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Microstructure tuning of epitaxial BaTiO_{3-x} thin films grown using laser molecular-beam epitaxy by varying the oxygen pressure

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ABSTRACT

Microstructural properties are found to be variant in the BaTiO_{3-x} films grown on $\text{SrTiO}_3(001)$ substrate under various oxygen pressures from 2×10^{-2} Pa to 2×10^{-5} Pa by laser molecular-beam epitaxy. Transmission electron microscopic studies reveal that the predominant defects in the films change from threading dislocations into (111) planar defects (i.e. stacking faults and nanotwins) by lowering the oxygen pressure. High density of these defects was observed in the BaTiO_{3-x} film prepared at the oxygen pressure of 2×10^{-5} Pa, which shows metallic behavior. The relationships between oxygen pressure, microstructure, and electrical properties are established on the basis of oxygen deficiency. The formation of nanotwins in highly oxygen-deficient BaTiO_{3-x} epitaxial thin films results from accommodating excess oxygen vacancies induced by lowering oxygen pressure.

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1. Introduction

Stoichiometric BaTiO_3 (BTO) thin films have potentially wide applications in ferroelectric random-access memories and electro-optic devices due to their high dielectric constant and low leakage current [1–4]. It is proposed that the performance of the thin films is strongly influenced by misfit strain and defect configurations in the epitaxial layers. The relief of misfit strain can be fulfilled by the formation of misfit dislocations when the film is above the critical thickness. In the previous work, thin films of stoichiometric BTO were grown on various substrates, and variant microstructural characteristics are reported. In a study of BTO films grown on SrTiO_3 (STO) (001) by pulsed laser deposition, Suzuki et al. [5] found that highly dense threading dislocations perpendicular to the interface between the film and the substrate constitute the major type of defects in the film. In contrast, Shigetani et al. [6] investigated the structure of BaTiO_3 thin films grown on a SrTiO_3 substrate by a molecular-beam epitaxy method at an oxygen radical source and found that the BTO thin films were oriented along the [001] direction without misfit dislocations along the interface. Both ferroelectric domains and {111} twins are structural peculiarities frequently found in stoichiometric bulk BTO and thin films [7,8]. When BTO films were prepared on polycrystalline Pt plate by radio-frequency magnetron sputtering, the BTO was polycrystallized, and (111) twins were found in the films [7].

Stoichiometric BaTiO_3 is insulating but electric conduction can be induced in BaTiO_{3-x} ceramic through impurity doping [9,10] or reduction [11,12] in which oxygen pressure plays an important role. Electrical properties of oxide materials are very sensitive to nonstoichiometry and structural defects. For instance, Zhao et al. [11] found that the electrical conductivity of the BaTiO_{3-x} thin films prepared by laser molecular-beam epitaxy (LMBE) under various oxygen pressure increases with decreasing the oxygen pressure. A metallic conduction is even observed in the most oxygen-deficient $\text{BaTiO}_{2.52}$ films, with the electrical resistivity of $6.0 \times 10^{-5} \Omega \text{ cm}$ and carrier density of 1.98×10^{22} , respectively. In a separate paper, they studied the thickness and oxygen pressure dependent structural characteristics on BaTiO_3 thin films prepared by LMBE [13]. Using multiple techniques including reflection high energy electron diffraction, atomic force microscopy, X-ray diffraction and high resolution transmission electron microscopy, the as-received BTO films are determined as highly *c*-axis or *a*-axis oriented single crystals. Although physical properties of the oxygen nonstoichiometric BTO films have been studied in a number of cases [11,13,14], structural and microstructural data in such films prepared under a broad range of oxygen pressures, are inadequate. In this paper, we present a spectrum of microstructures versus oxygen deficiency in the BaTiO_{3-x} films, which were prepared under various oxygen pressures from 2×10^{-2} Pa to 2×10^{-5} Pa. We found a variation in defect types and therefore the electric properties affected by the oxygen pressure. The present study is expected to shed some light on understanding the influence of oxygen pressure on microstructures in oxygen-deficient BTO films and may provide some useful information for the design of required devices.

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2. Experimental procedures

A series of BaTiO_{3-x} thin films with the thickness of 400 nm was deposited on $\text{SrTiO}_3(001)$ substrate by LMBE technique under various oxygen pressure from 2×10^{-2} Pa to 2×10^{-5} Pa. The base pressure of the epitaxy chamber was 1×10^{-8} Pa. Single crystal $\text{SrTiO}_3(001)$ substrate was heated at 630°C under various oxygen pressures. The output of a Lambda Physik LEXTRA200 excimer laser (308 nm, 20 ns, 2 Hz) was used as the laser source with an energy density of about 1 J/cm^2 . Detailed deposition procedure can be found elsewhere [11]. X-ray diffraction (XRD) measurements were used to obtain structural data. The θ - 2θ scan mode and asymmetric ω rocking curve evaluations were carried out on the RigakuD/Max-2400V diffractometer equipped with $\text{Cu K}\alpha$ irradiation. Cross-sectional samples were prepared for transmission electron microscope (TEM) observation. For cross-section samples, slices of $2 \text{ mm} \times 1 \text{ mm}$ in size were cut from the films along the [110] direction. Two of the slices were glued face to face and then embedded in epoxy resin. After the glue was cured, discs 3 mm in diameter were obtained by cutting away the redundant epoxy. Mechanical grinding, dimpling and finally ion-thinning were carried out on these discs. A Tecnai F30 transmission electron microscope at 300 kV was used to carry out the lattice imaging and contrast analysis.

3. Results and discussion

The as-received films, which were prepared under an oxygen pressure of 2×10^{-2} Pa, 2×10^{-3} Pa, 2×10^{-4} Pa, and 2×10^{-5} Pa, respectively, are colorless, light-grey, dark-grey, and black in appearance. The tendency in color also agrees well with the conduction behavior because the insulating BaTiO_3 is usually light-colored, while the n-type semiconducting BaTiO_3 is dark-colored, as reported by Chan et al. [15].

The oxygen content in the deposited BaTiO_{3-x} thin films was analyzed by Rutherford backscattering spectrometry (RBS) with an incident $^4\text{He}^+$ (3.016 MeV) ion beam, as described before [11]. It was also reported that grown under 2×10^{-2} Pa, the stoichiometric BaTiO_3 is obtained. When deposited at 2×10^{-5} Pa, the oxygen deficiency is as low as 0.48. However, the perovskite structure is preserved in $\text{BaTiO}_{2.52}$ thin film which shows metallic conduction behavior in electrical properties [11].

3.1. Oxygen pressure dependence of structural characteristics

From the previous studies [11], it is known that each of the four BTO films is a *c*-axis oriented tetragonal single crystal. There are two mechanisms to interpret the crystallographic orientation dependence on the gas pressure, 1) the residual hydrostatic compression process and 2) the difference in the thermal vibration under various oxygen pressures, as described in detail by the same research group [13]. To illustrate the variation of lattice constants and other structural parameters, the *c/a* ratios which are calculated as a function of oxygen pressure, the lattice constants *c* obtained from XRD θ - 2θ scan, *a* from $c/(c/a)$ and $V^{1/3}$ from $(a^2c)^{1/3}$ are all plotted in Fig. 1. The symbols (diamond, square, circle, and triangle) represent the experimental data and the solid lines are guided to eyes. For comparison, the *c/a* ratio, lattice parameters *a* and *c*, and unit cell volume $V^{1/3}$ of the bulk BaTiO_3 are also shown as dashed lines.

When the films were grown under relatively high oxygen pressure, the lattice constants tended to be close to the bulk values. Decreasing oxygen pressure, *a*, *c*, *c/a*, and $V^{1/3}$ all increase. It is generally accepted that the lattice misfit between film and substrate and different thermal expansion behavior may result in the lattice distortion in films [16]. But other factors may also contribute to the increments of lattice constants. According to Speck et al. theory [17], during thin film growth, additional stresses may arise that are independent of lattice mismatch and different thermal expansion. These so called growth

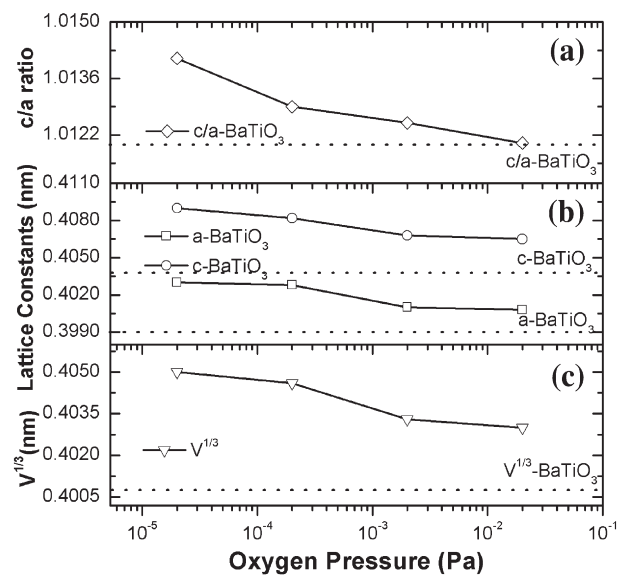


Fig. 1. (a) *c/a* ratio, (b) lattice constants *c* and *a*, (c) unit cell volume $V^{1/3}$ of BaTiO_{3-x} films versus oxygen pressure.

stresses are assumed to result from supersaturated point defect population. These stresses may be relaxed only by diffusional processes. Thus, the maximum relaxation rate will be at the thin film growth temperature or during subsequent high temperature annealing. The present investigated thin films were prepared under rather low oxygen pressures, nonequilibrium point defect such as oxygen vacancies, or interstitials, may be in large population. Unrelaxed residual growth stresses resulting from these point defects could change the lattice parameters of the film effectively. As to the enlargement of unit cell volume of $V^{1/3}$, excess oxygen vacancies are ascribed to this process [13]. As oxygen vacancies increase, the lattice volume of the BTO unit cell inflates accordingly.

3.2. Oxygen pressure dependence of microstructural characteristics

Fig. 2(a–d) shows the low magnification cross-section images of the four $\text{BaTiO}_{3-x}/\text{SrTiO}_3$ systems, corresponding to BTO films prepared under an oxygen pressure of 2×10^{-2} , 2×10^{-3} , 2×10^{-4} , and 2×10^{-5} Pa, respectively. These images were taken with the incident beam close to [110] direction of SrTiO_3 . The interface positions are denoted by a pair of arrows. It is seen that the interfaces between BTO thin films and STO are flat and sharp. Interfacial dislocations are visible along these interfaces. It is known that if the lattice mismatch is relatively small, films can grow coherently on substrates until a critical film thickness is reached. Within this thickness range, the misfit is accommodated by elastic strains. If the film thickness exceeds the critical value, misfit dislocations form to relieve the misfit strain. The critical thickness of BTO film epitaxially grown on STO substrate is around 5 nm [3,5]. The 400-nm-thick BTO films in the present study are almost fully relaxed by the formation of misfit dislocations, because the thickness is far beyond the critical value. On the other hand, high density threading dislocations would be generated concomitantly with misfit dislocations in the growth process of epitaxial perovskite films. In Fig. 2(a), besides misfit dislocations along the interfaces, we also see broad straight line contrasts along the film normal direction. These lines can be the images of threading dislocations, i.e. high density of the threading dislocations can be observed in the BTO film which was grown at an oxygen pressure of 2×10^{-2} Pa. A similar observation was reported in a previous study of BTO film prepared on STO substrate under the oxygen pressure of 0.1 Pa [5]. Composite electron diffraction patterns (not shown here) reveal that no extra spots can be identified, implying that the film is

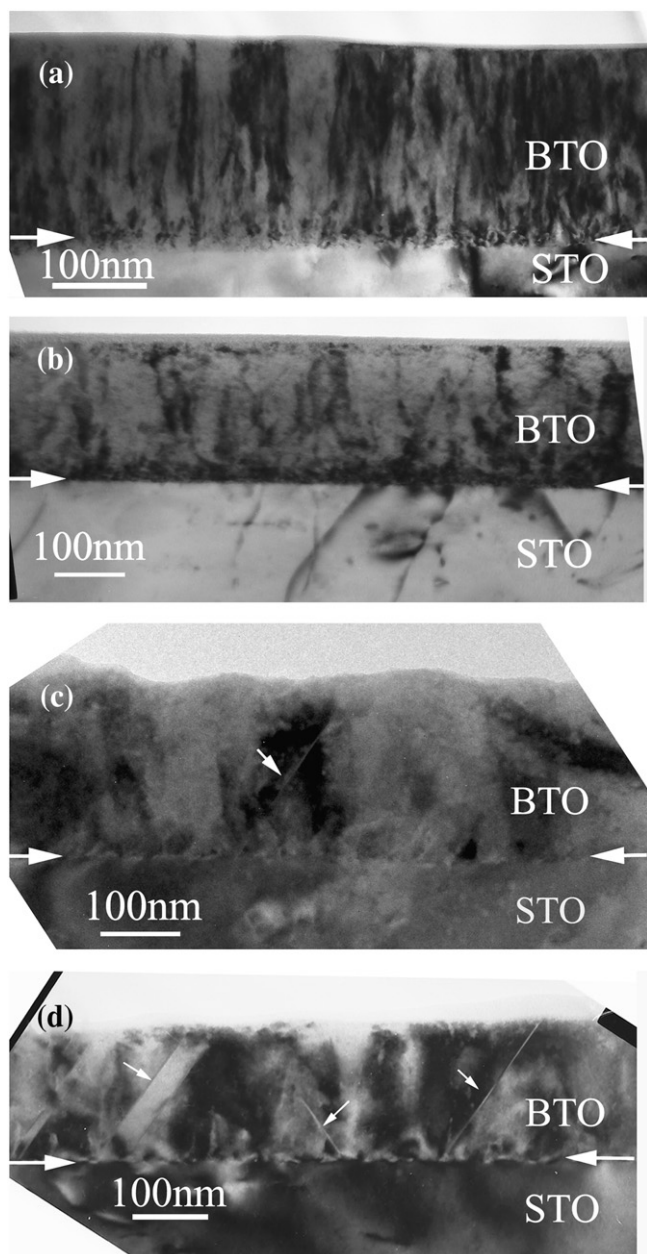


Fig. 2. (a)–(d) Bright field images of the four BTO films prepared under oxygen pressures of 2×10^{-2} , 2×10^{-3} , 2×10^{-4} , and 2×10^{-5} Pa, respectively.

free from a secondary phase. When the films were deposited under an oxygen pressure of 2×10^{-3} Pa (Fig. 2b), weaker contrast areas appear, indicating less threading dislocations in the film. With a further decrease in the oxygen pressure, threading dislocations are invisible. Instead, defects in the planes which are $\pm 35^\circ$ away from the interface normal are frequently observed (Fig. 2c and d). The defects are much denser in the most oxygen-deficient BTO thin film. They are identified as {111} planar defects marked with white arrows. Most of them in Fig. 2(d) originate from the interface between the film and substrate, some of which extend completely, penetrating through the whole film; while some terminate in the matrix. Fig. 3 is a composite electron diffraction pattern (EDP) corresponding to the area in Fig. 2(d), including both BTO thin film and STO substrate. Such an EDP displays that the present BTO film still remains the Perovskite-type structure, although it is highly oxygen-deficient. The splitting of diffraction spots results from the lattice difference between BTO film and STO substrate. The inner diffractions marked with white arrows are from the BTO

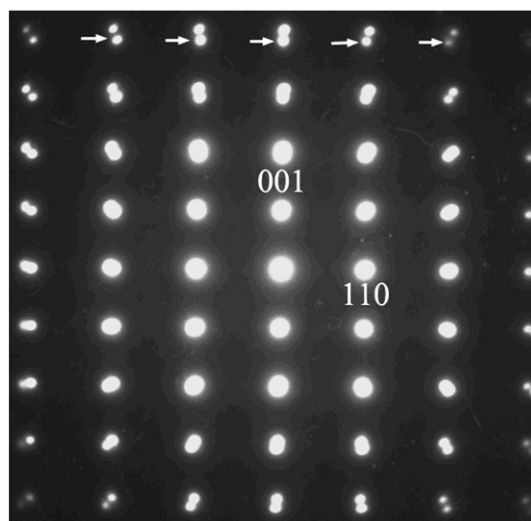


Fig. 3. A composite electron diffraction pattern taken from the area including both the BTO film and the STO substrate. The BTO film was grown at $P_{O_2} = 2 \times 10^{-5}$ Pa.

film, implying that the lattice parameter of BTO is larger than the lattice parameters of the STO substrate. The outer diffraction spots are from the STO substrate which has a lattice constant of $a = 0.3905$ nm. Using STO as a reference, the lattice constant of the present BTO thin films can be calculated as $c \approx 0.410$ nm which is 1.54% larger than the lattice constant in the bulk BTO ($c = 0.4038$ nm) [3]. From an EDP of [010] zone axis, the a value of the BTO film is calculated as $a = 0.403$ nm. The lattice values derived from the electron diffraction experiment agree with the values measured by X-ray diffraction (Fig. 1). The lattice constants calculation also verifies the tetragonal structure of the present film.

Although the film prepared at an oxygen pressure of 2×10^{-3} Pa does not show the existence of {111} planar defects at a low magnification image of Fig. 2(b), {111} planar defects can be identified at a high resolution (HR) image (Fig. 4). The lamella seems to consist of several segments separated by steps. It could be regarded as in the early stage of {111} planar defects formation.

A more detailed investigation indicates that the {111} planar defects are actually nanotwins with a width of about 1–2 nm. Fig. 5(a) is an HRTEM image of a BTO film grown at $P_{O_2} = 2 \times 10^{-5}$ Pa taken along $[\bar{1}10]$ direction showing {111} nanotwin lamella. The twin relationship can be verified by a Fourier transformation (FT) pattern

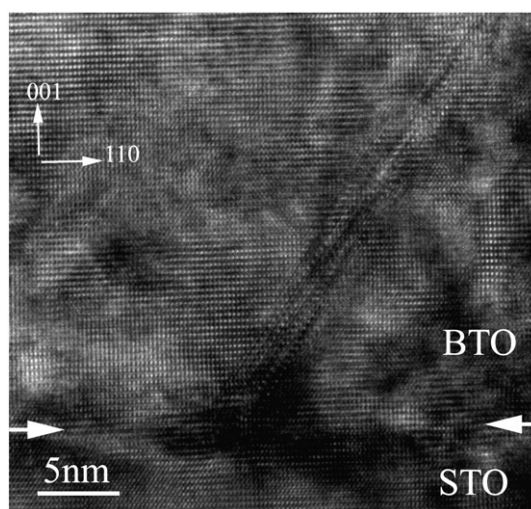


Fig. 4. A lattice image recorded along $[\bar{1}10]$ direction showing {111} planar defects in a BTO film prepared at $P_{O_2} = 2 \times 10^{-3}$ Pa.

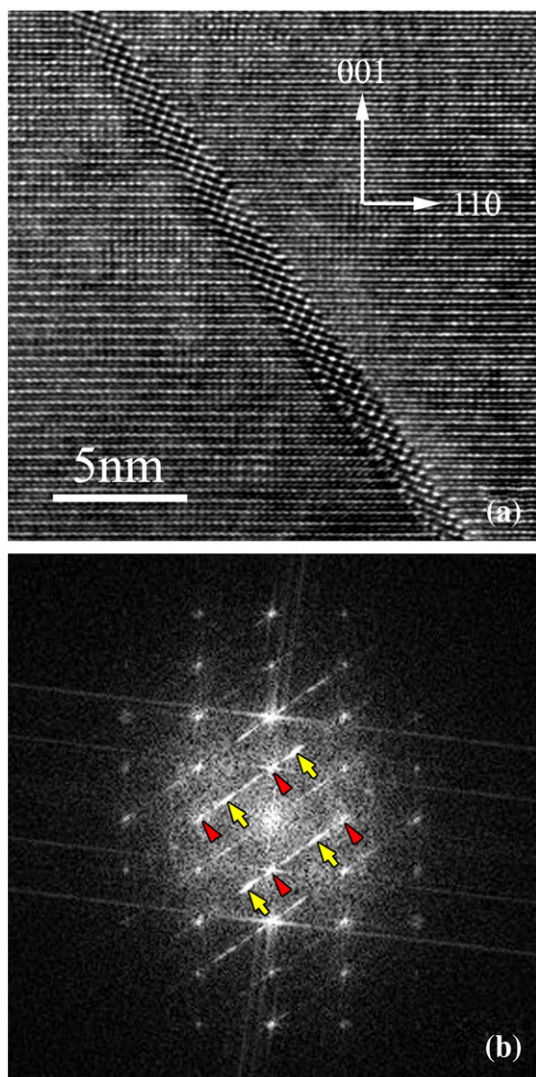


Fig. 5. (a) $[1\bar{1}0]$ lattice image showing $\{111\}$ nanotwins in $\text{BaTiO}_{2.52}$ thin films ($P_{\text{O}_2} = 2 \times 10^{-5}$ Pa). (b) An FT pattern corresponding to (a) indicating twin relationship. Red arrowheads represent the spots from the matrix, while the yellow arrows denote the spots from the twinning.

in Fig. 5(b) which corresponds to Fig. 5(a). In Fig. 5(b), the red arrowheads represent the spots from the matrix, while the yellow arrows denote the spots from the twinning. They form the typical $\{111\}$ twin relationship in the BaTiO_3 compound.

The four $\{111\}$ planes in the room-temperature BaTiO_3 are approximately equivalent, therefore, intersections between twin boundaries are also observed in the film prepared under an oxygen pressure of 2×10^{-5} Pa, as shown in Fig. 6. The morphology of the core area of such twin intersections differs from that of undisturbed single twin boundaries and shows more a complicated structure, as investigated by Jia et al. in BaTiO_3 polycrystalline films [18].

3.3. Discussions

From cross-section images (Fig. 2), it is learnt that the density of the threading dislocation decreases with a decrease in the oxygen pressure, and $\{111\}$ planar defect appears. It is believed that both misfit dislocations and threading dislocations greatly undermine the electrical properties of semi-conductive and conductive thin films, especially threading dislocation worsens the electrical properties more significantly. From the viewpoint of microstructural configura-

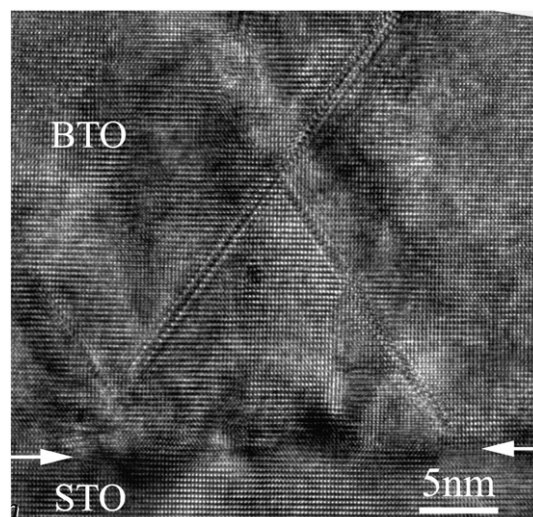


Fig. 6. A high resolution image of the $\text{BaTiO}_{2.52}$ thin film showing multiple twin variants viewed along the $[1\bar{1}0]$ direction.

tions in the present BTO films, the variety of electrical properties in the films is explicable. However, it must be clarified that the different electrical properties of BTO thin films are due to the different oxygen content in the films. The microstructures evolve with changing the oxygen pressure.

Several mechanisms have been proposed for the formation of the $\{111\}$ twins in BaTiO_3 . For single crystal and bulk BaTiO_3 ceramics, the twins observed were considered to be the growth twins. It is assumed by Eibl et al. [19] that the twins already exist in the nuclei since the temperature for the formation of single crystal and bulk is close to that for the transition from the cubic to the hexagonal phases, which share the same structural elements of Ti_2O_9 with $\{111\}$ twins. Another mechanism was proposed by Kästner et al. [20] that the mutual interaction of neighbouring grains with an orientation close to the twin relation may result in the formation of $\{111\}$ twins. For polycrystalline BaTiO_3 thin film, Jia et al. [21] found experimentally that twin nucleation from the dissociation of a perfect $a\langle 111 \rangle$ edge dislocation is one of the mechanisms for twin formation. Fahey et al. [22] also reported twin formation in a $\text{BaTiO}_3/\text{SrTiO}_3/\text{SrTiO}_3$ epitaxial system prepared by an oxygen-deficient environment and proposed a mechanism of stress induction of twins by large lattice misfit. Recently, it is proposed that $\{111\}$ nanotwins formation may be helpful to accommodate a large amount of oxygen vacancy [23]. In a previous report, Rečnik et al. [8] investigated the structural and spectroscopic properties of $\{111\}$ twins in reduced barium titanate by means of HRTEM combined with spatially resolved electron-energy-loss spectroscopy and found that the Ti atoms adjacent to the boundary plane occur in an oxidation state lower than the +4 on the stoichiometric compound. This suggests that the boundary plane is oxygen-deficient. In the $\Sigma 3$ $\{111\}$ twin boundary, the original TiO_6 octahedra change from corner- to face-sharing, forming a Ti_2O_9 group unit, which is a genuine element of the BaTiO_3 system because it is also the basic structural element of the hexagonal high temperature phase formed from the cubic phase at $\sim 1460^\circ\text{C}$ [24]. In this hexagonal BTO phase, those sites of the Ti_2O_9 group unit correspond to the oxygen sites in $\Sigma 3$ $\{111\}$ twin boundary planes and are partially vacant. By Cs-corrected HRTEM analysis, Jia et al. [23] measured the oxygen concentration in $\Sigma 3$ $\{111\}$ twin boundary in BaTiO_3 polycrystalline thin films at atomic resolution. They found that 68% of the boundary oxygen sites are occupied, and the others are left vacant. The modified Ti_2O_9 group unit thus formed to reduce the grain boundary energy and provides a way to accommodating oxygen vacancies occurring in oxygen-deficient materials by the formation of a nanotwin lamellae structure. The present BTO films were prepared under rather low oxygen pressures, oxygen vacancies may in large population. The

twin formation can accommodate the excess point defects in highly oxygen-deficient BTO systems. The lower the oxygen pressure is, the higher the density of nanotwins is. On the other hand, as mentioned in Section 3.1, decreasing the oxygen pressures, lattice parameters a and c become large, which may increase the lattice misfit between the films and the substrates. The large misfit strains can mainly be relaxed by the formation of misfit dislocation; however, the formation of {111} planar defects may also contribute to the relaxation process, as discussed in [25].

In comparison with the previous reports on the similar subject [11,13,14], the focus of this study is on the microstructural evolution of BTO thin films with oxygen pressure variations. The relationships between the electrical properties and structures as well as microstructures in the BTO films are tentatively established via oxygen pressure in the present study.

4. Summary

Microstructural characteristics were studied in a series of BaTiO_{3-x} thin films deposited under various oxygen pressures of 2×10^{-2} , 2×10^{-3} , 2×10^{-4} , and 2×10^{-5} Pa, respectively. It is found that the microstructures are dependent on the oxygen pressures under which the film was grown. The lattice constants and the volumes of BTO unit cells are inflated with oxygen pressure reduction. With the lowering of oxygen pressure, the major defects in the films change from threading dislocations into (111) nanotwins. The mechanism of {111} nanotwin formation in highly reduced BaTiO_{3-x} epitaxial thin films is discussed on the basis of oxygen vacancies accommodation.

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