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Nanometer-Scale Design and Growth of Ceramic Hetero-Junctions and Superlattices

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Fabrication technology of ceramic superlattices and hetero-junctions has been investigated by using pulsed laser MBE method. RHEED intensity oscillations observed during the growth of oxide films were used to control the growth thickness on an atomic scale. An anomalous metal-semiconductor transition was observed in the $SrVO_{3-x}/SrTiO_{3-y}$ superlattice.

1. INTRODUCTION

We are interested to explore nanometer-scale design of ceramic superlattices. Artificially designed nanometer-scale structures may add unexpected quantum size effects in conventional ceramics. Such effects can also be applied to the fabrication of tunnel type Josephson junctions as well as to the deposition of insulator or dielectric ultra-thin films on semiconductors.

Pulsed laser molecular beam epitaxy (laser MBE) has been proved by us to be a promising technique to stack ceramic epitaxial layers in a digitally controlled manner by monitoring the intensity oscillation of reflection high energy electron diffraction (RHEED) during the growth[1,2]. We aim to extend this technology to ceramic lattice engineering, i.e. the systematic designing and construction of ceramic superlattices.

2. EXPERIMENTAL

Pulsed laser MBE system we used is equipped with an RHEED for *in situ* surface monitoring and an X-ray photoelectron spectrometer (XPS) connected by a gate valve. Sintered targets of $SrVO_3$, $SrTiO_3$, and CeO_2 were ablated under a pressure below $1x10^{-7}$Torr by ArF excimer laser beam to deposit layered films on $SrTiO_3$(001) substrate heated at a temperature between 600 and 800°C. The deposited film structure was characterized by RHEED, X-ray diffraction (XRD), and XPS. Electrical conductivity was measured by the four probe method.

3. RESULTS AND DISCUSSION

3.1. *Perovskite Superlattice*

Since $SrVO_3$ and $SrTiO_3$ have perovskite structures with lattice parameters of 0.385 and 0.390nm, respectively, coherent epitaxial growth is expected. $SrVO_{3-\delta}$ is an electron carrier conductor, while $SrTiO_{3-\delta}$ changes its character from insulative to conductive and further to superconductive depending on the oxygen deficiency δ.

Fine RHEED streak patterns observed during the film growth at 650°C under $2x10^{-8}$Torr indicated clearly the epitaxial growth of $SrVO_{3-x}$ (SVO) and $SrTiO_{3-y}$ (STO) films with perovskite structure on $SrTiO_3$ substrates. Under optimized conditions, films were grown in layer-by-layer manner judging from the observation of RHEED intensity oscillation as shown in Figs. 1 and 2 for SVO and STO, respectively. The oscillation periodicity

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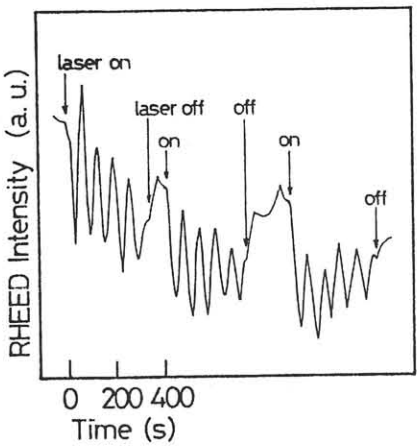

Fig.1. Typical RHEED intensity oscillation observed for $SrVO_{3-x}$ film growth monitored at the central streak. The oscillation periodicity was 0.36nm and was close to the *a*-axis length of $SrVO_3$, 0.38nm.

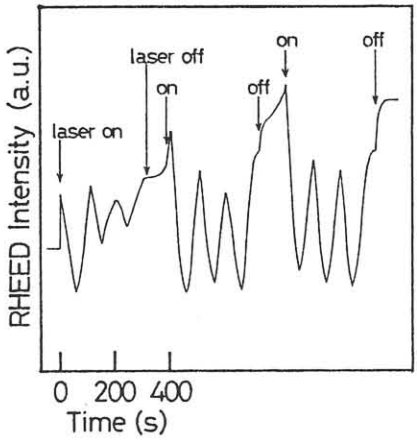

Fig.2. Typical RHEED intensity oscillation for $SrTiO_{3-y}$ homoepitaxial growth. The oscillation periodicity agreed well to an *a*-axis length of $SrTiO_3$.

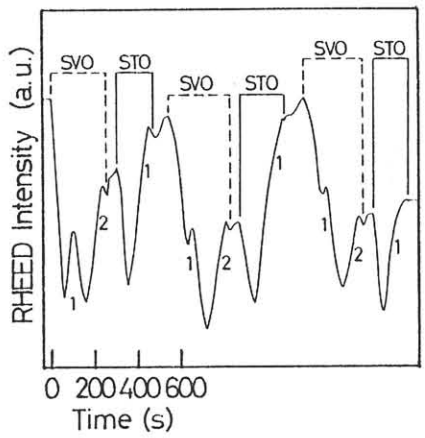

Fig.3. Variation of RHEED intensity monitored during formation of a $[(SVO)_2/(STO)_1]_9$ superlattice. The figure demonstrates a sequential deposition from the 3rd to the 5th periods.

corresponded well with the unit cell length of the perovskites. Therefore, we are able to fabricate SVO/STO superlattices with each layer thickness regulated on an atomic scale by counting the peak numbers of the RHEED intensity oscillation.

Figure 3 demonstrates the RHEED intensity oscillation monitored during the growth of a superlattice designed to have nine repeating units of two SVO and one STO cell lengths ($[(SVO)_2/(STO)_1]_9$). The coincidence between the designed and fabricated superlattice structures was confirmed by XRD; the superlattice was calculated to have 10.3nm thickness from angular position of XRD Laue peaks and the designed thickness was 10.4nm.

A superlattice with periodicity of 8nm, $[SVO(4nm)/STO(4nm)]_5$, was also prepared. In this case, layer thicknesses were regulated by both RHEED intensity oscillation and deposition duration because the oscillation decayed as the film was thickened as shown in Fig.4. Although the decaying oscillation suggests disturbance of layer-by-layer growth, XRD measurement indicated that superlattice structure was formed almost as designed. The superlattice periodicity calculated from XRD satellite peaks was 8.6nm, which was close to the designed value of 8.0nm. The film thickness was calculated to be 34nm from three Laue peaks observed clearly between neighboring satellite peaks. The values designed and measured by stylus method were 40 and 35nm, respectively.

Temperature dependences of resistivity of these superlattices were different from those of SVO and STO epitaxial films. SVO and STO films were metallic, i.e. their resistivities decreased with temperature decrease. On the other hand, the

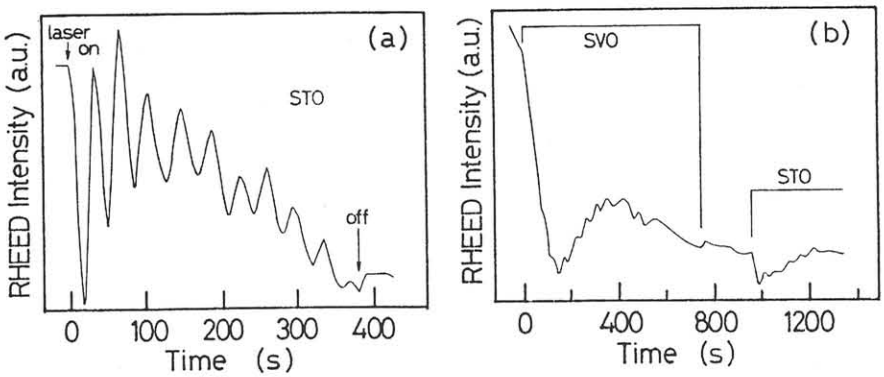

Fig.4. Variation of RHEED intensity monitored during formation of a $[SVO(4nm)/STO(4nm)]_5$ superlattice. (a) shows the oscillation for the first STO layer and (b) for the 2nd SVO/STO layer.

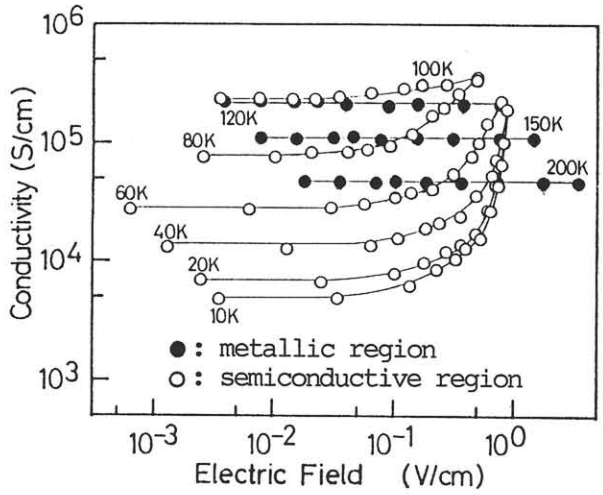

Fig.5. Electric field dependence of conductivity of the $[(SVO)_2/(STO)_1]_9$ superlattice at various temperatures.

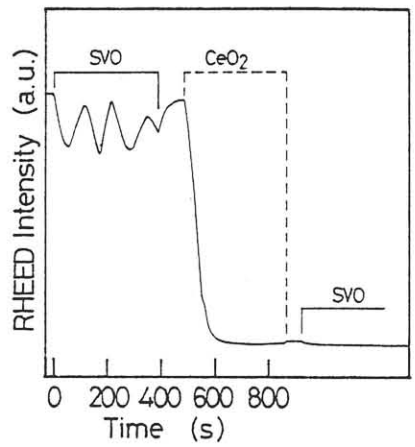

Fig.6. Intensity variation of RHEED 00 rod observed during sequential deposition of $SrVO_{3-x}$(SVO), CeO_2, and SVO layers.

superlattices changed their electric property upon cooling from metallic to semiconductive at about 100K. The resistivity at temperatures lower than 100K decreased as the measuring current was increased. Figure 5 shows the relationship between the conductivity and electric field applied to measure the conductivity of the $[(SVO)_2/(STO)_1]_9$ superlattice at various temperatures. Since similar phenomenon was observed in layered chalcogenides such as TaS_2 and VSe_2[3], we presume that the conducting path is also confined in the two-dimensional layers of our superlattice.

3.2. *Fluorite/Perovskite Hetero-Junction*

CeO_2 takes a fluorite structure and has a lattice parameter of a=0.541nm ($a/\sqrt{2}$=0.383nm). Therefore, CeO_2(001) was expected to grow epitaxially on $SrTiO_3$ and $SrVO_3$ (001)planes with lattice mismatches of 2 and 0.6%, respectively. However, at the perfect epitaxial interface, electric charge of atomic layers should be out of balance; for instance $(...O_2^{4-}/Ce^{4+}/O_2^{4-}/Ce^{4+}...)//(...SrO/VO_2/SrO/VO_2...)$ at $CeO_2/SrVO_3$ interface.

Figure 6 shows the intensity variation of RHEED 00 rod observed during CeO_2 deposition on SVO(001) film surface at 600°C. As soon as CeO_2 deposition started, the streaky RHEED pattern characteristic of the SVO film was obscured and was turned into broad spotty pattern of CeO_2(001), suggesting CeO_2 grew three-dimensionally. At 700°C, crystallinity of CeO_2 films was improved judging from sharp spotty RHEED and XRD patterns.

4. CONCLUSIONS

Ceramic superlattices have not yet been synthesized in a well controlled manner as in semiconductor superlattices. Our growth methods may open a new field of ceramic lattice engineering. The metal-semiconductor transition observed in the SVO/STO superlattice may indicate a quantum effect in ceramic superlattice. Further study is in progress to elucidate elementary features for ceramic lattice engineering as systematic approach to ceramic hetero-junctions and superlattices.

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