

## Physical properties of high quality anatase TiO<sub>2</sub> thin films using kinetic control

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### **Introduction**

Transition metal oxides have a rich variety of applications, such as transparent conducting thin films, high  $T_c$  superconductors, and solar cells. These functionalities strongly depend on the conductivity of the materials [1]. Thus techniques to control the conductivity are required for the development of devices. Thin films attract much attention for devices since there are various techniques to control precisely their growth, such as the thermodynamic conditions, the kinetic conditions and the substrate surface. In this thesis, we aimed to understand how these factors affect the conductivity of transition metal oxides.

The thermodynamic and kinetic conditions can control the conductivity by influencing the formation of crystalline defects that can work as dopants and scattering centers. The thermodynamic conditions determine the defect density based on the defect equilibria. In the oxide field, defect formation energy was extensively studied, and the defect density in the thermodynamic equilibrium state has been calculated from defect equilibria for many materials to control their defect densities [2]. However, the defect densities are not always determined by the thermodynamic conditions and it is necessary to consider other factors. Kinetic conditions like migration, adsorption and desorption, which can be modulated by the growth rate, are also influential on the formation of crystalline defects [3]. The effect of the kinetic conditions in the oxide field is still unclear. Previously, for example, the structural quality of Cr-doped anatase TiO<sub>2</sub> thin films grown by molecular beam epitaxy was found to directly correlate with the growth rate, implying that the defect density was changed by the growth kinetics [4]. In this thesis, we applied this approach to pulsed laser deposition (PLD) which is widely used to grow functional oxides, to control the conductivity of anatase TiO<sub>2</sub> which is a simple binary system.

The substrate surface, especially its composition, also strongly influences the conductivities in various ways [5]. Previously, Y. Nakanishi demonstrated a metal-insulator transition of anatase TiO<sub>2</sub> by changing the surface composition of substrate, using control of the termination of the LaAlO<sub>3</sub> substrate [6]. However, the detailed effect of this termination change is still unclear. One of the difficulties is that free carriers from crystalline defects prevent us from understanding the effect of surface composition control. In this thesis, we aimed to clarify the effect of termination control by controlling the crystalline defects.

### **Experimental Methods**

Anatase TiO<sub>2</sub> films were epitaxially grown on LaAlO<sub>3</sub> (001) substrates using PLD [6]. To control the growth rate, the laser fluence and repetition rate were changed in the range of 0.5 - 1 mJ/cm<sup>2</sup> and 0.25 - 1 Hz, respectively. The laser fluence was changed by fixing the spot size at the TiO<sub>2</sub> target, and varying the total energy. The termination control of the substrate was achieved by depositing a monolayer of LaTiO<sub>3</sub> on top of as-received AlO<sub>2</sub>-terminated LaAlO<sub>3</sub> substrates and monitoring the reflection high energy diffraction intensity oscillations. Single phase epitaxial (001)-oriented anatase TiO<sub>2</sub> thin films and atomically flat surfaces were

confirmed by X-ray diffraction measurements and atomic force microscopy respectively, for all growth conditions. Physical properties were characterized by resistance-temperature ( $R$ - $T$ ), Hall and photoluminescence (PL) studies.

### **[Growth rate dependence of the conductivity]**

Figure 1 shows the growth rate dependences of the carrier density and Hall mobility at  $T = 300$  K. Both of these parameters show a minimum around a growth rate of  $5-7 \times 10^{-3}$  nm/sec. Within the studied range of growth rates, the maximum change in the carrier density is almost two orders of magnitude, contrasting with a marginal variation in the mobility. In order to identify the origin of these carriers, the activation energy ( $E_a$ ) was evaluated by the fitting of  $R$ - $T$  data, which showed good agreement with an Arrhenius fit at high temperatures ( $100 \text{ K} < T < 300 \text{ K}$ ). These fits resulted in an  $E_a$  in the range 30 - 60 meV. Notably this value is of similar order to the energy level of oxygen vacancy ( $V_O^{\bullet\bullet}$ ) states obtained from first principles calculations [7].

As an independent confirmation for the origin of the carriers, PL measurements were performed using a He-Cd laser ( $\lambda = 325 \text{ nm}$ ) as the excitation source at  $T = 10 \text{ K}$ . PL is a powerful technique to detect crystalline defects, which work as recombination centers for excited photocarriers. The PL spectra of anatase  $\text{TiO}_2$  consist of two different peaks, originating from a surface state and a self-trapped exciton (STE) as shown in Fig. 2(a). When there are a number of  $V_O^{\bullet\bullet}$  states, a portion of the STE luminescence arises from a STE strongly coupled to  $V_O^{\bullet\bullet}$ . By increasing the excitation power, the number of photoelectrons increases, filling the  $V_O^{\bullet\bullet}$  sites and eventually a critical power ( $P_{crit}$ ) is reached above which the STE luminescence only occurs through direct emission from the STE. This is characterized by saturation in the plot of the integrated intensity from the STE peak against the excitation power. This critical power is then proportional to  $[V_O^{\bullet\bullet}]$ . The  $P_{crit}$  - growth rate relation shown in Fig. 2(c) closely follows the carrier density-growth rate relation in Fig. 1 confirming that the mobile carriers are generated from  $V_O^{\bullet\bullet}$  states.

The growth rate dependence of  $V_O^{\bullet\bullet}$  can be explained by the difference in the stable oxygen stoichiometry at the surface and in the sub-surface region; the sub-surface favoring a more reduced stoichiometry [10]. If the time to complete a monolayer growth of anatase  $\text{TiO}_2$  ( $\tau$ ) is shorter than the time to achieve surface stoichiometry  $\tau_S$ , the stoichiometry of the highly reduced ablated species is frozen inside the film. When  $\tau_S < \tau <$

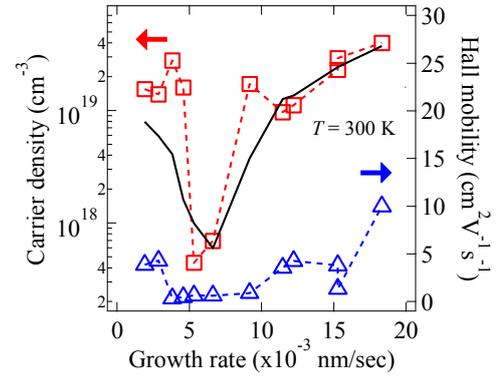


Fig. 1. Growth rate dependences of carrier density and mobility. Dashed lines are guide for the eye. Solid line is a carrier density obtained from calculated  $V_O^{\bullet\bullet}$ .

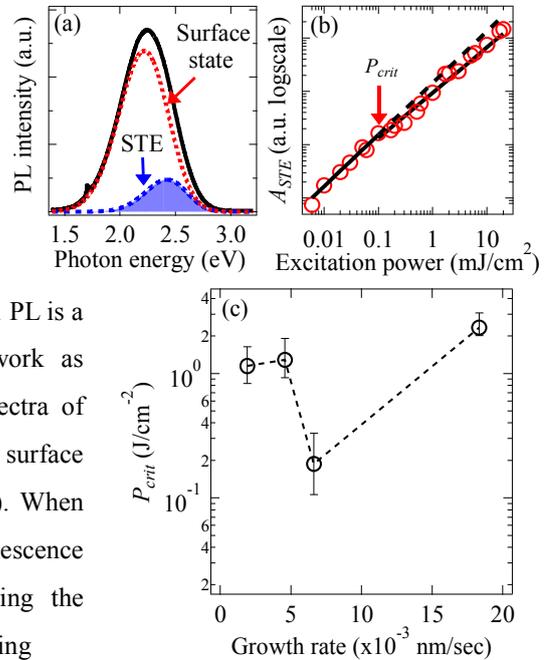


Fig. 2. (a) PL spectrum of anatase  $\text{TiO}_2$  with a growth rate of  $6.6 \times 10^{-3}$  nm/sec. Dotted and dashed curves show the fits for the surface state and the STE (b) Excitation power dependence of STE luminescence intensity ( $A_{STE}$ ) with the growth rate of  $6.6 \times 10^{-3}$  nm/sec. Solid line is a guide for the eye. Dashed line is  $A_{STE} \propto$  Excitation power. (c)  $P_{crit}$  - Growth rate relation. Dashed line is a guide for the eye

$\tau_B$ , where  $\tau_B$  is the time to achieve sub-surface stoichiometry, the less reduced surface equilibrium state is realized for each monolayer of growth resulting in smaller  $[V_O^{\bullet\bullet}]$ . When  $\tau > \tau_B$ , the growth proceeds after each monolayer achieves its surface/sub-surface  $V_O^{\bullet\bullet}$  exchange giving the bulk equilibrium state. The carrier density estimated by  $[V_O^{\bullet\bullet}]$  calculated from this model showed good agreement with experimental result as shown in Fig. 1 (solid line) assuming  $\tau_S = 30$  sec. and  $\tau_B = 1500$  sec.

### **[Termination control and conductivity]**

Anatase  $TiO_2$  was grown on LaO and  $AlO_2$  terminated  $LaAlO_3$  substrates using the above growth conditions which minimizes  $[V_O^{\bullet\bullet}]$ . As shown in the  $R$ - $T$  data shown in Fig. 3(a), a metal-insulator transition between the LaO and  $AlO_2$  terminations was found, qualitatively reproducing the results from Ref. [6], but with a much clearer resistivity difference. From the Hall measurements shown in Fig. 3(b), the sheet carrier density ( $n_{2D}$ ) in the  $AlO_2$ -terminated sample becomes two orders of magnitude smaller than the previous report emphasizing the effect of smaller  $[V_O^{\bullet\bullet}]$ . The LaO-terminated sample showed an increase in the mobility at 300 K from  $8.1$   $cm^2/V\cdot sec$  to  $14.1$   $cm^2/V\cdot sec$  [Fig. 3(c)], with negligible change in  $n_{2D}$ , suggesting a suppression of scattering by  $V_O^{\bullet\bullet}$ . This mobility is also higher than that of  $AlO_2$ -termination with almost the same  $n_{2D}$ . Given the large contrast in the resistivity and  $n_{2D}$  between the two terminations, these data strongly suggest that the metal insulator transition is not driven by  $V_O^{\bullet\bullet}$  generated carriers in the bulk of the film.

### **[Conclusion]**

A strong impact on the conductivity by the growth rate in the PLD process and the atomic control of the substrate surface was demonstrated. Through the study of epitaxial anatase  $TiO_2$  thin films on  $LaAlO_3$  (001), we discovered that the growth rate can vary the carrier density from  $V_O^{\bullet\bullet}$  by two orders of magnitude. Anatase  $TiO_2$  deposited on LaO-terminated  $LaAlO_3$  (001) showed a significant mobility and carrier density enhancement. These result show exceptional promise for conductivity control for applications.

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3 more presentations (2 international, 1 domestic) as a coauthor.

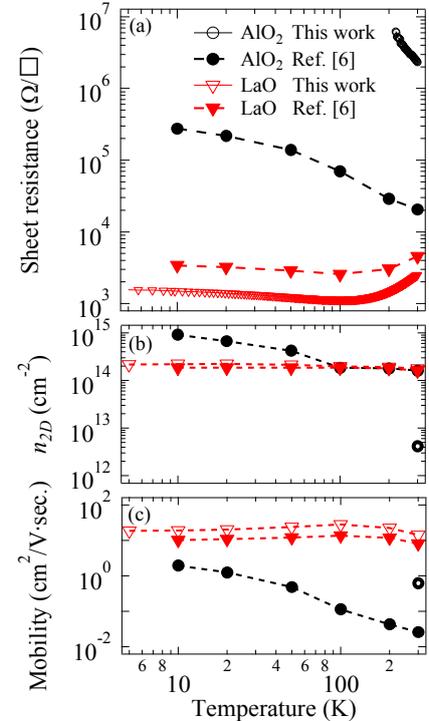


Fig. 3. Temperature dependences of (a) Resistivity, (b) sheet carrier density and (c) Mobility of anatase  $TiO_2$  deposited on LaO and  $AlO_2$  terminated  $LaAlO_3$  substrates.