**Fabrication of High Quality Perovskite Oxide Films by Lateral Epitaxy Verified with RHEED Oscillation**

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Epitaxial growth of SrTiO$_{3-x}$ and SrVO$_{3-y}$ films by Laser MBE has been controlled on an atomic scale. The RHEED intensity oscillation persisting more than 50 periods was observed during the homoepitaxial growth of SrTiO$_{3-x}$ film, indicating the lateral epitaxy in an unit cell layer-by-layer mode. The conductivity of SrTiO$_{3-x}$ ultrathin films was sensitive to the oxygen pressure at the deposition to far greater extent than that of SrVO$_{3-y}$ films.

1. INTRODUCTION

Ferroelectric perovskite oxides attract much attention not only as promising material for nonvolatile memory but also as dielectric layer components in high Tc superconducting devices because of their high capacitances and similar lattice parameters. For fabricating oxide films with atomically flat surface and high crystal quality, two-dimensional epitaxial growth of oxide films should be essential. As has been proved in molecular beam epitaxy (MBE) of semiconductor films, reflection high energy electron diffraction (RHEED) can provide us with a useful information on the crystal structure and morphology of growing film surfaces. Furthermore, in situ monitoring of RHEED intensity oscillation enables us to control the film thickness on a molecular or atomic scale.

Previously, we verified the ceramic layer epitaxy by using the laser MBE (pulsed laser deposition in ultra high vacuum). In this paper, we apply the in situ RHEED monitored laser MBE to the fabrication of atomically regulated perovskite oxide films.

2. EXPERIMENTAL

The laser MBE system employed in this study is composed of a UHV deposition chamber ($\sim 10^{-10}$Torr) containing ceramics targets and a heater, ArF excimer laser (193nm,20ns), and in situ RHEED and X-ray photoelectron spectrum (XPS) analyzers, as shown in Fig.1. A SrTiO$_3$(100) substrate was heated at a temperature of 600°C to 700°C under an oxygen pressure of 10$^{-5}$ to 10$^{-8}$

Fig.1 Laser MBE system with in situ RHEED and XPS apparatuses.
3. RESULTS AND DISCUSSION

3.1. Unit cell layer-by-layer growth in SrTiO$_{3-x}$ homoepitaxy

Fine streaky RHEED patterns and RHEED intensity oscillations were observed throughout the homoepitaxial growth of SrTiO$_{3-x}$ films in such a wide growth conditions as $T_{\text{sub}}$ from 600 to 700°C, $P_o$ from $10^{-8}$ to $5 \times 10^{-6}$ Torr, and D.R. (deposition rate) from 2A/min to 11A/min.

Under the condition of $T_{\text{sub}}$=630°C, $P_o$=5x10$^{-6}$Torr, and D.R. =10.6A/min, SrTiO$_3$ homoepitaxial growth exhibited the RHEED intensity oscillation lasting more than 50 periods at the specular beam spot as shown in Fig.2. After a few oscillation units growth, the once decreased intensity was recovered and shifted into stable oscillation. Every observed oscillation periodicity turned out to be $3.7 \pm 0.5$A, which is equivalent to the interplanar distance (3.905A) of SrTiO$_3$(100). The atomic force microscopy (AFM) demonstrated that the surface morphology was much improved from the root-mean-square roughness of 1.7A for the substrate before the homoepitaxy to that of 1.2A for the film after the 7 units homoepitaxial growth. Thus, the layer-by-layer growth monitored by RHEED oscillation is verified to be useful for the fabrication of high-quality ceramic films with atomically flat surfaces and digitally controlled thicknesses.

![Fig.2 A RHEED intensity oscillation observed during the SrTiO$_{3-x}$ homoepitaxial growth at $T_{\text{sub}}$=630°C and $P_o$=5x10$^{-6}$ Torr](image)

3.2. The persisting RHEED oscillation in SrVO$_{3-y}$ homoepitaxy

We already reported the fabrication of SrVO$_{3-y}$/SrTiO$_3$ superlattice by laser MBE. The lateral heteroepitaxy was further examined by RHEED monitoring for the growth of SrVO$_{3-y}$ films on SrTiO$_3$(100) substrate under various oxygen pressures.

Under the condition of $T_{\text{sub}}$=600°C and $P_o$=1x10$^{-8}$ Torr, RHEED intensity oscillation more than 20 periods was clearly observed, as shown in Fig.3. The oscillation periodicity (3.74±0.7A) agreed well with the lattice length of SrVO$_3$ (a-axis:3.846A). Under the atmosphere of $P_o$ exceeding 1x10$^{-8}$Torr, the RHEED intensity oscillation was observed only a few periods at $T_{\text{sub}}$=600°C.

3.3. Electric property of SrTiO$_{3-x}$ and SrVO$_{3-y}$ ultrathin films

SrTiO$_{3-x}$ is known to exhibit wide electric properties which depend on the oxygen deficiency $x$, stoichiometric SrTiO$_3$ has a high resistivity of ca.10$^{10}$Ω.cm, while reduced SrTiO$_{3-x}$ shows a high conductivity inclusive of the superconductivity below 0.4K.

The relationship between the growth condition and the conductivity of homoepitaxial SrTiO$_{3-x}$ film was examined. Figure 4 shows the oxygen pressure ($P_o$) dependence of conductivity at 150K for SrTiO$_{3-x}$ thin films (about 150A thick) prepared at 630°C. The films deposited at $P_o$ lower than 2x10$^{-8}$ Torr had conductivities higher than 10$^3$Scm$^{-1}$ due probably to significant oxygen deficiencies, whereas the film could be made insulative by the deposition at $P_o$=5x10$^{-7}$ and higher.

On the insulative SrTiO$_3$ layers grown at
630°C and 5x10^{-6} Torr O_2 to improve the surface morphology of substrate, conductive SrTiO_3-x ultrathin films were deposited at T_MBE=630°C and P_o_2=1x10^{-6} Torr under in situ monitoring of RHEED intensity oscillation. Figure 5 shows the resistivity vs. temperature for the films accumulating 5 units (~20A), 12 units (~50A), and 49 units (~190A) conductive SrTiO_3-x layers, together with those of Nb-doped SrTiO_3 single crystals depicted for comparison. The resistivity values and temperature dependences of the three thin films were almost the same. Thus, we could fabricate SrTiO_3-x films quite homogeneous both in the structure and electrical property. The conductive SrTiO_3-x ultrathin films prepared have the conductivities much higher than the Nb-doped SrTiO_3 crystals.

The conductivity of SrVO_3-y thin film (about 250A thick) was not so sensitive to P_o_2 as that of SrTiO_3-x. The film prepared at T_MBE=630°C and P_o_2=5x10^{-6} Torr had a conductivity of 1.63x10^{-2} S cm^{-1}, and the films deposited at P_o_2 lower than 5x10^{-6} Torr had conductivities higher than 1.63x10^{-2} S cm^{-1}. From this result, that at the condition of T_MBE=630°C and P_o_2=5x10^{-6} Torr, SrTiO_3-x was made to be an insulator and SrVO_3-y was a conductor, it is possible for us to fabricate the superlattices of SrTiO_3-x(insulator)/SrVO_3-y(conductor) and of SrTiO_3-x(conductor)/SrVO_3-y(conductor).

4. Conclusions
The persisting RHEED intensity oscillation lasting more than 50 periods was observed during the homoepitaxial growth of SrTiO_3 on SrTiO_3(100) substrate under optimized deposition conditions by laser MBE. The resistivity vs. temperature curves of SrTiO_3-x ultrathin (20A ~ 190A) films were substantially the same, indicating highly homogeneous and reproducible nature of our laser MBE method. During the heteroepitaxial growth of SrVO_3-y on SrTiO_3(100), we could observe the persisting RHEED intensity oscillation more than 20 periods only under an ultra-high vacuum (<2x10^{-8} Torr) condition. By controlling the oxygen pressure at the deposition, we can fabricate both conductive and insulative SrTiO_3-x epitaxial films as well as their superlattices with conductive SrVO_3-y epitaxial layers.

Acknowledgement
We are grateful to Dr. M. Kawasaki and Mr. K. Fujito of Tokyo Institute of Technology for their precious comments and experimental assistance. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, and by the Nissan Science Foundation of Japan.

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