PAPER

Strain effects on conductivity and charge transport in La-doped BaTiO$_3$ thin films

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1. Introduction

Conductivity and charge transport in traditional insulating ferroelectric oxides have been cutting-edge research topics with rich physical connotations and wide-ranging prospects for applications in the field of ferroelectric materials [1–5]. Semiconductor and even metallic conduction in insulating ferroelectric materials can be realized by various methods, such as ion doping [6, 7], oxygen reduction [8, 9], and so on. In the 1960s, Anderson and Blount developed a theory that introduced the idea of a polar metal [10], which suggested that two seemingly incompatible states, such as metallic conduction and ferroelectricity, could exist simultaneously in a material. Since then, significant theoretical [11–13] and experimental works [14–16] have been devoted to investigate the coexistence of a metallic phase and a ferroelectric or polar phase.

BaTiO₃ (BTO) is a classic ferroelectric perovskite that can be used in various applications ranging from piezo-sensors and nonvolatile memories to resistive switching memories and photovoltaic solar cells [2, 17, 18]. Although stoichiometric BTO is an insulator with a band gap of 3.2 eV [2], some results [3, 7–9, 19–21] indicate that BTO-based systems can
exhibit semiconducting behavior, metal conductivity, or even metallic ferroelectricity, extending their range of application to novel optoelectronic devices. For decades, considerable effort has gone into the fabrication of conductive BTO oxides in both the bulk polycrystalline [22–25] and thin films [3, 7–9, 15, 20, 21, 26–28] by inserting ions of unequal valence into the Ba\(^{2+}\) or Ti\(^{4+}\) sites. In such a doped BTO system, some Ti\(^{4+}\) ions must be changed to Ti\(^{3+}\) ions to balance the electric charge, and the resulting conductivity is due to the movement of 3d-orbital electrons among these Ti\(^{3+}\) and Ti\(^{4+}\) ions [19, 24]. For example, doping pentavalent (Nb\(^{5+}\), Ta\(^{5+}\)) ions into Ti sites in BTO has been well studied to understand the insulating and/or semiconducting behavior [21]. Conversely, trivalent-ion (La\(^{3+}\), Y\(^{3+}\), Gd\(^{3+}\)) doping into the Ba site has also been widely adopted [15, 22–25, 28]. La-doped BTO (Ba\(_{1-x}\)La\(_{x}\)TiO\(_3\)) is particularly intriguing. Takahashi et al prepared La-doped BTO epitaxial films with various doping contents and demonstrated the polar nature by band structure calculations in La-doped BTO with metallic conduction [15].

Strain in an epitaxial film, which is generated by the lattice mismatch between substrate and film, has been reported to significantly affect the structural, transport, and ferroelectric properties of materials [4, 29–36]. For example, Choi et al [4] and Lyu et al [34] reported enhanced ferroelectricity in strained BTO thin films. Such strain engineering has been extensively used to induce the metal-insulator transition [29] and to produce high-temperature perovskite ferromagnetic insulators [30]. In addition, epitaxial strain depends strongly on film thickness because strain relaxation occurs with increasing film thickness and the film relaxes beyond a critical thickness. In the present work, BLTO thin films of varying thickness were prepared to obtain various strains and to investigate how strain affects the conductivity and charge-transport properties of BLTO thin films. The systematic results presented herein demonstrate how epitaxial strain critically affects the conductivity and charge-transport of BLTO films, which should prove very helpful for clarifying the complex conduction and charge-transport mechanism in BLTO films and promote its application in various fields.

2. Experimental details

Ba\(_{0.5}\)La\(_{0.5}\)TiO\(_3\) (BLTO) films of varying thicknesses were grown epitaxially on (001) MgO single crystal substrates by using pulsed laser deposition with a KrF (\(\lambda = 248 \text{ nm}\)) excimer laser (Coherent COMPexPro 205). For the deposition, the substrate temperature was 650 °C, the laser energy density was 1.7 J cm\(^{-2}\), the laser repetition rate was 2 Hz, and the pressure of the ambient oxygen was 3.0 \times 10^{-4} \text{ Pa}. After deposition, films were cooled down at the rate of 10 °C/min in a high vacuum. The film thickness was controlled by the number of laser pulses (i.e., 500, 1000, 1500, 2000, or 2500) and the film was characterized by using small-angle x-ray reflectivity.

The crystal structure of the films was determined by using x-ray diffraction (XRD, PANalytical X’Pert Pro diffractometer) with Cu K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)). The surface morphology of the BLTO films was investigated by using atomic force microscopy (AFM, Asylum Research Cypher). The microstructure was determined by using cross-sectional high-resolution transmission electron microscopy (HRTEM, JEM2100F). The temperature dependence of the resistivity and the Hall Effect were determined by using a physical property measurement system (PPMS9, Quantum Design).

3. Results and discussion

Figure 1(a) shows x-ray diffraction patterns of BLTO films from 14.1 to 95.9 nm thick. All the films have (001) reflection planes, which correspond to the MgO (00l) planes, indicating epitaxial growth of all the BLTO films. The epitaxial quality was further investigated by rocking curve measurements, from which the full width at half maximum value is very small (<0.18°), implying very good epitaxial quality of the grown BLTO films. Note that the 14.1 nm-thick film has weak (001) and (002) peaks, and the (003) peak gradually appears with increasing film thickness. For clarity, the (001) and (002) diffraction peaks of BLTO films are presented on an expanded scale in figures 1(b) and (c), respectively. Note that both (002) and (001) reflection peaks are almost in the same 2θ value for the thinner films (14.1 and 28.5 nm-thick films). The reason is attributed to the high epitaxial strain. Further increasing the film thickness, they are shifted to a lower value of 2θ, which indicates an elongation of the out-of-plane lattice constant c due to the lattice relaxation [37]. Based on these reflection peaks and using Bragg’s law, the lattice constant c, defined as the out-of-plane orientation, increases from 4.089 Å for 14.1 nm-thick film to 4.099 Å for 95.9 nm-thick film. Figure 1(d) shows the small-angle x-ray reflectivity of BLTO films deposited on (001) MgO substrates. The thickness of each film is calculated to be 14.1, 28.5, 52.5, 62.2, and 95.9 nm, which corresponds to the use of 500, 1000, 1500, 2000, and 2500 laser pulses, respectively, in the pulsed-laser deposition.

Figures 1(e) and (f) show two representative surface morphologies of the thinnest and thickest BLTO films, respectively. Although the film thickness varies from 14.1 to 95.9 nm, the film surfaces of all the films are very smooth with a root mean square roughness ranging from 142 to 270 pm.

In addition to the out-of-plane lattice parameters, the in-plane lattice parameters should also be determined to investigate the epitaxial of BLTO/MgO heterostructures with different film thicknesses. Reciprocal space mapping (RSM) was done based on the (103) reflection, and the results are shown in figures 2(a)–(c) for the 14.1, 52.5, and 95.9 nm-thick films, respectively. These results reveal that all the BLTO films are of high epitaxial quality, and that the values of the epitaxial lattice parameters depend on the thickness.

On the basis of these RSM and XRD measurements, we confirmed all of the in-plane and out-of-plane lattice parameters, which are summarized in figure 2(d). Upon increasing the film thickness from 14.1 to 95.9 nm, the lattice constant a of the BLTO films gradually decreases from 4.216 Å for the 14.1 nm-thick film to 3.997 Å for the 95.9 nm-thick film. The
out-of-plane lattice parameter extracted by RSM is consistent with the results of XRD \( \theta-2\theta \) measurements (figure 1(a)). Note that the diffraction intensity of the BLTO (1 0 3) peak of the thinnest film (figure 2(a)) is undefined due to the low intensity as a result of the low film thickness. The in-plane lattice constant \( a \) is calculated to be 4.216 Å based on the TEM result, which is discussed in detail below (figures 3(a)-(c)). This result is the same as that for films deposited on MgO substrates \( (a = 4.216 \text{ Å}[27]) \), which suggests that the film has the highest epitaxial strain.

The epitaxial strain \( \varepsilon \) in BLTO films was calculated by using the formula \( \varepsilon = (a_f - a_{\text{min}})/a_{\text{min}} \times 100\% \), where \( a_f \) is the lattice constant of BLTO films of various thicknesses, and \( a_{\text{min}} \) is the minimum lattice constant of these films (i.e. for the completely relaxed BLTO film). The thinnest films are under tensile strain with \( \varepsilon \approx 6\% \), which decreases with increasing film thickness (see figure 2(e)). The strain \( \varepsilon \) approaches zero for the 52.5 nm-thick film, which indicates that the strain is completely relaxed at this thickness. The corresponding epitaxial stress of BLTO films with different thicknesses is also evaluated in figure 2(e). The 14.1 nm-thick BLTO film has the largest stress of 19.0 GPa.

Cross-sectional TEM was also used to evaluate the thickness and epitaxial quality of the BLTO films, and the results are shown in figure 3 for the thinnest and thickest films (14.1 and 95.9 nm, see figures 3(a) and (d), respectively). These results are consistent with those of figure 1(d). Note that the BLTO-MgO interfaces appear to be atomically sharp, as shown in figures 3(b) and (e) for the thinnest and thickest films, respectively. Moreover, figures 3(c) and (f) show the corresponding selected-area electron diffraction (SAED) patterns taken along the [0 1 0] MgO for the thinnest and the thickest film, respectively. The SAED spots from BLTO and MgO are sharp and identifiable, which indicates good single-crystal and epitaxial quality. Based on the TEM images and SAED results, we calculate the lattice parameters \( c \) and \( a \) for the two BLTO films to be \( c = 4.089 \) and \( 4.099 \) Å and \( a = 4.216 \) and \( 3.995 \) Å for the 14.1 and 95.9 nm-thick films, respectively, which is consistent with the RSM and XRD results.

To explore how strain affects the electrical transport properties, we plot in figure 4(a) the electrical resistivity \( \rho \) as a function of temperature \( T \) for the BLTO thin films with thickness ranging from 14.1 to 95.9 nm. The results show clearly that \( \rho \) depends strongly on thickness. Figure 4(b) plots \( \rho \) versus film thickness for temperatures of 80 K and 300 K. As the film thickness increases from 14.1 to 52.5 nm, \( \rho \) decreases for both low and high temperature, which is attributed mainly to strain relaxation. Upon further increasing the film thickness, the low-temperature resistivity increases slightly, whereas the high-temperature resistivity remains essentially constant. Clearly, the mechanism responsible for the resistivity depends on temperature, as is discussed below.

The resistivity is low for relatively thick films (>52.5 nm, \( \rho \sim 0.1 \Omega \cdot \text{cm} \)), which is consistent with the fact that the lattice

**Figure 1.** (a) \( \theta/2\theta \) x-ray diffraction patterns of BLTO/MgO heterostructure with different film thicknesses. Expanded view of XRD peaks for (b) (001) and (c) (002) reflections. (d) X-ray reflectivity of BLTO films with thickness ranging from 14.1 to 95.9 nm. AFM image of (e) 14.1 nm-thick film and (f) 95.9 nm-thick film.
constants in these films approach that of bulk BLTO. As demonstrated by Fritsch et al. in BLTO ceramics, a low resistivity $\rho$ may be due to increased mobility of Ba and La ions [22]. In relatively thin films, an enhanced resistivity $\rho$ may be due to the onset of tensile strain imposed by the substrate lattice. In a perovskite system, tensile strain is expected to increase the length and angle of the Ba–Ti or Ba–La bond and to influence the 3d–2p orbital hybridization, which reduces hopping by charge carriers [21, 22, 32]. Many studies have reported that strain relaxation in epitaxial ferroelectric films may be helpful for modulating the electric transport properties of these systems [38, 39]. Yang et al. reported that the compressive strain in an epitaxial ferroelectric film may induce an insulator–metal transition [39]. In contrast, a tensile strain
enhances the insulating property. Furthermore, atomic-scale disorder or defects may also affect the electrical properties [40], although this phenomenon may be neglected in the present work because of the good epitaxial quality of the thin films (<100 nm).

Note that the $\rho(T)$ curves reveal a clear semiconductor-metal transition. The transition temperature $T_{SM}$ and the strain state $\varepsilon$ as a function of the film thickness are summarized in figure 4(c). With increasing film thickness, the $T_{SM}$ first decreases rapidly and then increases slightly. Similar relationship is also found for the strain state. This implies that a direct relationship between $T_{SM}$ and strain state exists, and the dependence of $T_{SM}$ on the strain state is plotted in the inset of figure 4(c). It reveals that the larger is the strain, the higher is the $T_{SM}$. In addition, the substrate-film lattice misfit induced strain also plays a critical role in determining the conductivity and charge transport behaviors. To differentiate between various possible charge transport mechanisms in these BLTO thin films, we fit various models to the $\rho(T)$ curves.

Figure 4(d) shows that, at high temperatures ($T > T_{SM}$), $\rho(T)$ is well fit by the thermal phonon scattering model, which predicts [21, 27]:

$$\rho \propto T^{3/2},$$  

(1)

Note that, at lower temperatures ($T < T_{SM}$), the fit deviates from the thermal phonon scattering model, suggesting that this model is not valid at low temperatures. At low temperatures, carriers hop smaller distances and are affected by multiple activation energies, all of which is well described by the small-polaron hopping (SPH) model, which predicts [21, 41]:

$$\rho \propto T^{3/2} \exp\left(\frac{W_H}{k_B T}\right),$$  

(2)

where $W_H$ is the thermal hopping activation energy, and $k_B$ is the Boltzmann constant. Figure 4(e) shows that the low-temperature transport behavior fits well to the SPH model for all BLTO films studied.

Such a transition from thermally activated conduction to hopping conduction with decreasing temperature was previously reported for Nb-doped BTO film [35, 37]. Jing et al attributed this type of transition to strongly localized electron states below $T_{SM}$, which facilitates conduction in the SPH model [21]. The transition temperature $T_{SM}$ decreases with decreasing strain in the film, which implies that the charge-ordered state in films grows unstable with increasing strain. Based on theory, Li et al predicted a decrease in $T_{SM}$ in BLTO thin films as tensile strain is relaxed [30]. In addition, we plot in figure 4(f) the activation energy $W_H$ extracted from the fits to the data as a function of thickness. The activation energy
$W_H$ decays gradually with increasing thickness, implying that the energy band narrows as the film thickness increases, thereby allowing electrons to jump into the conduction band. The slight increase in $W_H$ for the thicker films is attributed to film defects and/or to disorder among Ba and La atoms.

Figure 5(a) shows the Hall coefficient $R_H$ measured as a function of temperature for BLTO films of various thicknesses (14.1–95.9 nm). Note that $R_H$ is negative, which indicates that electrons are the dominant carriers rather than holes, which is attributed to trivalent La$^{3+}$ ion doping into the Ba-site. The interesting feature is that $R_H$ decreases gradually with increasing temperature except for the 14.1 nm film, for which the opposite tendency is observed (below ~300 K), which proves that epitaxial strain strongly affects charge transport in these films. In addition, for BLTO films thicker than 52.5 nm, $R_H(T)$ is nearly independent of film thickness throughout the entire temperature range, which is attributed to the lack of strain in these thicker films (figure 2(e)).

Figure 5(b) shows the carrier density $n$ determined from the Hall data as a function of temperature and for various film thicknesses. For the 14.1 nm-thick BLTO film, $n(T)$ decreases with increasing temperature up to ~300 K, whereas $n(T)$ increases with increasing temperature for the thicker films. Note that $n$ for all the films is on the order of $10^{21}$ cm$^{-3}$, which is consistent with earlier reports [15].

Figure 5(c) shows the as-extracted carrier mobility $\mu_H$ as a function of $T$ for all films studied herein. The carrier mobility $\mu_H$ depends strongly on temperature for all the films. It increases with increasing $T$ below a critical temperature and then decreases with temperature above the critical temperature. The mobility of conduction-band electrons is typically thought to depend strongly on the scattering mechanism. At low temperatures, scattering from ionized impurities dominates. Above the critical temperature, acoustic phonon scattering becomes dominant, and the mobility follows $\mu_H \propto T^{-3/2}$. Based on the results shown in figure 5(c), the high-temperature scattering mechanism in these films is most probably acoustic phonon scattering, whereas small-polaron hopping dominates in the low-temperature range. These results are consistent with the resistivity results discussed above.

Figures 5(d)–(f) show the Hall coefficient, carrier density, and carrier mobility at 300 K as a function of epitaxial strain. It can be seen clearly that the thinner BLTO films with larger strain have a smaller carrier mobility, lower carrier density, and higher Hall coefficient, which implies that the epitaxial strain has a critical effect on carrier transport.

4. Conclusions

To summarize, we systematically investigated how epitaxial strain affects the microstructure and electrical transport nature of La-doped BTO films. The microstructural measurements, including AFM, HRTEM, and XRD, demonstrate that all the films studied were of good epitaxial quality, with atomic-level
flat surfaces. Measurements of resistivity versus temperature demonstrated that the conductivity gradually increases with decreasing epitaxial strain. All the BLTO films undergo a semiconductor-metal transition, and the transition temperature first decreases and then increases with increasing film thickness. Measurements of the Hall Effect revealed that the majority carriers in these BLTO films are electrons, and their transport is by small-polaron hopping in the semiconductor phase and by thermal phonon scattering in the metallic phase. In addition, the film thickness (i.e. epitaxial strain) clearly affects the carrier mobility and concentration. These findings provide deeper insights into the complex charge transport mechanism in conductive FE materials, which will boost potential applications in future information storage, sensors, and optoelectronic devices.

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