Nanoscale epitaxial growth control of oxide thin films by laser molecular beam epitaxy—towards oxide nanoelectronics

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Abstract

The nanoscale growth control of oxide thin films, such as ferroelectric and magnetic materials, were explored by a novel technique based on nanoscale substrate engineering as well as atomic layer control via laser molecular beam epitaxy (laser-MBE). Atomic-scale analysis of the terminating layer of perovskite oxide films was performed by in situ coaxial impact-collision ion scattering spectroscopy. The novel heteroepitaxies that could be attained were: (1) the termination-regulated molecular layer-by-layer epitaxy of BaTiO₃ and La₀.₇Sr₀.₃MnO₃ thin films and (2) the step-decoration epitaxy resulting in the nanowire or nanodot structures of magnetic oxides such as (Mn, Zn) ferrite on ultrasmooth sapphire substrates with straight atomic steps.

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1. Introduction

Epitaxial growth of oxide thin films has been attracting much attention from the viewpoint of development of oxide electronics utilizing the superior properties such as high-Tc superconductivity, ferroelectricity, ferromagnetism, magnetoresistance, and transparent conductivity [1]. In order to open new oxide electronics using nanoscience and technology, we have proposed an advanced oxide epitaxy technology based on nanoscale substrate-engineering as well as on the atomic layer control of oxide films by laser molecular beam epitaxy (MBE), i.e. pulsed laser deposition in ultrahigh vacuum (UHV) [2]. In the atomic layer control, we employed in situ monitoring of intensity oscillations in reflection high energy electron diffraction (RHEED) [3,4]. Laser MBE has also been desired for the low-temperature epitaxial growth, as we previously reported the room-temperature epitaxial growth of CeO₂ films on Si [5] and BaO films on SrTiO₃ [6].

The epitaxial growth manner of films is influenced by nanoscale surface morphology and terminating atomic planes of substrates as well as lattice mismatching. The mirror-polished single-crystal substrates have the nanoscale irregular surface, leading to the crystallographically heterogeneous terminations. The homogeneous terminations of substrate surfaces are considered to be essential for attaining the perfect epitaxy and interface [7,8]. We have proved that coaxial impact collision ion scattering spectroscopy (CAICISS) is a powerful tool to identify both atomic species and their arrangement on the terminating atomic plane of single-crystalline oxides [9]. CAICISS allows each atom at the topmost layer to be ‘seen’ in a real space by choosing the appropriate incident angle and azimuth [10].

For several years, memory device technology has been developing with rapid speed. As this technology has advanced, fabrication of magnetic nanostructure such as nanowires and nanodots has been attracting much attention because of their potential applications in ultra-high density memory devices [11–13]. Furthermore, nanoscale film processing is essential to open a new field of oxide spin-electronics [14]. Ultra-smooth sapphire (Al₂O₃ single crystal) substrates [15] have been used for the nanoscale growth control of films [4,16,17] as well as for atomic force microscopy (AFM) observation stage of organic molecules such as DNA [18,19]. Ultra-smooth sapphire substrates are expected to enhance the migration of film precursors on the atomic terraces for step flow growth mode resulting in the nanowires or nanodots along the atomic step edges.
Here we report the nanoscale control of surface morphology and termination of several perovskite single-crystal substrates by thermal processing and characterization via CAICISS and AFM. The heteroepitaxies through the nanoscale substrate engineering as well as laser MBE are also demonstrated for the molecular layer-by-layer growth of perovskite oxides such as La0.7Sr0.3MnO3 and BaTiO3, and for step-decoration epitaxy resulting in the nanostructure for the magnetic oxides of (Mn, Zn) ferrite and Fe3O4 (magnetite) on the ultra-smooth sapphire with atomic steps.

2. Experimental

Commercially available mirror-polished oxide single crystals were annealed in air or UHV at 1000–1400 °C for several hours to obtain atomically flat surfaces with molecular steps. The substrates were then introduced into an ultra-high vacuum chamber for laser MBE, which was equipped with a CAICISS (Shimadzu CAICISS-I) analyzer and a two-axis computer-controlled goniometer. The CAICISS measurements were carried out at a background pressure of less than 3 × 10⁻⁹ Torr. The He⁺ ion beam (2 keV) was chopped into pulses of 150 ns duration at a 100 kHz repetition rate. The backscattered ions and neutral species were detected with the microchannel plate, which giving the time-of-flight (TOF) spectra. The surface morphology of the specimens was observed with AFM (Seiko SPI-3700) in air.

A pulsed KrF excimer laser beam (248 nm, 20 ns, 1–10 Hz) was impinged with an energy density of about 1 J/cm² onto a sintered target, which has the same composition as the film to be deposited, leading to the condensation of the ablated species onto the substrate surface. Films were deposited under either UHV or oxidizing atmosphere of 10⁻⁷–10⁻⁴ Torr O₂. In situ monitoring of the RHEED pattern and intensity at the specular beam spot were performed using an incident electron beam of 25 keV and a CCD camera connected to an image processor and a personal computer. The film structure was characterized by X-ray diffraction (XRD).

3. Results and discussion

3.1. Atomic termination and molecular layer-by-layer growth of perovskite oxides

The perovskite-type single-crystal oxides are well known as a lattice-matched substrate suitable for the epitaxial growth of high Tc cuprate, magnetic and ferroelectric oxide films. A well-defined surface of the substrate is essential for fabrication of the high-quality thin films. The AFM surface images of the annealed single-crystal oxide substrates showed the ultra-smooth terrace with a molecular step [9]. Perovskite oxides with the formula of ABO3 have a common structure consisting of alternating layers of two kinds of nonpolar atomic planes, i.e. AO (A-site plane) and BO₂ (B-site plane), along the c-axis direction. From the measurements of CAICISS spectra taken at [111] and/or [001] directions for the surfaces of the molecular-stepped substrates, the dominant terminating atomic layers for the several perovskite substrates are determined as listed in Table 1. CAICISS studies proved that SrTiO₃ (100) surfaces of as-supplied substrates as well as of O₂-annealed substrates were predominantly terminated with the TiO₂ atomic plane. The La₀.₇Sr₀.₃MnO₃ are one of the promising magnetic materials because of such superior properties as ferromagnetism, colossal magneto-resistance, and tunneling spin-electronics. In a previous in situ CAICISS study, we reported that c-axis oriented La₀.₇Sr₀.₃MnO₃ thin films epitaxially grown on SrTiO₃(100) substrate was terminated with the MnO₂ plane [20].

BaTiO₃ is one of the most widely investigated ferroelectric oxides with a perovskite structure.

![Fig. 1. CAICISS-TOF spectra of BaTiO₃ films (0.4–20 nm) on SrTiO₃(001) at [111] direction.](image)

| Substrate | Dominate terminating layer | Coverage (%) |
|-----------|---------------------------|-------------|
| SrTiO₃(100) | TiO₂ (B-site) | 90–100 |
| LaAlO₃(100) | AlO₂ (B-site) | 90 |
| LSAT(100)⁺ | AlO₂/TaO₂ (B-site) | ~90 |
| NdGaO₃(001) | NdO (A-site) | 100 |

* LSAT: (LaAlO₃)₀.₃–(Sr₂AlTaO₆)₀.₇.
The typical RHEED intensity oscillations of 0.4 nm thick film growth were observed during the growth of the BaTiO$_3$ film on a stepped SrTiO$_3$ (100) substrate with TiO$_2$ termination at 700 $^\circ$C under $1 \times 10^{-6}$ Torr O$_2$ atmosphere. In order to examine the terminating atomic plane of the BaTiO$_3$ (001) film, in situ CAICISS spectra were taken in the [111] direction for the layer-by-layer grown films. Fig. 1 shows the CAICISS-TOF spectra taken at [111] direction for the BaTiO$_3$(001) films (0.4–20 nm thick) grown on SrTiO$_3$(100) substrate. CAICISS measurements were carried out in between the consecutive deposition runs of BaTiO$_3$. As for the SrTiO$_3$ substrate, dominant Ti peak is clearly observed, indicating the termination of TiO$_2$ plane on the topmost surface of the substrate. With increasing film thickness, Ba signal increases and Ti signal decreases. The Ti signal disappears for the film with thickness of about 20 unit-cell layers (~8 nm). This implies that the topmost layer consisted of mixed BaO/TiO$_2$ atomic planes at the initial growth stage and the terminating layer changed to BaO atomic plane with film growth. Further works are necessary to elucidate the nanoscale mechanism for this termination change.

The as-polished commercial SrTiO$_3$ (110) substrates had also the stepped surface structure after annealing at 1000 $^\circ$C in $1 \times 10^{-5}$ Torr O$_2$. The step height is about 0.27 nm, which is close to the (110) interplanar distance. This termination is thought to be (Sr,Ti)O plane. This stepped substrate enabled us to accomplish the (110)-oriented molecular layer-by-layer growth for the perovskite oxide films. Fig. 2(a) shows the RHEED intensity oscillations observed during the growth of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (110) epitaxial films on the stepped SrTiO$_3$ (110) substrate at 800 $^\circ$C under $1 \times 10^{-5}$ Torr O$_2$ atmosphere. One period of the oscillations corresponds to the growth of the 0.27 nm-thick film, which thickness coincides with the distance of (110) plane in La$_{0.7}$Sr$_{0.3}$MnO$_3$. Fig. 2(b) shows an AFM image of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ (110) film, indicating the stepped (about 0.3 nm-high) structure derived from the layer-by-layer growth.
3.2. Nanostructure construction of magnetic oxides through step-decoration epitaxy

Sapphire (corundum structure; \(a_0 = 0.476 \text{ nm, } c_0 = 1.30 \text{ nm}\)) substrates are widely used as insulating substrates for thin film growth of metals, compound semiconductors and superconductors. Commercial sapphire (0001) substrates have the roughened surfaces which corrugation ranges in size from 0.2 to 1.0 nm, suggesting the existence of the topmost atomic plane different from the (0001) plane in an atomic scale. Ultra-smooth sapphire substrates could be obtained by annealing the mirror polished ones at 1000–1400 °C for several hours in air [15]. We could also control the atomic step height from 0.2 nm (annealed at 1000 °C, as shown in Fig. 3(a)) to 2–3 nm (annealed at 1400 °C, as shown in Fig. 3(b)). The origin of the 2–3 nm high steps is thought to be step-bunching by higher temperature annealing. Atomically flat terraces in Fig. 3(a) were about 100 nm wide and the atomic step height was uniformly 0.2 nm.

Ferrimagnetic oxide thin films of (Mn, Zn) ferrite \([(\text{Mn}_{0.55}\text{Zn}_{0.35}\text{Fe}_{0.10})\text{Fe}_2\text{O}_4]\) and Fe\(_3\)O\(_4\) were deposited on the ultra-smooth sapphire (0001) substrates at 670 °C in \(1 \times 10^{-5} \text{ Torr O}_2\) atmosphere by laser MBE. Through the RHEED and XRD measurements, it was verified that (Mn, Zn) ferrite and Fe\(_3\)O\(_4\) could be grown epitaxially with (111) orientation. Fe\(_3\)O\(_4\) magnetite films exhibited the Verway transition at 119 K (close to that of bulk magnetite) in the conductivity versus temperature curve. Fig. 4 shows the AFM image of the (Mn, Zn) ferrite ultra-thin film (0.5 nm thickness of about 1 monolayer). It is noted that the ultra-thin film was grown in the two-dimensional growth mode, and the coverage of the film on the sapphire substrate is different alternately on the adjacent terraces. Taking account of crystallographic structure for 0.2 nm-high stepped sapphire (0001) plane along c-axis [0001] direction (c-axis length of 1.3 nm), the topmost atomic arrangements on the adjacent terraces of (0001) plane are thought not to be identical [15]. The alternately different coverage as shown in Fig. 4 might be caused by the different growth speed of (111)-oriented ferrite film on each other terrace. At present, it is difficult to state which terrace is preferential for film
growth. Further investigations are in progress to clarify the novel initial growth on the ultra-smooth sapphire substrates.

Here we could fabricate the magnetic oxide nanostructures by the step-decoration of the ultra-thin layer less than 1 ML on the 0.2 nm-high stepped ultra-smooth sapphire substrate as reported for Si or metal nanowires [21,22]. Fig. 5(a)–(c) show AFM images (1×1 μm²) of nanowires for (Mn, Zn) ferrite and Fe₃O₄, and the growth model, respectively. These nanowires are about 0.5 nm in height and about 15–20 nm in width; they are uniform and parallel with each other, due to growing selectively along the straight step edges. The height of 0.5 nm is close to an interplanar spacing of (Mn, Zn) ferrite (111) plane and Fe₃O₄ (111) plane. From the measurement of AFM line profile, the film precursors were seen to deposit selectively at the down step edge, probably due to Schwoebel barrier at the atomic edge [23].

We also succeeded in the fabrication of nanodots by changing the step height of ultra-smooth sapphire substrate from 0.2 to 2 nm. Fig. 6 shows the AFM image (1×1 μm²) of Fe₃O₄ nanodots. Fe₃O₄ nanodots have about 80 nm diameter and about 3 nm in height. Nanodots grow uniformly along straight step edges. Thus, we could control the nanoscale epitaxial growth via laser MBE and nanoscale substrate engineering.

4. Summary

The nanoscale growth control was explored using laser MBE for ferroelectric and magnetic oxide thin films. Atomic-scale analysis on the terminating layer of perovskite oxide films was performed by the in situ coaxial impact-collision ion scattering spectroscopy (CAICISS). The termination-regulated molecular layer-by-layer growths for BaTiO₃ and La₀.₇Sr₀.₃MnO₃ thin films were confirmed by in situ RHEED analysis. The nanoscale heteroepitaxy of ferrimagnetic oxides such as (Mn, Zn) ferrite and Fe₃O₄ magnetite could be attained, that is, the straight step-edge epitaxy resulting in (1) nanowire arrays on the single-stepped sapphire substrate, and (2) nanodots on the step-bunched substrate.

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References

[1] H. Koinuma, M. Yoshimoto, Controlled formation of oxide materials by laser molecular beam epitaxy, Appl. Surf. Sci. 75 (1994) 308–313.
[2] H. Koinuma, H. Nagata, T. Tsukahara, S. Gonda, M. Yoshimoto, Ceramic layer epitaxy by pulsed laser deposition in an ultrahigh vacuum system, Appl. Phys. Lett. 58 (1991) 2027–2029.
[3] H. Ohkubo, N. Kanda, M. Yoshimoto, H. Koinuma, Fabrication of high-quality perovskite oxide films by lateral epitaxy verified with RHEED oscillation, Jpn. J. Appl. Phys. 32 (1993) 689–692.
[4] T. Maeda, M. Yoshimoto, T. Ohnishi, G-H. Lee, H. Koinuma, Orientation-defined molecular layer epitaxy of α-Al₂O₃ thin films, J. Cryst. Growth 177 (1997) 95–99.
[5] M. Yoshimoto, K. Shimozono, T. Maeda, T. Ohnishi, M. Kumagai, T. Chikyow, O. Ishiyama, M. Shinohara, H. Koinuma, Room-temperature epitaxial growth of CeO₂ thin films on Sr(111) substrates for fabrication of sharp oxide/silicon interface, Jpn. J. Appl. Phys. 34 (1995) 688–691.
[6] T. Ohnishi, M. Yoshimoto, G.H. Lee, T. Maeda, H. Koinuma, Unit cell layer-by-layer heteroepitaxy of BaO thin films at temperatures as low as 20 °C, J. Vac. Sci. Technol. A 209 (1997) 2469–2474.
[7] J.P. Locquet, A. Catana, E. Machler, C. Gerber, J.G. Bednorz, Block-by-block deposition: a new growth method for complex oxide thin films, Appl. Phys. Lett. 64 (1994) 372–374.
[8] R.A. McKee, F.J. Walker, E.D. Specht, G.E. Jellison, L.A. Boatner, J.H. Harding, Interface stability and the growth of optical quality perovskites on MgO, Phys. Rev. Lett. 72 (1994) 2741–2744.
[9] M. Yoshimoto, T. Maeda, K. Shimozono, H. Koinuma, M. Shinohara, O. Ishiyama, F. Ohtani, Topmost surface analysis of SrTiO₃(001) by coaxial impact-collision ion scattering spectroscopy, Appl. Phys. Lett. 65 (1994) 3197–3199.
[10] M. Aono, C. Oshima, S. Zaima, S. Otani, Y. Ishizawa, Quantitative surface atomic geometry and two-dimensional surface electron distribution analysis by a new technique in low-energy ion scattering, Jpn. J. Appl. Phys. 20 (1981) L829–L831.
[11] J. Meier, B. Doudin, J. Anserrment, Magnetic properties of nanosized wires, J. Appl. Phys. 79 (1996) 6010–6015.
[12] L.A. Zheng, B.M. Lairson, Formation of nanomagnetic thin films by dispersed fullerenes, Appl. Phys. Lett. 77 (2000) 3242–3244.

Fig. 6. AFM image (1×1 μm²) of Fe₃O₄ nanodots grown on 2 nm-high bunching stepped sapphire substrate.
[13] M. Governale, D. Boese, Magnetic barrier in confined two-dimensional electron gases: nanomagnetometers and magnetic switches, Appl. Phys. Lett. 77 (2000) 3215–3217.

[14] H.Y. Hwang, S.W. Cheong, Enhancing the low field magnetoresistive response in perovskite manganites, Appl. Phys. Lett. 68 (1996) 3494–3496.

[15] M. Yoshimoto, T. Maeda, T. Ohnishi, H. Koinuma, O. Ishiyama, M. Shinohara, M. Kubo, R. Miura, A. Miyamoto, Atomic-scale formation of ultrasmooth surfaces on sapphire substrates for high-quality thin-film fabrication, Appl. Phys. Lett. 67 (1995) 2615–2617.

[16] G-H. Lee, M. Yoshimoto, H. Koinuma, Self-assembled island formation of LiNbO3 by pulsed laser deposition on α-Al2O3 substrate, Appl. Surf. Sci. 127–129 (1998) 393–397.

[17] M. Yoshimoto, K. Yoshiida, H. Maruta, Y. Hishitani, H. Koinuma, S. Nishio, M. Kakihana, T. Tachibana, Epitaxial diamond growth on sapphire in an oxidizing environment, Nature 399 (1999) 340–342.

[18] K. Ebihara, S. Koshihara, M. Yoshimoto, T. Maeda, T. Ohnishi, H. Koinuma, M. Fujiki, Direct observation of helical polysilane nanostructures by atomic force microscopy, Jpn. J. Appl. Phys. 36 (1997) L1211–L1213.

[19] K. Yoshida, M. Yoshimoto, K. Sasaki, T. Ohnishi, T. Ushiki, J. Hitomi, S. Yamamoto, M. Shigeno, Fabrication of a new substrate for atomic force microscopic observation of DNA molecules from an ultrasmooth sapphire plate, Biophys. J. 74 (1998) 1654–1657.

[20] M. Yoshimoto, H. Moruta, T. Ohnishi, K. Sasaki, H. Koinuma, In situ determination of the terminating layer of La0.67Sr0.33MnO3 thin films using coaxial impact-collision ion scattering spectroscopy, Appl. Phys. Lett. 73 (1998) 187–189.

[21] S. Yanagiya, S. Kaminura, M. Fujii, M. Ishida, Y. Moriyasu, M. Matsui, M. Yoshimoto, T. Ohnishi, K. Yoshida, K. Sasaki, Self-formed silicon quantum wires on ultrasmooth sapphire substrates, Appl. Phys. Lett. 71 (1997) 1409–1411.

[22] J. Hauschild, H.J. Elmers, U. Gradmann, Dipolar superferromagnetism in monolayer nanostripes of Fe (110) on vicinal W (110) surfaces, Phys. Rev. B 57 (1998) R677–R680.

[23] R.L. Schwoebel, E.J. Shipsey, Step motion on crystal surfaces, J. Appl. Phys. 37 (1966) 3682–3686.