

# Microstructural characteristics in the BaTiO<sub>2.52</sub> thin films showing metallic behavior

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## Abstract

BaTiO<sub>3-x</sub> films grown on SrTiO<sub>3</sub> substrate at the oxygen pressure of  $2 \times 10^{-5}$  Pa by laser molecular beam epitaxy result in a tetragonal BaTiO<sub>2.52</sub> compound which exhibits metallic behavior in physical properties. Such an oxygen-deficient compound remains in a perovskite-type structure, however, its lattice parameters are larger than those of the stoichiometric BaTiO<sub>3</sub>. Threading dislocations, which are frequently observed and are believed to undermine electrical properties in stoichiometric BaTiO<sub>3</sub> films, are rarely found. Instead, {111} nanotwins are found to be the major microstructural configuration in the present oxygen-deficient films. The mechanism for the defect configuration of these films is discussed on the basis of oxygen deficiency.

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**Keywords:** Microstructure; BaTiO<sub>3-x</sub> thin films; Oxygen deficiency

## 1. Introduction

Stoichiometric BaTiO<sub>3</sub> (BTO) thin films are of great interest due to their potential applications in ferroelectric random-access memories and electrooptic devices [1–4]. The performance of the devices is strongly influenced by the misfit strain and defect configuration in the epitaxial layers. The misfit strain can be relaxed by the formation of misfit dislocations depending on film thickness and growth condition. Through controlling of the oxygen pressure, the physical properties of BaTiO<sub>3-x</sub> thin films varied dramatically. Thin films of stoichiometric BTO have been grown on a number of various substrates by different deposition techniques. In the BTO films grown on SrTiO<sub>3</sub> (STO) by pulsed laser deposition, Suzuki et al. [5] found that the microstructural features in the epitaxial films are the formation of highly dense threading dislocations perpendicular to the interface between the film and substrate. In contrast, Shigetani et al. [6] studied the structure of BaTiO<sub>3</sub> thin films grown on STO substrate by 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 in-

terface. While films on polycrystalline Pt plate by radio-frequency magnetron sputtering, BTO were polycrystallized and (111) twins were found in the films [7].

Both ferroelectric domains and {111} twins are structurally peculiar frequently found in bulk BTO and stoichiometric BTO thin films [7,8]. Stoichiometric BaTiO<sub>3</sub> is insulating, however, through impurity doping [9,10] or reduction [11,12], electric conduction can be induced in BaTiO<sub>3-x</sub> ceramic. Although the physical properties of the oxygen nonstoichiometric BaTiO<sub>3-x</sub> thin films have been studied in a number of cases [11,13], the structural and microstructural properties in such films are rarely studied. Up to date there has been no report on the observation of {111} twins in oxygen-deficient BaTiO<sub>3-x</sub> thin films. In this letter, we present the microstructural characteristics of the BaTiO<sub>2.52</sub> compound, which has rather low oxygen content and shows metallic behaviors. We found that {111} nanotwins, rather than threading dislocations, are the major microstructural configuration in the present oxygen-deficient films.

## 2. Experimental

The present film was deposited on SrTiO<sub>3</sub>(001) substrate by laser molecular beam epitaxy at  $P_{O_2} = 2 \times 10^{-5}$  Pa. A detailed deposition procedure can be found elsewhere [11]. Cross-sectional

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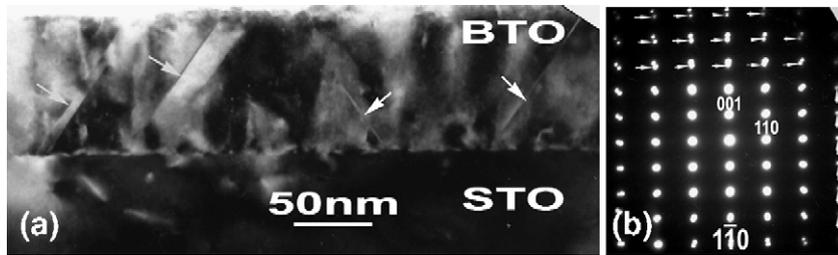


Fig. 1. (a) A low magnification cross-section image of the  $\text{BaTiO}_{2.52}/\text{SrTiO}_3$  system showing general distribution of  $\{111\}$  nanotwins in the  $\text{BaTiO}_{2.52}$  film. (b) A composite EDP corresponding to the area including both BTO thin film and STO substrate as in (a).

samples for transmission electron microscopic (TEM) observation were prepared by conventional slicing, grinding, dimpling and finally ion-thinning. A Tecnai F30 TEM, working at 300 kV, has been used to carry out lattice imaging and contrast analysis.

### 3. Results and discussion

The oxygen content in the present  $\text{BaTiO}_{3-x}$  films was measured by Rutherford backscattering spectrometry with an incident  $^4\text{He}^+$  (3.016 MeV in energy) ion beam, as described before [11]. When the films were grown at the oxygen pressure of  $2 \times 10^{-5}$  Pa, the oxygen deficiency in the  $\text{BaTiO}_{3-x}$  thin films is as high as 0.48. Such a highly oxygen-deficient  $\text{BaTiO}_{2.52}$  has electrical resistivity as low as  $6 \times 10^{-5} \Omega$  at 300 K; its electrical mobility and carrier density at 300 K are  $6.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $1.98 \times 10^{22} \text{ cm}^{-3}$ , respectively, which correspond to metallic behavior.

Fig. 1(a) shows a low magnification cross-section image of the  $\text{BaTiO}_{2.52}/\text{SrTiO}_3$  system. This image was taken with the incident beam close to the  $[11\bar{0}]$  direction of  $\text{SrTiO}_3$ .

It is seen that the interface between  $\text{BaTiO}_{2.52}$  thin film and STO is flat and sharp. Some interfacial dislocations are also visible along the interface. In this film, besides strong contrast areas, defects in the planes which are  $\pm 35^\circ$  away from the interface normal are frequently observed. They are identified as  $\{111\}$  planar defects marked with white arrows and it seems that nearly all of them originate from the interface between the film and substrate. Fig. 1(b) is a composite electron diffraction pattern (EDP) corresponding to the area including both  $\text{BaTiO}_{2.52}$  thin film and STO substrate in Fig. 1(a). Such an EDP confirms that the present film, although it is highly oxygen-deficient, still remains in a perovskite-type structure. The splitting of diffraction spots results from the lattice difference between  $\text{BaTiO}_{2.52}$  film and STO substrate. The inner diffractions marked with white arrowheads are from the  $\text{BaTiO}_{2.52}$  film, implying that the lattice parameter of  $\text{BaTiO}_{2.52}$  is larger than that of the STO substrate. The outer

diffraction spots are from the STO substrate which has a lattice constant of  $a = 0.3905 \text{ nm}$ . Using STO as a reference, the lattice constant of the present  $\text{BaTiO}_{2.52}$  thin films can be calculated as  $c \approx 0.410 \text{ nm}$ , which is 1.54% inflated than that in bulk  $\text{BaTiO}_3$  ( $c = 0.4038 \text{ nm}$ ) [3]. According to EDPs of  $[010]$  and  $[100]$  zone axis (not shown here), both  $a$  and  $b$  values of the  $\text{BaTiO}_{2.52}$  films are calculated as  $a = b = 0.403 \text{ nm}$ , which are larger than those in bulk BTO ( $a = b = 0.3992 \text{ nm}$ ) [3]. This confirms that, although the lattice parameters are larger than those of stoichiometric  $\text{BaTiO}_3$ , the present  $\text{BaTiO}_{2.52}$  film still keeps a perovskite-type tetragonal structure. The present film is  $[001]$ -oriented and has a parallel orientation relationship with the STO substrate. Such an electron diffraction experiment presents the agreeable values compared with X-ray diffraction measurement [14].

A more detailed investigation indicates that the  $\{111\}$  planar defects are actually nanotwins with the width of about 1–2 nm. Fig. 2(a) is a low magnification high-resolution transmission electron microscopic (HRTEM) image taken along the  $[11\bar{0}]$  direction showing how the  $\{111\}$  nanotwins developed in the film. It is seen that all these  $\{111\}$  planar defects originate from the interface. In the left part of this image, there are  $(111)$  and  $(11\bar{1})$  multiple nanotwins with the width of about 1 nm. Fig. 2(b) shows an HRTEM image of the  $(11\bar{1})$  twin. Such nanotwins are similar to those in stoichiometric  $\text{BaTiO}_3$  [15]. Misfit dislocations, which result from the lattice mismatch between the films and substrate, are also marked in Fig. 2(a) with vertical white arrowheads along the interface. It is seen that the distance of these dislocations is approximately 13 nm. Based on the lattice parameters of the present  $\text{BaTiO}_{2.52}$  film and STO substrate, theoretically the separation of misfit dislocations can be calculated as 12.5 nm. Therefore the lattice strain in the present film is mainly relaxed through the formation of misfit dislocations.

From the cross-section image (Fig. 1(a)), it is learnt that there are few threading dislocations in such an oxygen-deficient film, which shows a strong contrast to the work by Suzuki et al. who found highly dense threading dislocations in the stoichiometric BTO thin films grown on  $\text{SrTiO}_3$  [5].

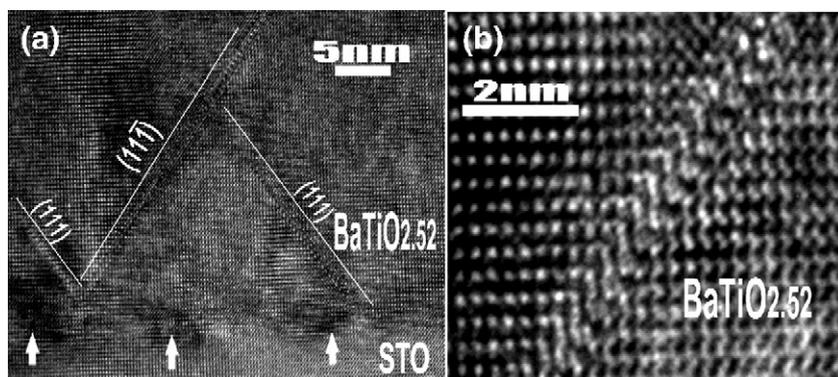


Fig. 2. (a) A low magnification high-resolution transmission electron microscopic image taken along the  $[11\bar{0}]$  direction showing  $\{111\}$  nanotwins in the  $\text{BaTiO}_{2.52}$  film and misfit dislocation at the  $\text{BaTiO}_{2.52}/\text{SrTiO}_3$  interface. (b) HRTEM image of  $(11\bar{1})$  twin.

It is generally believed that both threading dislocations and misfit dislocations greatly undermine the electrical properties of semi-conductive and conductive thin films, especially threading dislocation worsens the electrical properties more significantly. Therefore, the microstructural configuration in the present BaTiO<sub>2.52</sub> film, which is free from threading dislocations, is believed to be the key reason for its metallic behavior. The formation of nanotwins lamellae in the present film can be explained in terms of the tetragonality of the BTO stabilized by the large misfit strain between the film and substrate induced by high oxygen deficiency. It has been shown that the lattice constants of the oxygen-deficient film increase with decreasing oxygen pressure [14,16]. In the present most oxygen-deficient BaTiO<sub>2.52</sub> thin film, its lattice constant parallel to the interface increased to  $a=0.403$  nm, which makes the misfit strain  $\epsilon$  larger. In the ferroelectric heteroepitaxy system, the misfit strain between the film and substrate can be relieved either by the misfit dislocations or by the formation of domains [17]. Misfit dislocations are indeed observed along the interface in this epitaxy system, as shown in Fig. 2(a). However, in order to maintain the tetragonal structure in this highly reduced film, another misfit relaxation mechanism such as the formation of {111} nanotwins in the present case, is expected. Otherwise the tetragonal structure can be hardly preserved with such low oxygen content. For BaTiO<sub>3</sub> ceramics, it was proposed by Eibl et al. [18] that at (111) twin boundaries, TiO<sub>6</sub> octahedra share faces on a BaO<sub>3</sub> plane. With an oxygen content of 2.52, every two TiO<sub>6</sub> octahedra in BaTiO<sub>2.52</sub> films lack one oxygen atom. In order to keep the present BaTiO<sub>2.52</sub> tetragonal, twinning can occur so that the TiO<sub>6</sub> octahedra can be preserved. Fahey et al. [19] also reported twins formation in a BaTiO<sub>3</sub>/SrTiO<sub>3</sub>/SrTiO<sub>3</sub> epitaxial system prepared by an oxygen-deficient environment and proposed a mechanism of stress induction of twins by a lattice misfit. On the other hand, {111} nanotwins formation may be helpful to accommodate a large amount of oxygen vacancy. Reñik 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 charge is compensated by oxygen vacancies in the twin plane, which is composed of Ba–O<sub>3-x</sub>[V<sub>o</sub>]<sub>x</sub> instead of Ba–O<sub>3</sub>. In a study of polycrystalline BaTiO<sub>3</sub>, Kraševc et al. reported that the density of twinning was influenced by an appropriate heat treatment at a reducing atmosphere [20]. It is known that the electrical properties depend on the twins density. The oxygen deficiency, which is basically believed to be located at the twin boundary, should be the fundamental factor to be responsible for the metallic behavior in the present BaTiO<sub>2.52</sub> films.

#### 4. Conclusions

In conclusion, {111} nanotwins have been found in the highly oxygen-deficient BaTiO<sub>2.52</sub> films, which show metallic behavior

in electrical properties. Few threading dislocations, which are frequently observed and are believed to undermine electrical properties in stoichiometric BaTiO<sub>3</sub> films, are observed in these films. Such a structural configuration is believed to be responsible for the metallic conductive behavior in such an oxygen-deficient compound.

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