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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 non-volatile memory but also as dielectric layer components in high Tc superconducting devices because of their high capacitances and similar lattice parameters[1]. 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. Futhermore, in situ monitoring of RHEED intensity oscillation enables us to control the film thickness on a molecular or atomic scale[2]. Previously, we verified the ceramic layer epitaxy by using the laser MBE (pulsed laser deposition in ultra high vacuum)[3]. 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^{-8} to 10^{-5} Torr. Sintered targets of $SrTiO_3$ and $SrVO_3$ were ablated by a focused laser beam (2~10Hz,~0.5J/cm^2) to deposit films on the heated substrate. The deposition rate was about 5A/min for the laser frequency of 5Hz. In situ RHEED observation was conducted throughout the deposition using an incident beam energy of 19keV and glancing angle of 3° from [010] azimuth of the $SrTiO_3$ (100) substrate. The RHEED pattern and intensity were monitored through a CCD camera, and the intensity was analyzed by an image-processor. The temperature dependence of resistivity of the obtained films was measured by the standard four probe method.

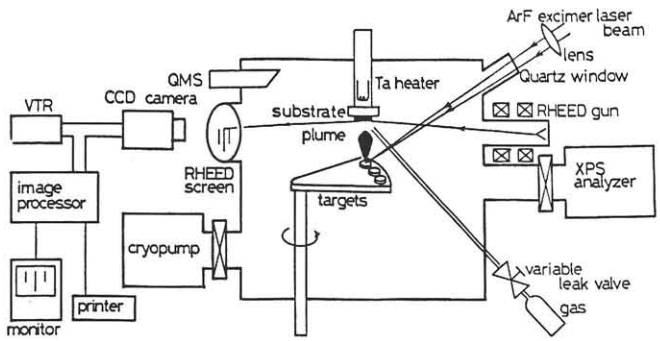

Fig.1 Laser MBE system with in situ RHEED and XPS apparatuses.

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_{sub} from 600 to 700°C, Po_2 from 10^{-8} to $5x10^{-6}$ Torr, and D.R. (deposition rate) from 2A/min to 11A/min.

Under the condition of T_{sub}=630°C, Po_2=$5x10^{-6}$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±0.5A, which was 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.

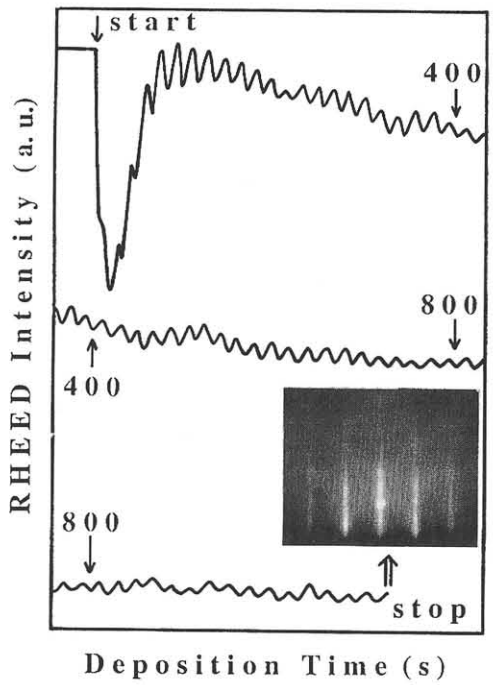

Fig.2 A RHEED intensity oscillaiton observed during the $SrTiO_{3-x}$ homoepitaxial growth at T_{sub}=630°C and Po_2=$5x10^{-6}$ Torr

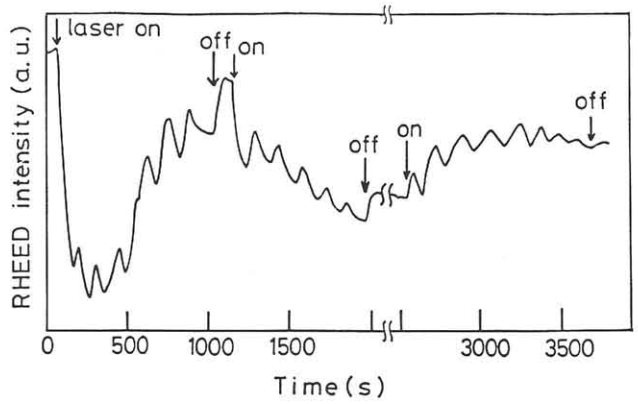

Fig.3 RHEED intensity oscillation observed during the $SrVO_{3-y}$ heteroepitaxial growth at T_{sub}=600°C and Po_2=$2x10^{-8}$ Torr.

3.2 The persisting RHEED oscillation in $SrVO_{3-y}$ heteroepitaxy

We already reported the fabrication of $SrVO_{3-y}/SrTiO_{3-x}$ superlattice by laser MBE[3]. 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_{sub}=600°C and Po_2=$1x10^{-8}$ Torr, RHEED intensity oscillation more than 20 periods was clearly observed , as shown in Fig.3. The oscillation periodicity (3.7±0.7A) agreed well with the lattice length of $SrVO_3$ (a-axis:3.846A). Under the atmosphere of Po_2 exceeding $1x10^{-8}$Torr, the RHEED intensity oscillation was observed only a few periods at T_{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.$10^{10}\Omega$.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 (Po_2) dependence of conductivity at 150K for $SrTiO_{3-x}$ thin films (about 150A thick) prepared at 630°C. The films deposited at Po_2 lower than $2x10^{-8}$ Torr had conductivities higher than 10^3Scm^{-1} due probably to significant oxygen deficiencies, whereas the film could be made insulative by the deposition at Po_2=$5x10^{-7}$ and higher.

On the insulative $SrTiO_3$ layers grown at

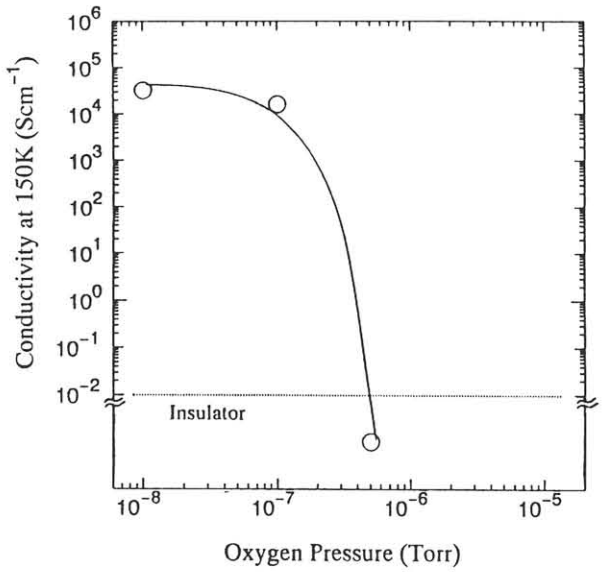

Fig.4 Conductivity of $SrTiO_{3-x}$ thin films (150A) dependent on Po_2 at the deposition.

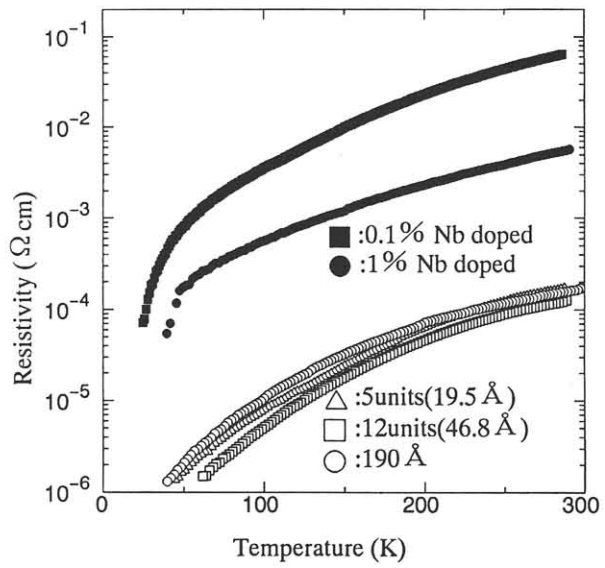

Fig.5 Resistivity vs. Temperature for $SrTiO_{3-x}$ ultrathin films and Nb-doped $SrTiO_3$ crystals

630°C and $5x10^{-6}$Torr O_2 to improve the surface morphology of substrate, conductive $SrTiO_{3-x}$ ultrathin films were depostited at T_{sub}=630°C and Po_2=$1x10^{-8}$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 49units(~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 homogenous 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 Po_2 as that of $SrTiO_{3-x}$. The film prepared at T_{sub}=630°C and Po_2=$5x10^{-6}$Torr had a conductivity of $1.63x10^{-2}Scm^{-1}$, and the films deposited at Po_2 lower than $5x10^{-6}$Torr had conductivities higher than $1.63x10^{-2}Scm^{-1}$. From this result that at the condition of T_{sub}=630°C and Po_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 homogenous 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.

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