Microstructure defects mediated charge transport in Nb-doped epitaxial BaTiO₃ thin films

Jian Zhou¹, Xiaosai Jing¹, Marin Alexe², Jiyan Dai³, Minghui Qin¹, Sujuan Wu¹, Min Zeng¹, Jinwei Gao¹, Xubing Lu¹ and J-M Liu¹, 4

¹ Institute for Advanced Materials and Guangdong Provincial Laboratory of Quantum Engineering and Quantum Materials, South China Normal University, Guangzhou 510006, People’s Republic of China
² Department of Physics, University of Warwick, Coventry CV4 7AL, West Midlands, UK
³ Department of Applied Physics, The Hong Kong Polytechnic University, Hunkom, Hong Kong, People’s Republic of China
4 Laboratory of Solid State Microstructures, Nanjing University and Innovation Center of Advanced Microstructures, Nanjing 210093, People’s Republic of China

E-mail: luxubing@scnu.edu.cn

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Abstract
Nb-doped BaTiO₃ (BNTO) films were deposited on MgO substrates at different substrate temperatures by pulsed laser deposition. The temperature dependence of their resistivity, carrier mobility and carrier concentration were systematically investigated. It reveals that the BNTO films deposited at lower temperature show higher resistivity and lower carrier mobility, and only show semiconductor characteristics at measurement temperatures ranging from 10 to 400 K. There is a metal–semiconductor transition at about 20 K for the films grown at relatively higher temperature. The intrinsic mechanism responsible for the different charge transport behavior was revealed by microstructure studies. Low crystal quality and high density of microstructure defects, observed for BNTO films grown at low temperatures, are, in particular, massively affecting the charge transport behavior of the BNTO films. The mediated charge transport of the microstructure defects is dominated by the thermal excitation process.

Keywords: BaTiO₃, charge transport, microstructure defects, conductivity, carrier mobility

(Some figures may appear in colour only in the online journal)

1. Introduction
BaTiO₃ (BTO) is a classical perovskite oxide material with wide potential applications based on its ferroelectricity, piezoelectricity and photo-refractivity [1, 2]. Stoichiometric BaTiO₃ is an insulator with a bandgap in the range of 3.2–3.4 eV and a resistivity of about $10^{19} \Omega \cdot \text{cm}$. The bandgap is located between a valence band composed primarily of oxygen 2p levels and an empty conduction band derived from the titanium 3d $t_{2g}$ orbitals [3, 4]. While the ferroelectricity of insulating BaTiO₃ has been the focus mainly for applications related to ferroelectric memories, little attention has been paid to the conductivity, except its unique positive resistivity-temperature coefficient [5]. Recently, considerable attention has been paid to the ferroelectric semiconducting oxide materials for their applications in resistive switching memory and photovoltaic solar cells [6–9].

Insulating BaTiO₃ can become conductive either through doping with trivalent rare-earth ions on a Ba²⁺ site [10–12] or pentavalent ions on a Ti⁴⁺ site [13] or through reduction (BaTiO₃−δ) [14]. Many conduction mechanisms spanning from thermal excitation, hopping conduction to polaron conduction have been brought forward to describe charge transport in conductive BaTiO₃. In the case of Ti⁴⁺ site doping, especially the case of Nb doping, considerable effort has been paid to study the electrical transport in BTO bulk or epitaxial
films [13, 15–19]. The results obtained show wide discrepancies. Kahn et al [19] pointed out a variable range hopping conduction mechanism for 2% at Nb-doped BTO thin film in the range of 150 to 300 °C. Shao et al [13] provide evidence of the small singlet bi-polaron mechanism in their single phase BaTi1−xNbO3 (0.2 ≤ x ≤ 0.75). Liu et al [18] brought evidence of the small polaron conduction mechanism in single phase BaTi1−xNbO3 (0.01 ≤ x ≤ 0.5). The majority of these studies favor small polaron conduction which generality consists of three regimes as discussed by Appel [20] and Klinger [21]. At low temperature, the polarons behave as heavy particles in a band, showing metallic transport behavior. At intermediate temperature, hopping motion dominates the conduction, leading to an activated behavior. Finally, the polaron states are thermal dissociated as the temperature is higher than the activation energy, leading to a thermal activation charge transport behavior.

When compared with the SrTiO3 (STO) system, which has a similar crystal structure and electronic structure [22], the BTO system exhibits very different charge transport behaviors. For example, the reported carrier mobility value is much lower than that of the STO system. For La-doped STO epitaxial films, the carrier mobility can reach as high as 32 667 cm² V⁻¹ s⁻¹ [23]. However, for single crystal BTO the reported carrier mobility is usually below 1.0 cm² V⁻¹ s⁻¹ and the reported highest value is only 15 cm² V⁻¹ s⁻¹ [12, 24]. Another noticeable difference is that the conductivity of the STO system can be easily transformed among insulator–semiconductor–metallic behaviors, whereas for the BTO system it is not easy to obtain very high conductivity or metallic transport. The bulk BTO always has a critical doping point. That is the conductivity increases with the doping concentration of the dopants, and it will decrease again above a certain doping concentration. Moreover for BTO films, the situation is even more complicated. For instance, MOCVD-grown BTO films show similar critical doping phenomena, while this critical doping concentration disappears for films deposited by pulsed laser deposition (PLD). The above mentioned charge transport behavior suggests that the charge transport behaviors of the BTO system and the corresponding intrinsic mechanisms need to be further investigated, which will be very important for potential applications such as photovoltaic and resistive switching memory.

In the past, most of the studies [13, 15–18, 25] focused on the effect of chemistry defects on the conductivity and charge transport behaviors of BTO. Unfortunately, studies on the effect of microstructure on the conductivity of BTO, especially for thin films, are rather limited [13, 26]. In this work we focus on the less explored effect of microstructure defects on the conductivity and charge transport behaviors of BTO. We targeted different microstructures by depositing the BTO films by PLD at various temperatures and we have been able to show that the conductivity and charge transport can be significantly tuned by the microstructure defects.

2. Experimental details

BaNb0.5Ti0.5O3 (BNTO) films were deposited on MgO (001) single crystal substrate using the pulse laser deposition (PLD) technique. The Nb doping concentration of 50% at was chosen in this work to obtain reliable Hall effect measurement results at low temperature. The MgO substrate was chosen to avoid the interfacial oxygen vacancy diffusion effect, which was always found to play a critical role on the conductivity and charge transport for BTO deposited on the STO substrate. Details on the Nb-doping concentration effect and the interface oxygen vacancy diffusion effect on the BTO/STO structure will be discussed in our other work. BNTO thin films with a thickness of ~80 nm were grown in a temperature range from 500 to 700 °C and at oxygen ambient pressure of 3.0 × 10⁻⁴ Pa. A polycrystalline BaNb0.5Ti0.5O3 ceramic pellet (Goodwill) was used as the ablation target. During the deposition, a KrF excimer laser with a wavelength of 248 nm was operated at 3 Hz and the laser fluence was fixed to 1.0 J cm⁻². After the deposition, the films were cooled down in vacuum to avoid the compensation of oxygen. X-ray diffraction (XRD) analyses were carried out using a PANalytical X’Pert Pro diffractometer with Cu Kα radiation (λ = 1.5406 Å). The surface morphology of the samples was investigated using a Cypher Asylum Research atomic force microscope (AFM). A JEOL JEM2100F high resolution transmission electron microscope (HRTEM), with point resolution of 0.194 nm and working voltages of 200 kV, was used to carry out cross-section analysis and selected area electron diffraction (SAED) measurement. The cross-sectional and planar view specimens for transmission electron microscopy (TEM) observation were prepared by the conventional processes of slicing, grinding and finally ion-milling. The temperature dependence of the resistivity and Hall effect measurements were performed by the van der Pauw method using a physical property measurement system (PPMS 9, Quantum Design).

3. Results and discussion

Figure 1(a) shows the 2θ/θ scans of samples grown at temperatures of 500 °C, 550 °C, 600 °C, 650 °C and 700 °C. From the figure, (001) peaks of BNTO with no other diffraction peaks originate from the impurity phase can be clearly observed for all of the samples. (002) and (003) peaks can be observed only for the films grown at 700 °C. The disappearance of (002) peaks for these films grown below 700 °C is most probably due to the fact that their out-of-plane lattice constant is very close to that of the MgO substrate. The (002) diffraction peaks for BNTO films are hard to distinguish from the diffraction peak of the MgO substrate. Another possible reason for the disappearance of (002) and (003) peaks is that the crystallinity of the BNTO films is not good enough to obtain clear diffraction peaks for films grown below 700 °C. Figure 1(b) especially shows the diffraction patterns for (001) peaks. The (001) peaks shown in figure 1(b) revealed a clear shift to the larger angles for the 700 °C grown sample compared with that of the other four samples. Correspondingly, the out-of-plane lattice constant shrinks from 4.162 to 4.135 Å. The absolute diffraction intensity of the (001) peak increases with the increase of growth temperature and the full width at half maximum (FWHM) values decrease with the increase of the growth temperature, both of which imply an enhancement of
crystal quality with increase of deposition temperature. In addition to the 700 °C grown sample, the other four samples exhibit no clear shifts of the (001) peaks, which implies that the low temperature below 700 °C did not bring clear effects on their out-of-plane lattice constants. The surface morphologies measured by AFM revealed a slight increase of the surface roughness with the increase of the growth temperature.

Figure 2 shows the typical AFM surface morphology images of the samples grown at different temperatures. Very flat surfaces have been observed for all of these samples. For films with ~80–100 nm physical thickness, their surface root of mean square (RMS) is as small as ~0.2 nm. Another feature shown in figure 2 is that growth temperature did not significantly affect their surface roughness. All the RMS values are between 0.1 and 0.2 nm. The microstructures of three representative BNTO films grown at 500, 600 and 700 °C were studied by cross-sectional TEM along the [010] crystal direction. Figures 3(a)–(c) show the low-magnification TEM images of the three samples. Clear interface between MgO substrate and BNTO film can be observed, and the film thicknesses are determined to be ~80 nm. Figures 3(d)–(f) show the high-resolution TEM images of the same samples. The main difference among the TEM images is that the 700 °C grown film shows more perfect crystal structure compared to the other two films. The epitaxial quality increases with the increase of the growth temperature. In 500 °C grown film, some amorphous and disordered structures can be clearly seen.
Figure 4(a) shows the temperature dependent resistivity characteristics of the BNTO films. The dc resistivity of BNTO films shows a clear dependence on the growth temperature. The sample grown at 500 °C exhibits the highest resistivity during the whole measurement temperature range. The resistivity gradually decreases with the increase of the growth temperature. Films deposited at low temperatures of 500 and 550 °C show semiconductor transport behaviors spanning the whole range of measurement temperature (10–400 K). For films grown at 600, 650 and 700 °C, the resistivity exhibits entirely the semiconductor transport behaviors. However, a metal–semiconductor-like transition occurs at a low temperature of around 20 K. When the temperature is lower than 20 K, the transport behaviors of the three samples are metallic-like, as shown in figure 4(b). This low temperature metal–semiconductor transition has also been observed in the BaTi0.8Nb0.2O3 ceramics, which implies a crossover from band to hopping transport of the charge carriers [27]. In the work performed by Shao et al [13] and Liu et al [18], the charge transport behaviors of the BNTO films exhibit to be either semiconductor or...
metal behaviors in the whole temperature range depending on the Nb-doping concentration. One result shown in figure 4(a) should be mentioned is that the 700 °C grown film shows a higher resistivity than that of the 650 °C grown film. This is assumed to be due to the electron trapping effects from cation vacancies. According to the experimental results by Radaelli et al [28], Ba re-evaporation occurs above 680 °C for BaTiO₃ films, which will result in the increase of the cation vacancies in the BNTO film. The cation vacancy will trap free electrons [16, 29] and the free carrier concentration in 700 °C grown film reduces leading to the increase of its resistivity.

Figure 5(a) shows the temperature dependent Hall coefficient $R_H$ for all of the Nb-doped BTO films. The negative Hall coefficient indicates the majority of carriers in the BNTO films are electrons. The Hall coefficient shows obvious temperature dependence for all of the samples. The absolute values of $R_H$ decreases with the increase of measurement temperature. The different temperature behaviors of Hall coefficient implies that the microstructures, which is controlled by the growth temperature, plays an important role on their charge transport behaviors of BNTO films. Figure 5(b) shows the temperature dependence of carrier concentration, which is calculated according to the formula: $R_H = \frac{1}{en}$. Similar to $R_H$, the carrier concentration also exhibits a slight temperature dependence. Unlike $R_H$, the carrier concentration increases with the increase of the measurement temperature, which implies that the thermal excitation may dominate the movement of the carriers. It is demonstrated that the carrier is localized in the defect energy levels at low temperature. At higher temperature localized carriers will be excited to the conduction band leading to the increase of the carrier density. The overall carrier concentration is in the $\sim 10^{21}$ cm$^{-3}$, which is similar to the reported values [18]. Figure 5(c) shows the temperature dependence of the carrier mobility as a function of growth temperature. The mobility does not show a significant variation on the entire temperature range. Only a slight increase of the carrier mobility at high temperatures can be observed. The most noticeable result shown in figure 3(c) is that the films grown at low temperatures of 500 °C and 550 °C exhibit a clear smaller mobility than that of the films grown at a high growth temperature of above 550 °C. It has been shown that the carrier scattering in the semiconductors is dominated by phonon scattering and impurity scattering [13]. The temperature stability of carrier mobility in the present BNTO films suggests that the phonon scattering may not be the important scattering factor. The clear mobility difference between high and low grown temperature samples implies that the impurity scattering, which is most probably induced by the microstructure defects, prevails the charge transport in the BNTO films.

Figure 5. Temperature dependence of (a) Hall coefficient; (b) carrier concentration; (c) Hall mobility as a function of growth temperature.
We analyzed the charge transport mechanisms further by fitting the resistance–temperature ($R$–$T$) using various charge transport models. The small polaron hopping and variable range hopping models do not reasonably fit the data for all five samples. The $R$–$T$ curves at some specified temperature range can be well fitted by using the thermal activation models, which is expressed as follows:

$$\rho = \rho_0 \exp\left(\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (1)

where $E_a$ is the activation energy, $k_B$ is Boltzmann’s constant.

From figure 5, it should be noticed that the carrier mobility as well as carrier concentration and Hall coefficient does not strictly increase/decrease with the change of BNTO film growth temperatures. For films grown at 500, 600 and 700 °C, the carrier concentration and carrier mobility increases exactly with the increase of the growth temperature, while the absolute value of the Hall coefficient decreases with the increase of the growth temperature. Considering the XRD and cross-sectional TEM results, these carrier transport characteristics exhibit a direct relationship with their film microstructures. For films grown at 550 and 650 °C, their carrier transport characteristics somewhat deviate from the changing tendency of the other three samples. The reason is still not very clear now. We assume that it should be closely related to the complex growth dynamics in BNTO films. Theoretical [30] and experimental [28] results have demonstrated that the growth temperature will affect the cation stoichiometry in BaTiO$_3$ films and cation vacancy concentration. Cation vacancy will contribute to BNTO films’ oxidation state due to different growth temperature may also be well fitted by using the thermal activation models, which is expressed as follows:

$$\rho = \rho_0 \exp\left(\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (1)

where $E_a$ is the activation energy, $k_B$ is Boltzmann’s constant. In the Arrhenius plot from figure 6(a) for films grown at low temperatures like 500 and 550 °C, the fit is good only at temperatures higher than 200 K, while for the films grown above 550 °C, the fitting range can extend down to about 100 K. The activation energy is shown in figure 6(b). The overall activation energy is around ~20 meV or smaller, suggesting that the electrons provided by oxygen vacancies or doped Nb$^{5+}$ are localized at a comparatively shallow energy level in the forbidden gap. The activation energy also shows a strong dependence on the growth temperature, which decreases as the growth temperature increases. Except for growth temperatures, other growth parameters are the same for all these samples, the only possible mechanisms to affect the difference of the activation energies is the film microstructures controlled by their growth temperatures.

To further confirm the above proposed influence of the microstructure, we carried out HRTEM investigations. Figures 7(a) and (b) show the planar-view TEM images of samples grown at 500 and 700 °C, respectively. The sample grown at 500 °C exhibits a rather disordered crystal structure, in which many defects and large grain boundaries can be seen clearly. Polycrystalline phase and even amorphous phase coexist, and grain boundaries can be clearly found. Increasing the growth temperature to 700 °C massively improves the crystallinity and film quality, as can be seen in figure 7(b). The density of grain boundaries and defects were greatly reduced.

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structure of the 700 °C grown BNTO sample. Since all the growth parameters of all five BNTO films are the same except the growth temperatures, the differences of resistance, carrier mobility, Hall coefficients implies that the microstructure defects controlled by the growth temperature is one of the critical mechanisms affecting the charge transport behavior. It provides new insights to clarify the big differences of charge transport behaviors between the BTO and STO systems. At least the imperfect epitaxial quality should be one of the reasons leading to the low carrier mobility of the BTO system, although the carrier scattering effect due to the dipoles in BTO cannot be excluded.

4. Conclusion

In summary, we made a systematical investigation on the charge transport behaviors of the Nb-doped BTO films. The BNTO films deposited at different temperatures clearly show different charge transport behaviors. The mechanisms affecting the charge transport are mainly related to the film microstructure, which is significantly affected by their growth temperatures. Generally, low temperature grown films have a low crystallinity and high defect density, while at high temperatures the films show good epitaxial quality with lower defect density. The films grown at ~650 °C show a higher carrier mobility and conductivity compared to films grown at other temperatures. The mediated charge transport of the microstructure defects is dominated by the thermal activation process during the main measurement temperature range and the conductivity and charge transport of BTO films can be significantly tuned by the microstructure defects. In addition to widely studied chemical defects, our work proved that physical microstructure defect is another important mechanism to affect the conductivity and charge transport in BaTiO₃ films. Our work will deepen the understanding on the complex charge transport mechanisms in BTO films and will be beneficial to their future resistive memory and photovoltaic applications.

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