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Nanostructure growth on termination-controlled $SrTiO_3$ surfaces

終端面を制御した $SrTiO_3$ 上の構造成長

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1. Background

Recently, ultra-thin oxide films only a few nanometers thick have found broad use in miniature electronic devices. Therefore it is obvious that improving the control over the crystal structure, electronic structure, and composition of oxide surfaces and interfaces is gaining importance in the design and development of new electronic devices.

Strontium titanate ($SrTiO_3$) is one of the common substrate materials used for atomic level growth of oxide thin films, mainly because of its simple crystal structure and good quality of commercially available single crystals. Atomic-scale modification and control of the terminating layer of $SrTiO_3$ substrates can thus lead to a variety of novel applications.

The goal of this study is to study the transport properties of single-monolayer oxide films and nanowires.

The specific goal of this study was to fabricate conducting $LaTiO_3$ nanowires. In order to achieve this goal, I studied the growth of $SrO/SrTiO_3$, $LaTiO_3/SrTiO_3$ and $LaTiO_3/SrO/SrTiO_3$ material systems, focusing on the atomic-scale growth mechanism of SrO layers and the transport properties.

2. Experiments

Pulsed Laser Deposition (PLD) is a form of physical vapor deposition, which can be used to fabricate high-quality oxide thin films when the laser ablation conditions are under precise control. All substrates used in this study were wet etched to obtain a regular atomic-scale step-and-terrace surface structure. The crystals were further annealed before film growth to obtain straight and parallel surface steps. The etched and annealed substrates had surfaces that were predominantly terminated by the TiO_2 atomic layer of the perovskite structure.

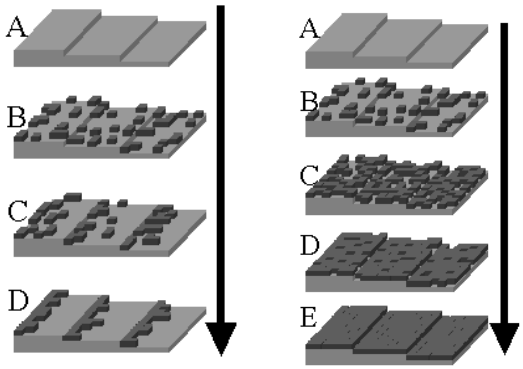

Fig.1 **a.** Step-flow growth mode
b. Layer-by-layer growth mode

Less than one atomic layer of $LaTiO_3$ was grown on $SrTiO_3$ (001) surfaces in the form of wires by PLD in step-flow growth mode. The nanowires were capped with a layer of $SrTiO_3$ to protect the 0.4 nm-thick nanowires from atmospheric degradation. The step-flow growth mode is illustrated in Fig. 1a. Step-flow growth of titanates can only be done at relatively high temperatures and low oxygen pressures. Such crystal growth conditions result in a

large density of oxygen vacancies in the heterostructures. In order to refill the oxygen vacancies in the $SrTiO_3$ capping layer and substrate, samples were annealed for 6 hours at 400°C in a furnace in air.

Similar nanowire samples were grown on SrO-terminated surfaces. SrO was deposited by atomic-layer growth on as-supplied $SrTiO_3$ (001) substrates (Fig.1 b).

In order to study how the surface morphology changes with SrO coverage, two kinds of samples were fabricated: with a 1 u.c. and a 0.5 u.c. SrO layer. Changes of surface morphology were observed by AFM. After SrO layer deposition, $LaTiO_3$ nanowires were grown on the surface in step-flow mode. Anisotropic conduction was observed after capping layer deposition.

3. Results and discussions

A) $LaTiO_3$ wires on a TiO_2-terminated $SrTiO_3$ substrate

Fig. 2 shows the in-plane anisotropy of sheet resistance of a sample containing an array of $LaTiO_3$ wires on a TiO_2-terminated $SrTiO_3$ substrate. The angle is measured between the measurement direction and the direction of the surface steps. Although the resistance measured at 0°appears to be the lowest, the variation of resistance is less than 40%, which can be neglected because there may be other sources of error in resistance values.

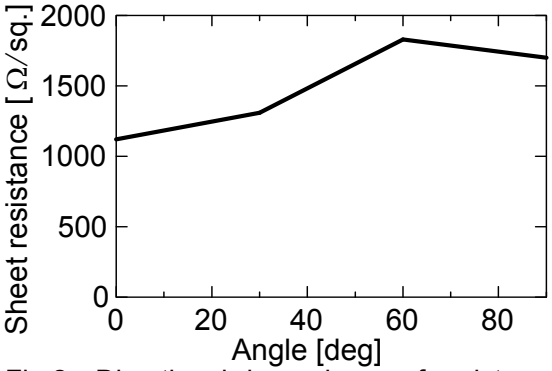

Fig.2 Directional dependence of resistance of an array of $LaTiO_3$ nanowires grown on a TiO_2-terminated $SrTiO_3$ substrate

B) Termination control of a $SrTiO_3$ substrate

In order to improve wire isolation, the substrate termination was controlled by atomic-layer growth of SrO thin films. The number of SrO deposition pulses was selected so that the estimated film coverage was 1 u.c. or 0.5 u.c. based on the RHEED oscillation period. SrO films were grown at 550℃. After growth, samples were annealed at various temperatures of up to 1000 °C, which is the temperature where the $LaTiO_3$ nanowire structures were grown. Fig. 3 shows topography images observed after annealing the surfaces at various temperatures.

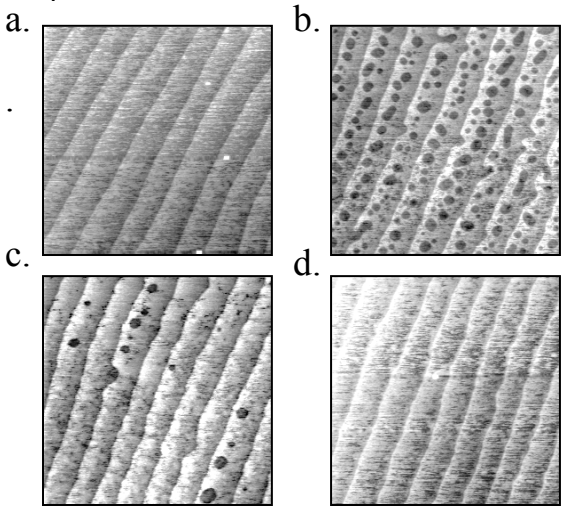

Fig. 3 Topography of a 1 u.c. SrO film on $SrTiO_3$ (1μm×1μm) Annealing temperature and time: **a.** 0 min. **b.** 800 °C 1hour **c.** 900 °C 1 hour **d.** 1000 °C 1hour.

Fig. 4 shows the results of a similar annealing experiment after 0.5 u.c. SrO deposition.

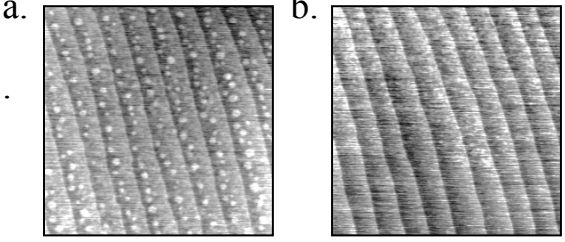

Fig. 4 Topography of a 0.5 u.c. SrO film on $SrTiO_3$ (1μm×1μm). Annealing temperature and time: **a.** 900 °C 10 min. **b.** 1000 °C 1 hour.

From these result, it was found that the surface morphology changes during annealing after SrO deposition although the samples had already been annealed once in order to obtain straight steps. The conclusion is that an additional high-temperature anneal is needed between SrO deposition and $LaTiO_3$ wire deposition to obtain straight wire structures.

C) *$LaTiO_3$ wire growth on SrO-terminated $SrTiO_3$ substrate*

C)-1 AFM measurement

The number of $LaTiO_3$ deposition pulses was selected so that the estimated average film coverage was 0.2 u.c. This should form a wire structure that covers one fifth of each substrate terrace. The AFM topography and phase images were measured before capping layer deposition. The images in Fig. 4 illustrate the phase contrast that corresponds to a chemical difference between parts of the substrate covered by $LaTiO_3$ and $SrTiO_3$.

$LaTiO_3$ wires were observed on both 1u.c. and 0.5 u.c. SrO deposited $SrTiO_3$ surfaces.

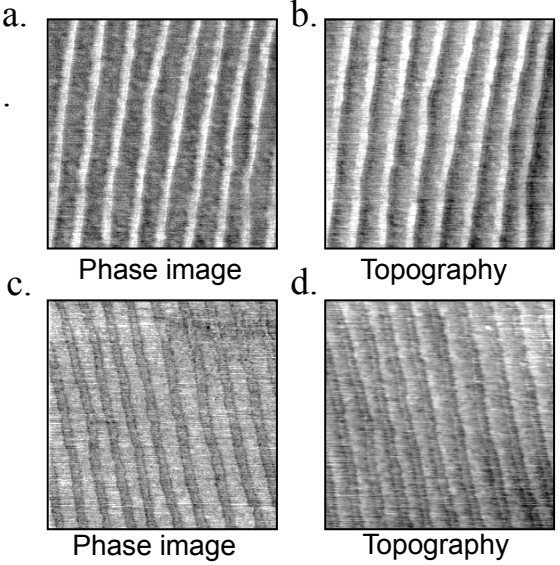

Fig. 5 AFM topography and phase image (1μm×1μm) **a** and **b**: $LaTiO_3$ wires on 1 u.c. SrO layer, **c** and **d**: $LaTiO_3$ wires on 0.5 u.c. SrO layer.

C)-2 Electrical characterization

It was found that the sheet resistance ratio between directions perpendicular and parallel to the wires were very different. While the ratio was 4.8 on the 1u.c. SrO buffered substrate, 6.1×10^5 was seen on the 0.5u.c. SrO deposited substrate. Both were measured 4nder room light exposure. After the 0.5 u.c. SrO sample was kept in darkness to eliminate the effect of photo-induced carriers, the ratio of anisotropy started to increase. The final in-plane anisotropy reached 2.6×10^7.

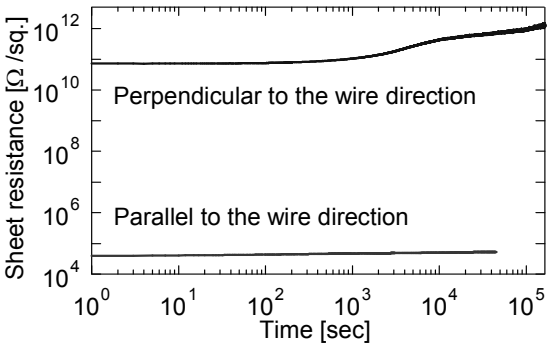

Fig. 6 Sheet resistance of wires in dark field

4. Conclusions

AFM measurements indicated that the wire structure could be obtained by controlling the temperature and the laser repetition rate so that pure step-flow growth is obtained. Although the wire structure was obtained on both 1u.c. and 0.5 u.c. SrO layer, the anisotropy of conductance, which should be a characteristic of the conducting wires, was considerably different. These results suggest that changing the surface termination layer is not the critical step needed for anisotropic wire conductivity. It is more likely that SrO deposition compensated the Sr vacancies that were generated during initial substrate annealing to obtain straight steps and this prevents Lanthanum diffusion into the substrate surface. Excess Sr may prevent $LaTiO_3$ from surface migration in step-flow growth, resulting in small anisotropy of conductance on the 1 u.c. SrO layer.