論文内容の要旨

論文題目　Atomic-scale observation of epitaxial growth process of oxides using ultrastable scanning tunneling microscope

(超安定走査型トンネル顕微鏡を用いた
酸化物エピタキシャル成長過程の原子スケール観察)

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[Introduction]

Transition metal oxides have attracted great interest as a stage in which a wide variety of unique physical properties, such as metal-insulator transition, high-T_c superconductivity and colossal magnetoresistance and, appear, particularly at low temperatures. For applying these materials to electronics, it is of essential importance to make them in high-quality thin film form, which requires comprehensive knowledge of their initial growth processes on lattice matched substrates. The initial growth processes have been studied using atomic force microscopy (AFM) in ambient atmosphere at ten-nm scale or diffraction methods, such as reflection high-energy electron diffraction (RHEED) in vacuum. Although real-space observations using scanning tunneling microscopy (STM) are thought to provide more direct information about the initial growth processes, such attempts have been scarcely made so far, mainly due to dull-contrast STM images caused by ionic nature of metal-oxygen bonds and poor surface preparation techniques for epitaxial growth on an atomic scale, compared to Si or III-V compound semiconductors. To overcome these difficulties, an ultrastable STM instrument with enhanced signal-to-noise ratio and well-established oxide substrate preparation methods are highly desired.

The purpose of the present study is to observe homoepitaxial growth process of perovskite $SrTiO_3$ (STO) on the truly atomically-ordered STO substrate at the atomic level, using ultrastable STM. What I have done in this study covers three topics. The first issue is development of vibration-free STM to overcome thermal drift for long-time measurements and to enhance the STM image contrast. The second issue is establishment of surface preparation methods for oxide substrates from the viewpoint of thin film growth, as well as of surface science. The final subject is atomic-scale observation of homoepitaxial growth process of sub-ML $SrTiO_3$ using pulsed laser deposition (PLD) technique.

[Vibration isolation for ultrastable STM]

Figure 1 shows a schematic illustration of the newly-developed STM system combined with a PLD chamber. Based on the general principles, the STM has the following outstanding features for vibration isolation. First, the STM head and the damping system are located on a foundation completely separated from a building floor to eliminate vibration from the building. Second, the STM system is equipped with a two-stage damping system composed of a typical passive table and actively-controlled damping legs. In general, double passive suspension springs are considered to be most effective for vibration isolation [1]. However, the two passive dampers were found to enhance original vibrations below 20 Hz, rather than to reduce them, because their resonant frequencies are around a few Hz. To avoid this problem, I replaced the lower passive damper with actively-controlled damping legs, which can suppress vibration transfer even around the resonant frequency and also work similarly to usual passive one above a few ten Hz. Moreover, suspension springs supporting the STM head were also replaced with firm poles for obtaining higher rigidity, resulting in higher resonant frequency near the head.

Figure 2 shows a typical fast-Fourier-transformed dark current noise spectrum with a preamplifier-gain of 10^9 acquiring on the STM. As can be seen, there are no significant peaks compared with the reference spectrum [2], and the noise level is lower than 10 fA/$\sqrt{\text{Hz}}$ in a whole frequency range, which is one of the lowest values in the world.

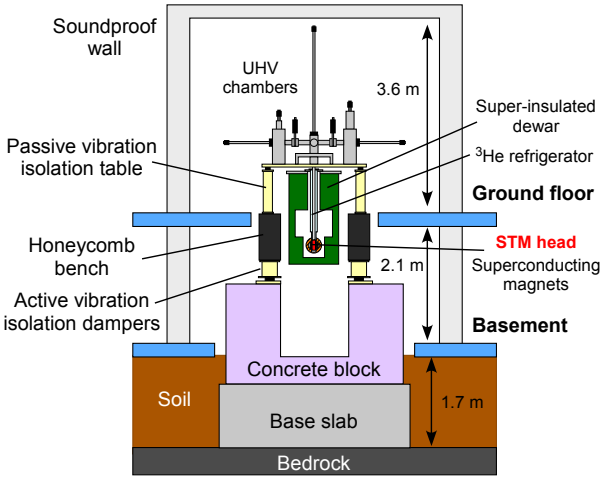

Figure 1: Schematic of newly-developed STM system.

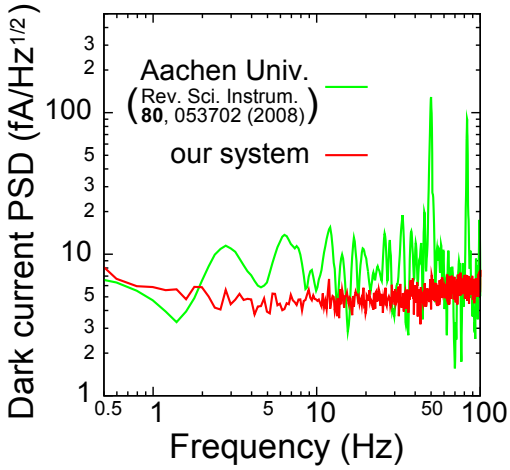

Figure 2: A fast-Fourier-transformed dark current noise spectrum with a reference one [2]. The preamplifier is the same as that of the reference.

[Preparation of $SrTiO_3$(001)-($\sqrt{13} \times \sqrt{13}$) substrates]

Strontium titanate ($SrTiO_3$) has been widely used as a single crystalline substrate for epitaxial growth of perovskite oxides due to its well-defined surface with wide terraces separated by equidistant steps, hereafter called as step/terrace structure. However, I found that the step/terrace structure does not assure atomic-scale structural ordering on the topmost surface and that the structural ordering strongly depends on the amount of oxygen deficiencies, manifesting the importance of controlling oxygen vacancies in surface preparation. Here, to establish the preparation process for obtaining atomically-ordered STO substrate surfaces in a PLD chamber, I have examined the thermal and chemical stability of STO substrates by means of ultrastable STM, low-energy electron diffraction (LEED) and RHEED.

Single crystalline substrates of $SrTi_{1-x}Nb_xO_3$ (x = 0.001) (Nb:STO) (001) were chemically-etched with buffered-HF solution for TiO_2-single termination, and then loaded into a PLD chamber with a background pressure of 5×10^{-9} Torr. Figs. 3(b) and 3(c) are a RHEED pattern and an STM image, respectively, taken on the STO surfaces prepared by a typical heat-treatment as shown in Fig. 3(a). Although a clear step/terrace structure is visible from the wide-scan STM image (inset), the close-up picture shows structural disordering on an atomic scale. This is consistent with the corresponding RHEED pattern which shows only bulk-like (1×1) sharp streaks. Such structural disorder is possibly due to oxygen deficiencies, which are easily introduced into substrate surfaces during heating in a vacuum condition. This suggests that a heat-treatment process under a more oxidative condition is required to reduce the density of oxygen deficiencies.

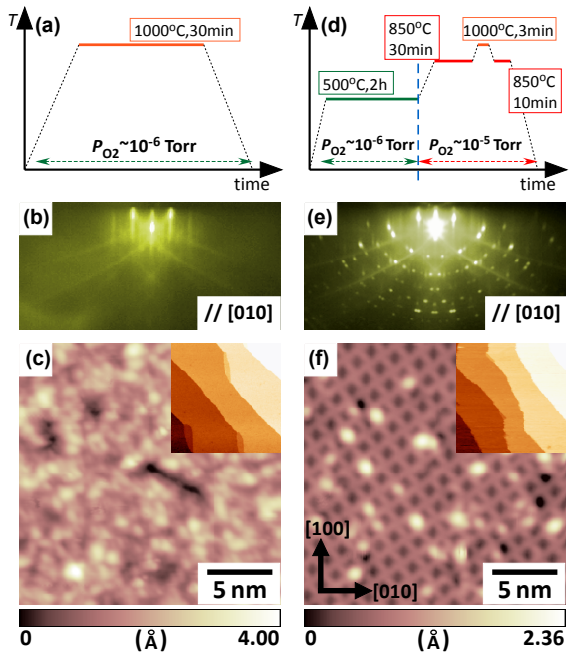

Figure 3: Schematic diagram of (a) typical and (d) new annealing processes. (b), (e): RHEED patterns (c), (f): STM images (20×20 nm^2, $V_s = +1.5$ V, $I_t = 30$ pA at 77 K) on the surfaces annealed by process (a), (b), respectively. Insets show wide-view STM images (400×400 nm^2, $V_s = +2.0$ V, $I_t = 0.2$ nA at RT).

As a consequence, I developed a new annealing process, as shown in Fig. 3(d). The annealing in oxygen partial pressure (P_{O_2}) of 10^{-6} Torr at 500°C is a degassing process for sample and sample holder without the removal of surface carbon-contamination. Heat-treatment at 850°C in $P_{O_2} = 10^{-5}$ Torr is for preparing a single wider domain, and short pulse-like heating at 1000°C in $P_{O_2} = 10^{-5}$ Torr makes steps straight. The contaminated carbon can also be removed at 850°C. The STO surface prepared by the new procedure shows a clearer RHEED pattern and STM image, characterized by well-ordered surface reconstruction (Fig. 3(e), (f)). This reconstructed surface can be identified as $R33.7°$-$(\sqrt{13} \times \sqrt{13})$ structure, being consistent with LEED observations (data not shown) [3,4]. It should be noted that the $(\sqrt{13} \times \sqrt{13})$-reconstructed surface can be prepared in an oxide-growth chamber in a reproducible manner. Thus, the STO $(\sqrt{13} \times \sqrt{13})$ surface is suited as a template on which oxide thin films epitaxially grow.

The $(\sqrt{13} \times \sqrt{13})$ surface shows strong bias-dependent STM images as shown in Fig. 4. It is of great surprise that contrast reversal occurs with increasing sample bias voltages (V_s), where the darker areas at $V_s < +1.5$ V get brighter with V_s increasing. Recent DFT calculation with transmission electron microscopy measurements proposed a $(\sqrt{13} \times \sqrt{13})$ reconstruction model composed of additional TiO_2 topmost layer (TiO_2 double-layer model) [4]. Based on the model, Hamada *et al.* simulated STM images with theoretical calculation [5]. However, the STM sim-

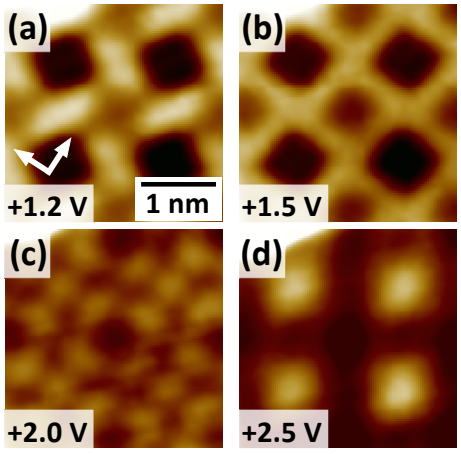

Figure 4: Bias-dependent STM images of the STO(001)-$(\sqrt{13} \times \sqrt{13})$ surface (2.9×2.9 nm^2, $I_t = 30$ pA at 77 K).

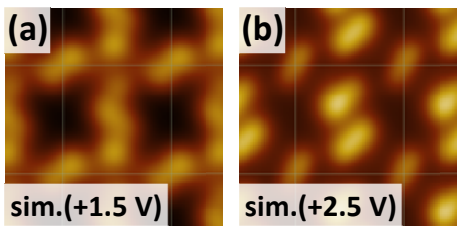

Figure 5: Simulated STM images at (a): $V_s = +1.5$ V and (b): $V_s = +2.5$ V based on the proposed model [5].

ulation cannot reproduce the experimental bias-dependent STM images in the empty states (Fig. 5). Further structural studies on the $(\sqrt{13} \times \sqrt{13})$ surfaces are needed.

[Atomic-scale investigation of initial stage of STO homoepitaxial growth]

It is of peculiar interest to elucidate how the thin film is grown on the truly atomically-controlled substrate surfaces in the initial stage of oxide growth. I have observed the initial stage of homoepitaxial growth of STO on the $(\sqrt{13} \times \sqrt{13})$ substrate surface by using atomic-resolution STM. Two STO thin films with 0.3- and 1.6-monolayer (ML) thickness were homoepitaxially grown on the Nb:STO(001)-$(\sqrt{13} \times \sqrt{13})$ substrates by PLD at a substrate temperature of 700°C under $P_{O_2} = 10^{-6}$ Torr. The film thickness was monitored *in-situ* by RHEED intensity oscillation during deposition. STM measurements were carried out at 77 K on the deposited thin film surfaces without exposing them to air.

Figure 6 shows an STM image taken on the STO film with 0.3 ML coverage at 77 K. The $(\sqrt{13} \times \sqrt{13})$-based mesh structure is clearly recognizable not only on the substrate surface but also on the first layer of the STO film. The mesh structure can also be seen on the second layer of the 1.6-ML thick film (not shown here). Thus, the STO(001)-$(\sqrt{13} \times \sqrt{13})$ substrate can be used as an atomic-scale template to grow single-crystalline perovskite-type oxides even with 1-ML thickness, leading to further studies on the mechanisms of initial growth processes.

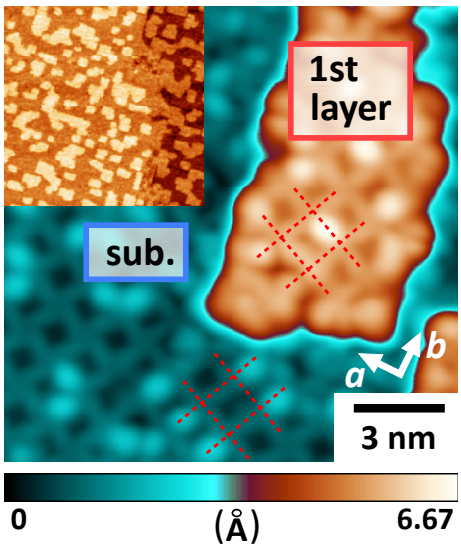

Figure 6: STM image (15×15 nm^2, V_s = +1.5 V, I_t = 30 pA at 77 K) taken on the ultrathin STO film with thickness of 0.3 ML. Red broken lines are guides of the $(\sqrt{13} \times \sqrt{13})$ mesh structure.

[Summary]

In this study, I have developed a new vibration-free STM with a two-stage damping system consisting of a typical passive table and actively-controlled damping legs. I have also established a preparation process for obtaining truly atomically-controlled $SrTiO_3$(001) step/terrace substrates. Furthermore, the initial growth processes of STO homoepitaxial ultrathin films grown on the $(\sqrt{13} \times \sqrt{13})$ substrate surfaces were observed on an atomic scale using the ultrastable STM. The same $(\sqrt{13} \times \sqrt{13})$ reconstruction structure was observed on the mono-layer STO film surface as well as on the original substrate. This growth technique is widely applicable to heteroepitaxial growth of perovskite-type functional materials, which would help to fabricate higher-quality epitaxial thin films with well-defined interfaces.

[References]

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