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# Effects of compressive and tensile stress on the growth mode of epitaxial oxide films

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**Abstract**

Oxide films were deposited on different substrates by laser molecular beam epitaxy. Reflection high-energy electron diffraction was performed to in situ investigate the change of growth mode and the lattice relaxation during the growth. An asymmetrical phenomenon was found in the two kinds of strain states, compressive stress and tensile stress of heterostructures with different lattice mismatch. In the case of $BaTiO_3/SrTiO_3$ (2.2%), 2D layer-by-layer growth mode without lattice relaxation can be maintained for a longer period for BTO films on STO with compressive stress, comparing to STO films on BTO with tensile stress. When MgO films were deposited on $SrTiO_3$ with a large mismatch of 7.8%, compressive stress leads to rapid lattice relaxation with a very thin wet layer, and 3D strained island were observed. As a comparison, $SrTiO_3$ films on MgO with tensile stress were configured. No RHEED patterns can be observed duo to a large tensile stress.


*Keywords:* B. Interface; Oxide films; Stress; Epitaxy

## 1. Introduction

Oxide thin films have been widely investigated as functional materials for the microelectronic devices such as dynamic random access memory, bypass capacitors, infrared detectors, and tunable-microwave devices [1]. Enormous strain can exist in the films in the heterostructures, which might lead to a significant change of structure and properties markedly different from the corresponding intrinsic unstrained materials [2–4]. Recently, strain behavior in heterostructures has attracted more attention due to both scientific and technological significance. An extensive understanding of the growth of oxide films was explored, and to seek a good route to construct high-performance oxide films by controlling strain extent [5,6].

The influence of stress on the film growth and their microstructures is complicated, which is dependent on the degree of mismatch and different stress states. According to Frank and Van der Merwe mode, the lattice of the film can be suppressed by the lattice of the substrate through elastic strain and epitaxial growth can continue in a layer-by-layer manner if the lattice mismatch is less than 7% [7]. In general, there are two kinds of stress states, compressive stress and tensile stress. Although the investigation on stress behavior in the epitaxial growth was carried out by some groups [5,6], the understanding about the growth behavior for films under two kinds of stress with different degree was still limited.

Reflection high-energy electron diffraction (RHEED) is one of the most useful techniques to study epitaxial growth of thin films [8–10]. The in situ real-time study of the characteristics of the diffraction patterns during the growth can provide useful information of the microstructure and morphology. By tracking the relative ‘‘streakiness’’ of the diffraction pattern, it is possible to study the evolution of the atomic scale roughness and strain relaxation [11].

In this work, $BaTiO_3$ films were deposited on $SrTiO_3$ (1 0 0) substrate, and $SrTiO_3$ films subsequently were alternately deposited on underlayed BTO films by laser molecular beam epitaxy (LMBE) to investigate the effect of two kinds stress states. In addition, MgO films on $SrTiO_3$ substrates with a larger mismatch were fabricated. As a comparison, $SrTiO_3$ films were also deposited on MgO substrates. Thus, the two kinds of stresses, compressive stress and tensile stress, in the heterostructures with different lattice mismatch were investigated.

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## 2. Experimental procedure

Oxide films were deposited by laser molecular beam epitaxy (LMBE) using commercial single crystal targets of BTO, STO and MgO. A LAMBDA PHYSIK KrF excimer laser (248 nm wavelength and 30 ns pulse duration) with a repetition rate of 1–10 Hz was used as a laser source for the ablation of targets. The laser beam was focused on the target surface with a fluency of about 3 J/cm$^2$. The deposition details were described elsewhere [12].

The in situ RHEED diagnosis during the growth was performed in anti-Bragg condition using 20 keV electron beam under a grazing incidence of 1–3° towards the substrate surface. RHEED patterns are collected with a charge coupled device camera (8 bit, 380 × 280 pixels), which is interfaced to a PC data collection system. Strain can be derived from the in-plane lattice constant as a function of the film thickness, which is inversely proportional to the spacing between the reciprocal lattice rods (streaks) in the RHEED image. The in-plane epitaxy relationship was also revealed by XRD $\psi$ scan with Cu K$\alpha$ radiation (D1 SYSTEM, BEDE).

## 3. Results and discussion

### 3.1. BTO/STO (small mismatch of 2.2%)

The lattice parameter for cubic structure STO is 3.905 Å, and that of tetragonal BTO is 4.030 Å. The lattice mismatch is 2.2%. Obviously, compressive stress exists at the interface when BTO films are deposited on STO substrates, while there is tensile stress at the interface when STO films are deposited on BTO substrates. Fig. 1 demonstrates the evolution of RHEED diffraction patterns of the BTO/STO multilayer heterostructure at 500 °C. As pointed out in our recent work, the easily observed azimuth is ⟨1 0 0⟩, ⟨1 1 0⟩ and ⟨1 2 0⟩ for the (0 0 1) surface [13]. In this work, ⟨1 2 0⟩ azimuth was chosen to collect RHEED patterns due to the large streak spacing. Due to the small incident angles, the lateral spacing of the diffraction streaks corresponds to the reciprocal space scattering vector, which is inversely proportional to the in-plane surface lattice constant. In-plane lattice constant of the films BTO and STO can be computed using the RHEED spacing. Firstly, about 10 monolayers STO film were homoepitaxial grown on single crystal STO substrate. Sharp streaky diffraction patterns can be observed, as shown in Fig. 1(a), indicative of 2D layer-by-layer growth with atomically smooth surface of STO which can minimize the effect of substrate quality.

The interval growth of BTO/STO multilayer was then carried out to investigate the influence from different stress. BTO and STO films were deposited in turn with a thickness of about 40 monolayers (ML). RHEED patterns remained to be streaky, as shown in Fig. 1(b)–(d). In addition, the periodic intensity oscillation curve was obtained during the growth process (not shown here). It reveals that both BTO film and STO film were in 2D layer-by-layer growth mode. One period of oscillation corresponded to the growth of one unit cell of BTO or STO. The growth rate is estimated to be 0.02 ML/s by the analysis of the oscillation period, where 1 monolayer (ML) corresponds to a layer thickness of 0.403 nm and 0.3905 nm, the value of the *c*-axis lattice constant of bulk BTO and STO, respectively. Fig. 1(b) is the RHEED pattern for 1 ML BTO on homoepitaxial STO. Due to compressive stress, BTO film was constrained with respect to STO and was completely coherent epitaxial grown. But the streak for BTO is slightly dispersed

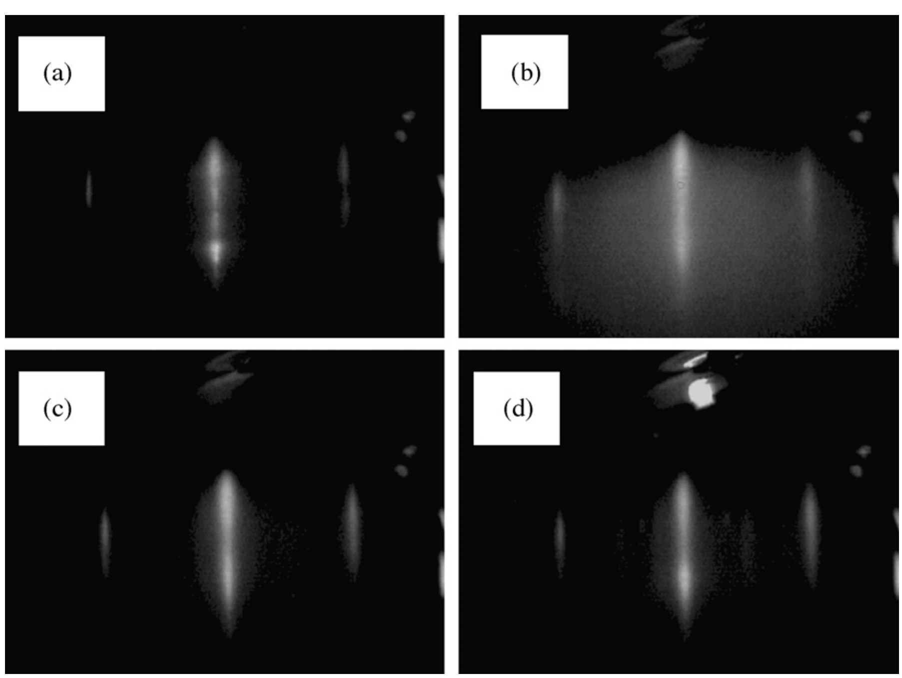


Fig. 1. Evolution of RHEED diffraction patterns for BTO/STO multilayer heterostructure on STO (0 0 1) substrate recorded with the incident electron beam parallel to [1 2 0] direction. (a) 10 ML STO homoepitaxial layer, (b) 1 ML BTO, (c) 40 ML BTO, (d) 20 ML STO films subsequently grown on 40 ML BTO layer at various periods.

comparing with that of STO in Fig. 1(a). It was suggested that compressive stress resulted in the slight roughness of the growing surface for strained BTO film. Fig. 1(c) demonstrates the pattern for 40 ML BTO, i.e.16.12 nm, which was completely relaxed. It can be attributed to the growth behavior for the free-standing BTO film. Fig. 1(d) is the RHEED patterns for 20 ML STO films on 40 ML BTO film. The streaky patterns also revealed the 2D growth. But it can be observed that the streak spacing is slight smaller than that of Fig. 1(a). It suggested that the in-plane lattice was enlarged due to the tensile stress for STO on BTO.

During the interval growth of BTO/STO multilayer heterostructure, the evolution of lattice parameters for the two films was indicated in Fig. 2. The changing tendency of lattice parameters at the different interfaces of BTO/STO and STO/BTO is quietly different between BTO and STO films under different strain states. As shown in Fig. 2, the BTO lattice was rapidly relaxed to reach the free-standing bulk value after eight unit cells were deposited on STO. In contrast, STO film can be epitaxially deposited on the full-relaxed 40 ML BTO. STO film was slowly relaxed to STO bulk lattice with about 10 unit cells as a relaxed buffer layer. This asymmetrical phenomenon can be attributed to the different stress states at the interface for BTO/STO and STO/BTO systems.

The observed asymmetrical effect of interfacial strain was related to the release of stress caused by lattice mismatch. As we have reported, $ABO_3$ perovskite oxide films can be deposited with a unit-cell migration mode [14]. When BTO or STO films were heteroepitaxially grown in 2D layer-by-layer mode, unit cells were enforced a stress which leads to lattice distortion. In-plane unit cells were clamped to fit the underlayer, and *c*-lattice parameter of in-plane biaxially strained films was subsequently elongated or shortened. The tensile stress can enlarge the in-plane lattice consequently, and the area of growth surface became larger to enhance surface energy and to release strain energy, which can result in a smooth surface. In contrast, rough surface of BTO films was formed by compressive stress, revealed in Fig. 1(b).

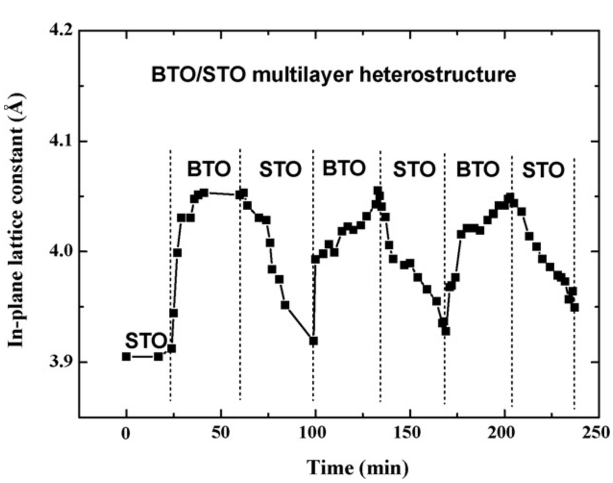


Fig. 2. The change of the in-plane lattice relaxation of BTO/STO multilayer heterostructure during the film growth.

In general, tensile stress can be released by enlarging the in-plane lattice parameter with a smooth growth surface, while compressive stress can be released by changing the surface structure, especially for the constrained film whose thickness is less than critical thickness, which was estimated as eight unit cell of about 3.2 nm which is consistent with theoretical calculation by using Matthews–Blakeslee formula [7]. The relaxation process for compressive stress is quicker than that for tensile. In both cases, strain energy can decrease by enhancing surface energy.

### 3.2. MgO/$SrTiO_3$ (large mismatch of 7.8%)

MgO films were deposited on STO (1 0 0) substrate at 600 °C, the deposition rate is about 0.5 nm/min. The lattice parameter for the rocksalt structural MgO is 4.216 Å. Comparing with the BTO/STO system, there is a larger lattice mismatch of about 7.8%. The in-plane epitaxial relationship of full-relaxed thick MgO films on STO substrate was investigated by XRD $\psi$ scans, as shown in Fig. 3. The (1 0 3) plane was selected. The four peaks at 90° intervals to each other have nearly the same intensity, indicating a fourfold rotational symmetry along the STO (1 0 3) plane normal. Furthermore, the full width at half-maximum (FWHM) of each peak is very small. Thus, the XRD $\psi$ scans of the heterostructures reveal that MgO unit cells were epitaxially deposited on (0 0 1) STO substrates with a cubic-on-cubic arrangement in the mode of MgO[1 0 0]//STO[1 0 0]. Due to this larger mismatch, RHEED periodic intensity oscillation has not been observed. The azimuth of the incident electron beam is parallel to the [1 0 0] axis of STO substrate. The insets in Fig. 3 are the RHEED diffraction pattern for 2 ML MgO film and 8 ML MgO film on STO (100) substrate, respectively. The streaky pattern for 2 ML MgO film is observed but not as clear as that of Fig. 1. In contrast, dot plus streak mode for 8 ML MgO film appears, which is the typical diffraction pattern of rocksalt structural MgO (1 1 0) plane. The change of RHEED patterns indicates

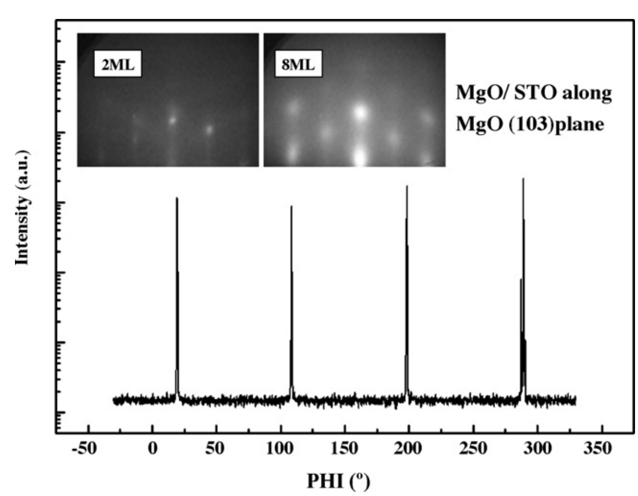


Fig. 3. XRD $\phi$ scan curve of MgO film on STO substrate along MgO (1 0 3) plane. The insets are the RHEED patterns of MgO thin film on STO substrate at 600 °C with 2 ML cubic structural MgO film and 8 ML rocksalt structural MgO film, respectively.

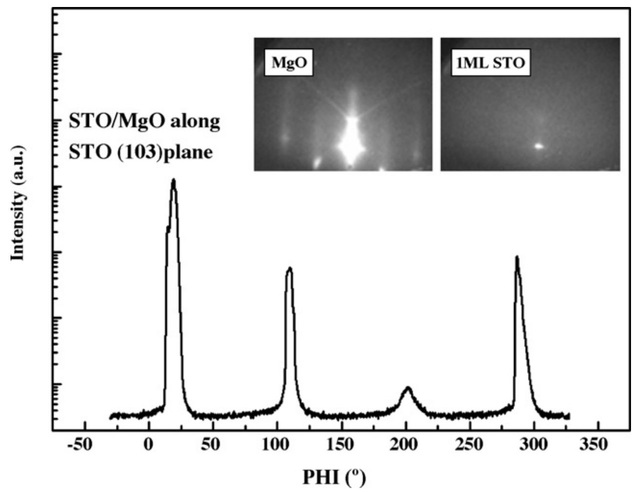


Fig. 4. XRD $\phi$ scan curve for STO film on MgO substrate along STO (1 0 3) plane. The insets are the RHEED patterns of MgO substrate and 1 ML STO film on MgO substrate, respectively.

that the critical thickness for coherent epitaxial growth of MgO film is very small, about 2 ML, comparing with BTO/STO.

STO films were inversely deposited on (0 0 1) MgO substrate at 600 °C with the tensile stress at the interface. XRD $\psi$ scans in Fig. 4 reveals that the four peaks at 90° intervals to each other existed, but showed a large intensity difference. FWHM of each peak for STO/MgO is very larger than that of MgO/STO. RHEED patterns in the insets of Fig. 4 indicate that RHEED patterns disappear completely when only 1 ML STO film was deposited on MgO. No RHEED patterns of STO films appear hereafter, indicating a rough surface of STO on MgO due to large tensile strain. The rough STO film under a large tensile stress can decrease strain energy, and also result in the extinction of RHEED diffraction condition.

## 4. Conclusions

Two kinds of oxide heterostructures with different lattice mismatch values were fabricated by laser molecular beam epitaxy (L-MBE). An asymmetrical phenomenon was found by in situ investigation of RHEED. In the case of $BaTiO_3/SrTiO_3$ with a small mismatch of 2.2%, 2D layer-by-layer growth mode can be maintained for a longer period. Lattice relaxation process for STO/BTO with tensile stress is slower than that of BTO/STO with compressive stress. Compressive stress for $MgO/SrTiO_3$ with a large mismatch of 7.8% can lead to rapid lattice relaxation with a very thin wet layer and 3D strained island growth mode. No RHEED diffraction patterns can be observed due to a large tensile stress for $SrTiO_3/MgO$. XRD $\psi$ scans investigation reveals that epitaxial quality of films under compressive stress was better than that of films under tensile stress in the MgO/STO heterostructures.

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