Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1659–1662

www.elsevier.com/locate/jeurceramsoc

Phase shift behavior of RHEED intensity oscillation in intermediate growth mode between layer-by-layer mode and step flow mode

G.H. Lee*, B.C. Shin

Research Center for Electronic Ceramics, Dong-Eui University, Gaya-Dong 24, Busanjin-Ku, Busan 614-714, South Korea

Abstract

Phase shift behavior of the first oscillation of reflection high-energy electron diffraction specular beam intensity was observed in the process of the resumption after growth interruption during epitaxial growth of $SrTiO_3$ on $SrTiO_3$ (001) substrate with the misorientation angle of 1°. The growth proceeded in intermediate mode between layer-by-layer mode and step flow mode. Using an exactly oriented substrate, the phase shift phenomena disappeared, when the growth was a perfect layer-by-layer mode. The phase shift appears to be closely related to the growth mode. This is the first observation of phase shift of intensity oscillation in the growth mode between 2D nucleation on the terraces and step propagation. By observing the period of the first oscillation, initial surface roughness on the substrate can be identified.

Keywords: $BaTiO_3$ and titanates; Films; Perovskites; RHEED intensity oscillation; Surfaces

1. Introduction

Oxides with perovskite structure have attracted great attention due to the many versatile properties such as high temperature superconductivity, magnetism, optical nonlinearlity, dielectricity and so on. This enables many practical applications of the oxides in electronic devices such as high Tc superconductor devices, nonvolatile memory, and dynamic random access memory. $SrTiO_3$ (STO) and $BaTiO_3$ (BTO) have emerged as important materials in the field of microelectronic devices owing to their useful ferroelectric properties. Besides, these are also potential candidates for the insulator layer in the high Tc oxide superconducting device due to their similar perovskite structure and small lattice mismatch with high Tc oxide superconductors. To exploit oxide properties in the electronic devices, it is necessary to prepare these oxides in the form of thin films. Furthermore for high quality oxide thin films, the surface and interface of thin films should have atomic level smoothness which demands precise atomic scale control of the thickness.

For controlling film thickness on atomic scale during molecular beam epitaxial (MBE) growth, reflection high-energy electron diffraction (RHEED) is a widely used technique.[1,2] In a layer-by-layer growth mode during the growth process, the intensity of RHEED specular beam oscillates regularly, which has been explained by a growth model of formation and coalescence of two-dimensional (2D) nuclei. With the beginning of 2D nuclei formation, the number of electrons scattered on the surface increases, which decreases the intensity of the RHEED specular beam. As the growth proceeds, the coalescence of the 2D nuclei starts, which eventually recovers the flatness of the growing surface and in turn increases the RHEED intensity again. Owing to the repetition of the formation and coalescence of two-dimensional (2D) nuclei, RHEED intensity shows oscillatory behavior. It has been established that one period of RHEED intensity oscillations corresponds exactly to the deposition of one molecular layer or atomic layer.[3–5] Thus, by monitoring the oscillation during epitaxial growth, growing layers can be controlled on atomic scale and growth rate can be determined digitally. But, our results show that one period of these oscillations does not exactly correspond to the growth of one complete monolayer and the period can be changed by initial surface coverage as well as growth mode.

In this paper, we report the first interesting observation of phase shift phenomenon in the RHEED intensity

* Corresponding author. Tel.: +82-51-890-1722; fax: +82-51-890-1619.
E-mail address: ghl@dongeui.ac.kr (G.H. Lee).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00391-1

oscillations during STO and BTO growths on atomically smooth STO (001) substrate.

2. Experimental

Films were grown by pulsed laser deposition method using a pulsed KrF excimer laser. The PLD system is schematically represented in Fig. 1. The focused laser beam with a typical fluence of 1 J/cm^2 and a repetition rate of 1 Hz was used as the energy source for the ablation of single crystal STO or sintered BTO targets. The laser beam was impinged onto the targets and the plume fraction ablated from the target was condensed into the film on a substrate heated at 600 °C. For oxidizing atmosphere, oxygen gas was flushed onto the substrate during the film growth. RHEED pattern was monitored throughout the deposition with the incident energy of 19 KeV. The electron beam of RHEED was incidented on STO (001) substrates at a glancing angle of about 3°. A charge coupled device (CCD) camera was used to monitor the RHEED diffraction pattern image. A personal computer was used to record the specular beam intensity and control the growth procedures. During the growth, the specular beam intensity exhibited a clear oscillation behavior presenting a layer-by-layer growth.

The substrates with the surface both exactly oriented ($<\pm 0.3°$) and intentionally misoriented with the angle of 1° toward [100] with respect to the crystallographic (001) plane were used. The substrates were prepared by etching as-polished substrates chemically with a buffered (pH = 4.5) NH_4F–HF (BHF) solution, the surface of which has one unit cell high (0.4 nm) steps and atomically flat terraces.[6] Fig. 2 demonstrates the AFM image of the surface on a BHF-treated $SrTiO_3$ (001) substrate. Atomic steps with the height of 0.4 nm and atomically flat terraces are clearly observed on the whole surface. This surface becomes smooth enough to realize atomic and (or) molecular layer epitaxy of various oxide materials. In reality, RHEED intensity oscillation persisting over 300 periods was observed in a homoepitaxial $SrTiO_3$ growth using the BHF-treated $SrTiO_3$ substrate, which indicated molecular layer-by-layer epitaxial growth continued to give 120 nm thick film.[4] In this study, epitaxial growths were carried out using the BHF-treated $SrTiO_3$ (001) substrates.

Before the epitaxial growth, the substrates were annealed at the temperature of 600 °C for 2 h in O_2 atmosphere of 1×10^{-10} Torr for removing carbon and contaminant from the surface. The annealed STO (001) substrate showed fine diffraction spots on the 0th and 1st Laue circles and Kikuchi lines. Epitaxial growths of STO and BTO were performed at an oxygen pressure of 10^{-6} Torr maintaining the substrate temperature at 600 °C.

3. Results and discussion

The intensity behavior of RHEED specular beam observed during homoepitaxial STO growth is shown in Fig. 3. The growth was carried out at 600 °C under oxygen atmosphere of 1×10^{-6} Torr and on a substrate with a misorientation angle of 1°. The quite regular intensity oscillation is observed indicating a layer-by-layer growth under this experimental condition. One period of the oscillation was 0.4 nm, which corresponds to the *c*-axis single unit cell layer of STO as estimated from the deposition rate. During the film growth, the growth was halted at various stages of RHEED intensity oscillations and restarted after some relaxation time. As shown in Fig. 3, when the growth was stopped,

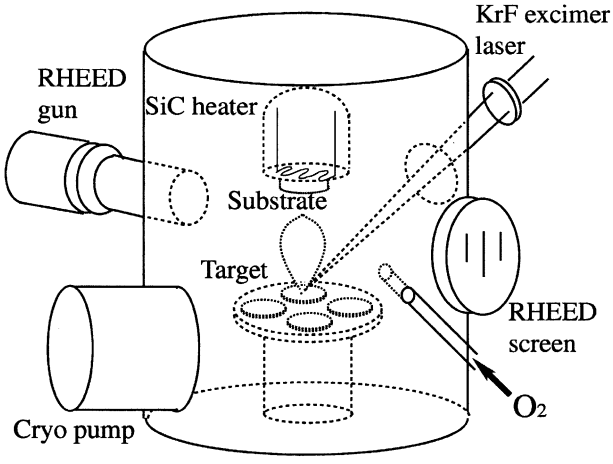

Fig. 1. Schematic diagram of the pulsed laser deposition (PLD) system used.

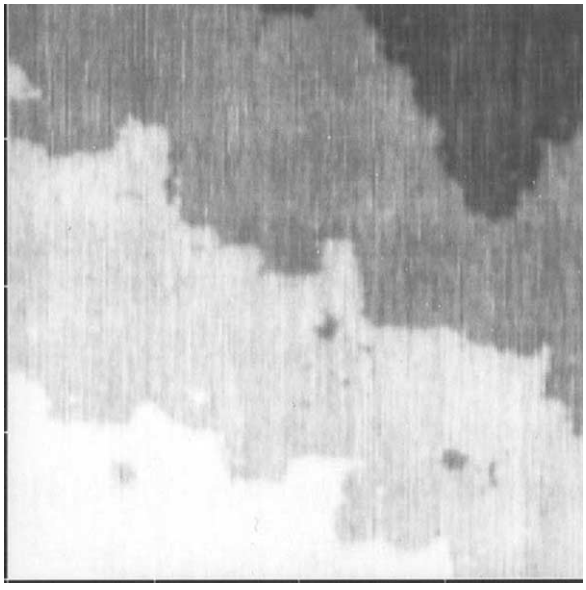

Fig. 2. AFM image (1×1 μm) of the surface on a BHF-treated $SrTiO_3$ (001) substrate.

significant recovery in the intensity was observed. Restarting the growth, the RHEED intensity starts to oscillate again from the maximum intensity level. This implies that just after the deposition, surface adatoms not enough to cover the surface were randomly distributed. During the relaxation, migration of the adatoms to the pre-existing step edges occurred, which improves the surface smoothness leading to the intensity recovery. Therefore, the growth mode under this deposition condition could be considered as intermediate stage between a layer-by-layer mode and step-flow mode. It is well known that the RHEED intensity oscillations reflect the oscillations of the surface coverage. The growth was stopped at the points that coincided approximately with 0.5, 0.75 and 0.25 ML. When the growth was restarted after relaxation, the periods of the first oscillation to the next maximum level were in close agreement with the growth time of 0.5, 0.25 and 0.75 ML, respectively. This indicates a phase shift of the first oscillation to the next intensity maximum level. Thus, under the employed experimental conditions, initial surface smoothness on substrate can be estimated by observing the phase shift of the first intensity oscillation.

The layer-by-layer growth of STO on an exactly oriented STO (001) substrate is represented in Fig. 4. The film was grown at 600 °C under oxygen atmosphere of 1×10^{-6} Torr. Typical oscillation behavior of RHEED specular beam intensity was clearly observed. The oscillation period was in accordance with one molecular layer of [SrO/TiO_2]. The film growth was interrupted at the intensity levels of 0.75 and 0.5 ML as shown in Fig. 4. There is very little intensity recovery when the growth is stopped. This implies that surface diffusion of adatoms is negligible, which indicates that the growth proceeded in a perfect layer-by-layer mode. When the growth was restarted after the relaxation time, the RHEED intensity started to oscillate from the points of 0.75 and 0.5 ML. After re-growth, the oscillation time necessary for reaching the next maximum intensity level agreed well with the growth time corresponding to 0.25 and 0.5 ML, respectively. The RHEED intensity oscillation started from the stopped level, after which phase shift phenomenon of RHEED intensity oscillation was not observed.

RHEED intensity oscillation started at different oscillation position according to the misorientation angles of the substrate used for each growth in the process of re-growth after growth interruption. This can be understood from the relationship between surface diffusion length of adatom and terrace width. The terrace width of a substrate with the misorientation angle of 1° is estimated as 22 nm while the terrace width of the exactly oriented substrate was about 200 nm from the observation by atomic force microscopy (AFM). Higher the misorientation angle is, higher is the step density on the substrate. This leads to the enhancement of step-flow growth because the steps act as dominant sites for adatom incorporation. Accordingly, with increasing the misorientation angle, the contribution due to step flow at step edges to RHEED intensity becomes larger than that when using an exactly oriented substrate. This leads to stronger intensity recovery. However, 2D nuclei still remain on the terrace and the roughness variation on the terrace causes the RHEED intensity oscillations. It has been reported that in the growth proceeding via a combination of step flow and 2D island nucleation, many islands were still observed near steps even after

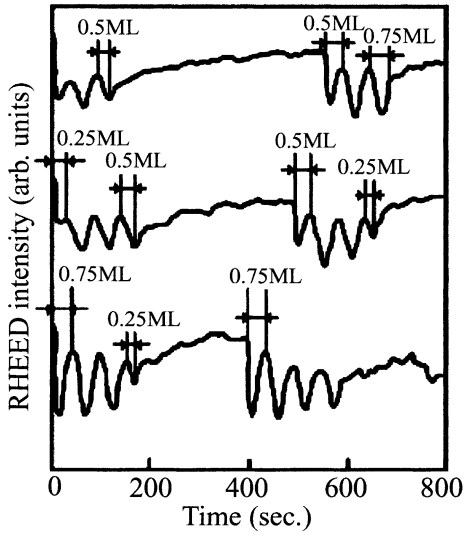

Fig. 3. Variation of the RHEED intensity oscillations observed during the homoepitaxial growth on an atomically smooth $SrTiO_3$ (001) substrate with misorientation angle of 1°. The film was repeatedly regrown after some relaxation time.

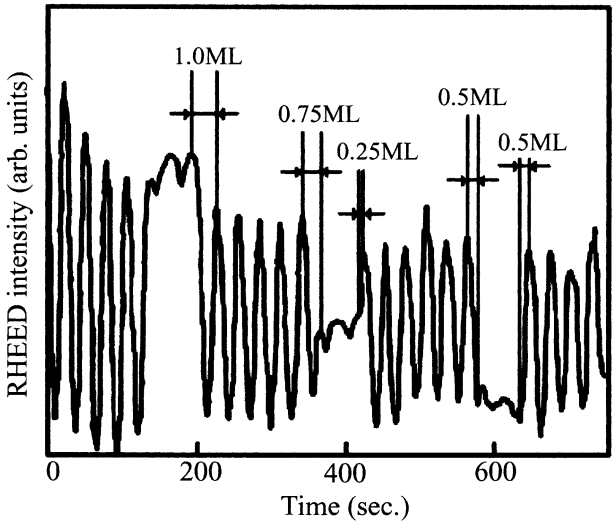

Fig. 4. Variation of the RHEED intensity oscillations observed during the homoepitaxial growth on an exactly oriented $SrTiO_3$ (001) substrate with atomically smooth terraces and steps. The film growth was repeatedly restarted after some relaxation time.

enough relaxation time after the deposition.[7,8] During the relaxation time, the steps advance by the incorporation of preexisting 2D islands into step edges. Therefore the zones devoid of 2D islands (in short, denuded zones) were formed near descending steps and 2D islands were observed near ascending steps. Then the denuded zone length on the terrace corresponds to the surface diffusion length of adatom. When the growth was restarted after relaxation, all of the flux incident on a terrace within a denuded zone diffused to 2D islands existing on the remainder of the terrace due to the sufficient surface diffusion length. Hence, the remainder of the terrace needs to be filled before the surface coverage is recovered, which implies that the period of the first RHEED intensity oscillation depends on the surface coverage on the terrace except the denuded zone. This resulted in the phase shift phenomenon of the first RHEED oscillation after re-growth. After the completion of surface coverage, the period of RHEED oscillation again corresponds to the completion period of one monolayer.

In contrast, in the epitaxial growth of STO on an exactly oriented substrate, the RHEED intensity mainly reflected the roughness on the terrace because of lower step density without showing any substantial recovery of the intensity. Thus, after re-growth, RHEED intensity oscillation started from the stopped level and the period of oscillation is essentially preserved. In reality, as shown in Fig. 5, for heteroepitaxial BTO growth using an exactly oriented substrate, similar experimental result as in homoepitaxial STO growth was observed. After the interruption of growth, no substantial recovery and restart of RHEED intensity at interrupted points were observed under the same growth conditions as applied here.

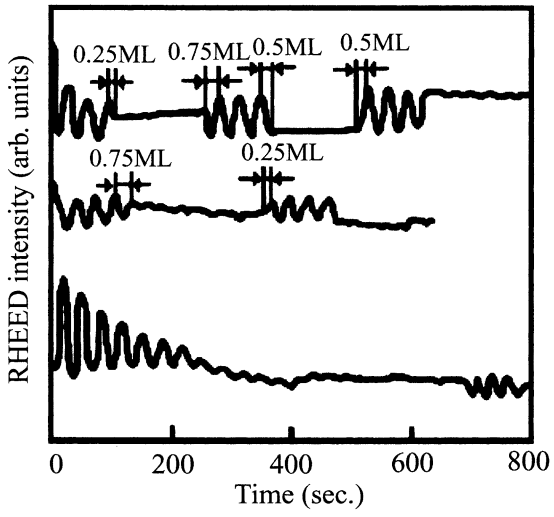

Fig. 5. Variation of the RHEED intensity oscillations observed during the growth of $BaTiO_3$ film on an exactly oriented $SrTiO_3$ (001) substrate with atomically smooth terraces and steps. The film growth was repeatedly restarted after some relaxation time.

4. Conclusion

Oscillatory behaviors of RHEED intensity were observed for epitaxial growths of STO and BTO on atomically smooth STO substrates. In homoepitaxial STO growth using a substrate with a misorientation angle of 1°, RHEED intensity recovered to maximum level and the period of the first RHEED intensity oscillation after restarting the growth was different according to the intensity points halted in the oscillation. The periods of the first oscillation were in excellent agreement with the growth time requisite for returning from the intensity level just after growth-interruption to the maximum intensity level. The phase shift of the first oscillation was observed, apparently due to the enhancement of step flow component contributing to RHEED intensity. On the other hand, with the use of an exactly oriented substrate, the RHEED intensity oscillation resumed at the stopped level when restarting the growth after relaxation as in this case RHEED intensity reflected mainly the surface roughness on the terrace.

Acknowledgements

This work was financially supported by Research Center for Electronic Ceramics (RCEC) of Dong-Eui University funded by Korea Science and Engineering Foundation (KOSEF), Ministry of Science and Technology (MOST) and the Busan Metropolitan City Government.

References

1. Egelhoff, W. F. Jr and Jacob, I., Reflection high-energy diffraction (RHEED) oscillations at 77 K. *Phys. Rev. Lett.*, 1989, **62**, 921–923.
2. Stroscio, J. A., Pierce, D. T. and Dragoset, R. A., Homoepitaxial growth of iron and a real space view of reflection high energy electron diffraction. *Phys. Rev. Lett.*, 1993, **70**, 3615–3617.
3. Lee, G. H., Yoshimoto, M., Ohnishi, T., Sasaki, K. and Koinuma, H., Epitaxial $BaTiO_3$ thin films grown in unit-cell layer-by-layer mode by laser molecular beam epitaxy. *Mater. Sci. Eng. B*, 1998, **56**, 213–216.
4. Maeda, T., Lee, G. H., Ohnishi, T., Kawasaki, M., Yoshimoto, M. and Koinuma, H., Molecular layer-by-layer growth of $SrTiO_3$ and $BaTiO_3$ films by laser molecular beam epitaxy. *Mater. Sci. Eng. B*, 1996, **41**, 134–137.
5. Neave, J. H., Dobson, P. J., Joyce, B. A. and Zhang, J., Reflection high-energy electron diffractions from vicinal surfaces. *Appl. Phys. Lett.*, 1985, **47**, 100–102.
6. Kawasaki, M., Takahashi, K., Maeda, T., Tsuchiya, R., Shinohara, M., Ishiyama, O., Yonezawa, T., Yoshimoto, M. and Koinuma, H., Atomic surface modification and characterization of $SrTiO_3$ single crystal. *Science*, 1992, **266**, 1540–1542.
7. Naito, M., Yamamoto, H. and Sato, H., Reflection high-energy electron diffraction and atomic force microscopy studies on homoepitaxial growth of $SrTiO_3$(001). *Physica C*, 1998, **305**, 233–235.
8. Kim, D. W., Kim, D. H., Kang, B. S., Noh, T. W., Shin, S. and Khim, Z. G., Atomic control of homoepitaxial $SrTiO_3$ films using laser molecular beam epitaxy. *Physica C*, 1999, **313**, 246–248.