electrons contributing to the 2DEG. The ALD process used for the fabrication of ultrathin Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures has a high technological maturity in the present semiconductor technology and a low process temperature (<300 °C), which would enable the mass production of 2DEG devices and present new opportunities for sequential three-dimensional integration.

### EXPERIMENTAL SECTION

Ultrathin Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Heterostructure. The TiO<sub>2</sub> thin films (5-20 nm) were grown by ALD on a thermally grown SiO<sub>2</sub> (300 nm)/Si substrate at 300 °C in a 4 inch travelling wave-type ALD reactor (CN-1 Co., Atomic Classic) at 300 °C. The purge/carrier gas was highpurity N<sub>2</sub> (99.999%) with 200 sccm flowing horizontally along the reactor. Titanium tetraisopropoxide [TTIP, Ti $\{OCH(CH_3)_2\}_4$ ] and H<sub>2</sub>O were used as the Ti precursor and oxygen source, respectively. The pulse times of TTIP and H<sub>2</sub>O were 1 and 2 s, respectively. The  $Al_2O_3$  films (1-6 nm-thick) were grown by ALD at 300 °C on the  $TiO_2$  films using TMA [Al(CH<sub>3</sub>)<sub>3</sub>] and H<sub>2</sub>O as the Al precursor and oxygen source, respectively, for the formation of the  $\mathrm{Al_2O_3/TiO_2}$ heterostructure. The pulse times of TMA and H<sub>2</sub>O were 1.5 and 2 s, respectively. The precursor and reactant purge times were 30 s for both purge steps. The growth rates of  $Al_2O_3$  and  $TiO_2$  were ~1.19 and 0.38 Å/cycle, respectively. A rapid thermal annealing process was performed at 600 °C for 1 min under N2 atmosphere prior to the ALD of the Al<sub>2</sub>O<sub>3</sub> thin film to enhance the crystallinity of TiO<sub>2</sub> thin films. The thickness of each film was measured by ex situ spectroscopic ellipsometry (Nano-View Co., MG-1000).

Electrical Measurements and Physicochemical Analysis. In the electrical measurements, the TiN (50 nm)/Ti (100 nm) top electrodes were deposited through a shadow mask at four corners of square samples ( $20 \text{ mm} \times 20 \text{ mm}$ ) using dc magnetron sputtering. The sheet resistance, carrier density, and mobility were measured using the Hall measurement system (Ecopia Co., HMS-5500) using the standard Van der Pauw method working at a constant magnetic field of 0.56 T. The specific Hall measurement method is described in Figure S5, Supporting Information.<sup>39</sup>

In situ resistance measurement with a four-point probe was performed using a specially designed ALD reactor, which was modified based on a microvacuum probe station system equipped with an ultra-high-vacuum compatible ceramic heater. The electric power of the heater is supplied through the nine-pin electric feedthrough, which is separated from signal feedthrough. The surface of the probe tip is coated with Au to prevent oxidation during the ALD process.

The crystallinity of the films was estimated by XRD (Rigaku, Dmax 2500) in the glancing incidence mode with a 1° incidence angle using a Cu K $\alpha$  radiation. The microstructures of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures including crystallinity were observed by HRTEM (JEOL, JEM-2100F) with SAED, operating at 200 kV with the bright-field imaging mode. Samples for HRTEM imaging were prepared by focused ion beam (FEI Co., Nova Nanolab FC-FI10) sectioning.

XPS (Thermo Fisher Scientific Co., Al K $\alpha$ , 1486.6 eV, pass energy 20 eV) was performed to determine the valence state of Ti ions at the interface of the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure. All XPS spectra were calibrated with respect to the C 1s core-level peak at 285 eV. Electronic states were determined by XAS at Ti L<sub>2,3</sub>- and O K-edges at the 2A beamline of the Pohang Light Source using a total electron yield mode. The directions of the incident X-rays were set to be normal to the sample planes. PL analysis was performed using a helium–cadmium laser operating at 325 nm (3.82 eV) in association with a spectrophotometer at room temperature. The optical transmittance of Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructures grown on a quartz substrate was measured at wavelengths from 200 to 1000 nm using a UV–vis spectrometer (JASCO, V-670).

### ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01572.

 $TiO_2$  surface atomic force microscopy, HRTEM image, XPS spectra, transmittance, and Hall measurement configuration (PDF)

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# Author Contributions

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### Notes

The authors declare no competing financial interest.

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