# Effects of donor concentration on the electrical properties of Nb-doped BaTiO<sub>3</sub> thin films

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Thin films of  $\text{BaNb}_x \text{Ti}_{1-x} O_3$  ( $0 < x \le 0.5$ ) were epitaxially grown on MgO substrates by laser molecular beam epitaxy. The thin films undergo tetragonal to cubic and semiconductor to metal transitions with Nb concentrations as shown by x-ray diffraction and electrical resistivity measurements. Room temperature resistivities are found to decrease monotonically with increasing Nb concentration and range from  $10^1$  to  $10^{-4} \Omega$  cm. The fact that the temperature dependence of resistivity of the thin films can be fitted well using a small polaron model reveals the polaronic nature of the charge carriers in the thin films. This conclusion is further confirmed by the existence of localized states within the band gap of BaTiO<sub>3</sub> as revealed by synchrotron radiation-based ultraviolet photoelectron spectroscopy. © 2005 American Institute of Physics. [DOI: 10.1063/1.1858056]

### I. INTRODUCTION

Barium titanate has been one of the most intensively studied materials owing to its rich optical and electrical properties. Stoichiometric BaTiO<sub>3</sub> is an insulator with a resistivity of about  $10^{10} \Omega$  cm. Insulating BaTiO<sub>3</sub> can become *n*-type conductive either by substituting trivalent rare-earth ions such as  $Y^{3+}$  or  $La^{3+}$  for  $Ba^{2+}$  (A-site doping) (Refs. 1 and 2) or by substituting pentavalent ions such as Nb<sup>5+</sup> for  $Ti^{4+}$  (B-site doping).<sup>3</sup> In the case of A-site doping, it is reported that  $R_x Ba_{1-x} TiO_3$  (R = Y, Nd, and La) series all have a metallic region. The metallic region is from x=0.2 to 0.4 for the yttrium series, from 0.28 to 0.9 for neodymium series, and from 0.2 to 1.0 for lanthanum series.<sup>4</sup> In the case of B-site doping, particularly in the case of Nb doping, there are few reports on the doping-induced metal-semiconductor transition. Sintered bulk ceramics of Nb-doped BaTiO<sub>3</sub> show semiconducting behavior when doped with small amount of Nb, but when Nb concentration exceeds 0.4-0.5 mol %, the specimens revert to insulator.<sup>5</sup> Single crystals of  $BaNb_{x}Ti_{1-x}O_{3}$  with x ranging from 0.005 to 0.1 have also been investigated and were found to be semiconducting.<sup>6</sup> Nagano *et al.*<sup>7</sup> have fabricated BaTiO<sub>3</sub> thin films with 1.5–7.5 at. % Nb using metal-organic chemical-vapor deposition technique. They found that the thin films showed semiconductor behavior and the resistivity increased rapidly when Nb content exceeded 5.7%. Lemée et al.<sup>8</sup> have also studied the influence of Nb content on the resistivity of Nb-doped BaTiO<sub>3</sub> thin films and found similar results. The main reason for the increase of resistivity when donor concentration exceeds a certain value is the fact that the compensation mechanism changes from one that mainly involves electrons to one that primarily involves cation vacancies.<sup>9,10</sup> It is known that the cation vacancies will reduce when samples are prepared under low oxygen pressure.<sup>11</sup> Therefore, to further increase conductivity, thin films should be grown under low oxygen partial pressure. Laser molecular beam epitaxy (L-MBE) is a powerful tool for growing oxide thin films and it is easy to control oxygen partial pressures on the system. We have grown a series of  $BaNb_xTi_{1-x}O_3$  (x=0.01-0.5) thin films using L-MBE and found that heavily Nb doped  $BaTiO_3$ showed metallic behavior, which is quite different from the reported results mentioned above. In this paper, we report on the evolution of the conducting behavior of the thin films with different concentrations of Nb. First, the crystal structures of the thin films are described. Next the resisitivity measurement results are presented and discussed in the frame of small polaron. Finally the relationship between the valence bands and electrical properties of the thin films is discussed.

#### **II. EXPERIMENTS**

Thin films of BaTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> with nominal composition x=0.01, 0.05, 0.1, 0.2, and 0.5 were deposited on MgO (100) single crystal substrates by L-MBE system. Ceramic targets used here were prepared by standard solid-state reaction using BaCO<sub>3</sub>, TiO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub> powders. An excimer laser with a wavelength of 308 nm operated at 3 Hz was employed to ablate the targets. During the deposition the substrate temperature and oxygen pressure were maintained at 680 °C and  $3 \times 10^{-4}$  Pa, respectively. The thickness of each film was  $\approx 3000$  Å, as estimated from oscillation numbers of reflection high-energy electron diffraction (RHEED) intensity.

Phase purity and structural characteristics of the films were studied by x-ray diffraction (XRD)  $\theta/2\theta$  scan and asymmetric rocking curve method. Temperature dependence of electrical resistivity was measured between 77 and 600 K using van der Pauw method. The carrier density and mobility of the thin films were estimated from the Hall measurement under a magnetic field of 1 T. The stoichiometry of the films was examined by x-ray photoelectron spectroscopy and found to deviate from the nominal value within 10%.

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FIG. 1. XRD patterns of BaNb<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> thin films with x=0.01-0.2 (a) and x=0.5 (b). Lattice parameters **a** and **c** (c), **c**/**a** ratios (d) of BaNb<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> thin films as a function of Nb concentrations *x*.

Valence bands were measured at the 4B9B beam line at the Beijing Synchrotron Radiation Facility in the Beijing Electron Positron Collider National Laboratory. The measurements employed photons with the energy of 37.4 eV delivered by a spherical grating monochromator. The total resolution of the experimental system was about 0.2 eV. The surfaces of the samples were sputtered by  $Ar^+$ , followed by annealing at 500 °C in the UHV for 10 min.

## **III. RESULTS AND DISCUSSION**

Our previous work<sup>12</sup> on XRD  $\theta/2\theta$  scan patterns and asymmetric rocking curves were used in this work. As shown in Fig. 1(a), only (00*l*) peaks of BaTiO<sub>3</sub> together with (*l*00) peaks of substrate MgO were observed for BaNb<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> thin films with  $x \le 0.2$ , indicating that the thin films are of single phase and orientation. For thin films with x=0.5, two more peaks (101) and (111) of BaTiO<sub>3</sub> phase with weak intensity were observed [see Fig. 1(b)]. This reflects a minor loss of crystalline orientation perpendicular to the substrate's plane. From XRD  $\theta/2\theta$  measurements, the lattice parameter perpendicular to the substrates can be extracted. From asymmetric XRD {103} rocking curves, the ratios between out-ofplain and in-plain lattice parameters can be inferred. Combining these results, we can get the two lattice parameters *a*  and *c* of BaTiO<sub>3</sub>. Detail of the discussion is in Ref. 12. The calculated parameters *a* and *c*, and their ratios are shown in Figs. 1(c) and 1(d). Lattice parameters *a* and *c* increase with Nb content, but lattice parameter *a* increases more rapidly than *c*. This is consistent with the theoretical work conducted by Patino and Stashans.<sup>13</sup> According to their computational results, in tetragonal phase the optimization of crystal geometry of BaTiO<sub>3</sub> after doping with Nb is attained by the impurity-outward displacements of barium. The movements are mainly in the *ab* plane while the motion along the *c* axis is practically negligible. The ratio of lattice *c* and *a* decreases with Nb concentration and finally reaches 1 at x=0.5, as shown in Fig. 1(b) indicating the transition of BaTiO<sub>3</sub> crystal phase from tetragonal to cubic.

Figure 2(a) shows the temperature dependence of electrical resistivity of the thin films. When dopant concentration is less than x=0.2, the resistivity of the thin films decreases with temperature, showing semiconductor behavior; while the resistivity of the thin films with Nb concentration above 0.2 increases with temperature, showing metallic behavior. The thin films with x=0.2 exhibit transitional conduction behavior. The metallic region is similar to the results of  $R_xBa_{1-x}TiO_3$  series reported by Eylem *et al.*<sup>4</sup>

Table I gives the result of the Hall measurement at room



FIG. 2. (a) Temperature dependence of resistivity for a series of  $BaNb_xTi_{1-x}O_3$  thin films (*x* ranges from 0.01 to 0.5). (b) Temperature dependence of carrier density of the thin films with *x*=0.2 and 0.5. (c) Temperature dependence of the resistivity and reciprocal of mobility of the thin films with *x*=0.5.

temperature (RT). The Hall coefficients of all samples are negative, indicating that electrons contribute to conduction as major carriers. As Nb concentration increases, the resistivity drops monotonously, which is quite different from earlier published results.<sup>5,7,8</sup> The resistivities of thin films (with x > 0.2) are between  $10^{-2}$  and  $10^{-4} \Omega$  cm, a behavior of poorly conducting metallic oxides.<sup>14</sup> Carrier densities also increase with an increase in dopant concentration. On the other hand, mobilities are not remarkably different between the samples in spite of the differences in dopant concentration. Therefore, the result indicates that the differences in resistivity at RT are mainly derived from the difference in the carrier density.

Figure 2(b) shows the temperature dependence of carrier densities of the thin films with x=0.2 and 0.5. The carrier densities are almost constant in the temperature range from 70 to 300 K. Hence the temperature dependence of resistivity

TABLE I. Resistivity, carrier density, and Hall mobility of  $BaNb_{x}Ti_{1-x}O_{3}$  thin films at room temperature.

Samples	$\rho_{RT} \left( \Omega \text{ cm} \right)$	$n ({\rm cm}^{-3})$	$\mu_H ({ m cm^2/Vs})$
x=0.01	13.78	$1.2 \times 10^{17}$	3.5
x = 0.05	5.48	$3 \times 10^{17}$	3.3
x = 0.1	1.82	$6.3 \times 10^{17}$	5.3
x = 0.2	$1.08\times10^{-2}$	$6.4 \times 10^{19}$	9
x = 0.5	$2.70 \times 10^{-4}$	$4.6 \times 10^{21}$	5.2

does not depend deeply on that of carrier density. Figure 2(c) plots the temperature dependence of the resistivity and reciprocal of mobility of the thin films with x=0.5. Two sets of data show almost the same behavior with temperature, indicating the temperature dependence of resistivity deeply depends on that of mobility.

Though the nature of charge carriers in BaTiO<sub>3</sub> is a subject of discussion as to whether it is band electron or small polaron, our experimental results favor small polaron conduction scheme. In the common wisdom, polaronic transport in solids is synonymous with activated conductivity. Actually, small polaron conduction consists of three regimes as pointed out by Appel<sup>15</sup> and Klinger.<sup>16</sup> At low temperatures, the polarons behave as heavy particles in a band, showing "metalliclike" resistivity. At intermediate temperature, hopping motion prevails, leading to an activated behavior. Finally, when temperature is higher than the activation energy, the polaron states are thermally dissociated and the residual electrons are scattered by thermal phonons, leading to  $\rho$  $\sim T^{3/2}$ . Taking into account these three regimes, the temperature dependence of resistivity data can be consistently interpreted using small polaron model.

Conduction in semiconducting thin films (x < 0.2) should mainly take place by the hopping motion of polaronic carriers between neighboring Ti ions. The resistivity due to the small polaron hopping obeys the following law:<sup>17</sup>

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FIG. 3. (a) Arrhenius relations between  $\ln(\rho/T^{1.5})$  and 1/T of thin films with x=0.01, 0.05, and 0.1. (b) Temperature dependence of resistivity for x=0.2. The solid lines are fitted curves by Eq. (2) in the temperature interval 78 K < T < 200 K and by the form  $\rho=\rho_0 e^{\Delta/k_B T}$  in the activated regime. (c) Resistivity  $\rho(T)$  vs *T* for x=0.5. The solid lines are fitted curves by Eq. (2) at temperatures below 300 K,  $T^{1.5}$  in the interval 300–500 K, and  $T^5$  above 500 K.

$$\rho \propto T^{3/2} \exp(W_H / k_B T), \tag{1}$$

where  $W_H$  is the hopping energy; the disorder energy is omitted since it is negligibly small compared to  $W_H$  in crystalline materials. The above expression should yield a linear relation between  $\ln(\rho/T^{1.5})$  and the reciprocal of temperature T. This is confirmed in the semiconducting thin films as shown in Fig. 3(a). The hopping energies are 0.22, 0.18, 0.18 eV for thin films with x=0.01, 0.05, 0.1, respectively. The values agree well with the thermal activation energy obtained in a number of previous studies.<sup>18-21</sup> With the approximation  $W_p \cong 2W_H$  ( $W_p$  is the polaron binding energy), we can estimate the electron-phonon coupling constant  $\alpha$ . The theoretical expression for the relation between  $W_p$  and  $\alpha$  is  $W_p$ =0.1 $\alpha^2 \hbar \omega_{0L}$ , where  $\omega_{0L}$  is the frequency of the longitudinal optical mode for which we employed the experimental value,<sup>22</sup>  $\omega_{0L} = 7 \times 10^{13} \text{ s}^{-1}$ . From the expression, we obtain values of  $\alpha$  ranging from 8.8 to 9.7, which is quite close to 10 indicating there is strong coupling between electrons and phonons.

At temperatures below 245 K, thin films with x=0.2 show metallic behavior, but if the traditional  $\rho \propto T^n$  law was used to fit to the data, no meaningful fitting parameters could be obtained. So we try to fit the data using small-polaron metallic conduction theory.<sup>23</sup> The theory states that, for  $k_BT < 2t_p$ , the resistivity is given by

$$\rho(T) = \rho_0 + E\omega_s / \sinh^2(\hbar\omega_s / 2k_B T), \qquad (2)$$

where  $t_p$  is the hopping integral of polarons,  $\omega_s$  is the average frequency of the softest optical phonon mode, *E* is a constant, which is proportional to the effective mass of polarons, and  $\rho_0$  is the residual resistivity due to impurity scattering. The resistivity below 200 K can be well fitted by Eq. (2) with  $\hbar \omega_s/k_B = 194$  K, as shown in Fig. 3(b). This suggests that a soft optical phonon mode with  $\hbar \omega_s/k_B$  of about 194 K has a strong coupling with the carriers and thus contributes to scattering. Upon increasing the temperature, the mean free path of polarons is rapidly reduced until the picture of coherent motion breaks down. There is a maximum in the resistivity around 245 K, indicating the crossover from coherent to hopping motion. At high temperatures, the activated behavior prevails. The activation energy was found to be 0.034 eV by fitting to the data using the activation form  $\rho = \rho_0 e^{\Delta/k_B T}$ . The value of 0.034 eV is much smaller than those for the thin films with x < 0.2, indicating the decrease in electron-phonon coupling.

As for the thin films with x=0.5, below 300 K, the situation is similar to the case of thin films with x=0.2. That is, the data has to be fitted by Eq. (2) in order to get meaningful fitting parameters. The fit is excellent with  $\hbar \omega_s / k_B = 210$  K. However, in this case, the coupling between electrons and phonons is so weak that there is no crossover from coherent to hopping motion. Instead, as temperature increases, the polaron states are dissociated, and the contribution to the resistivity is mainly from thermal phonon scattering. At temperatures between 300 and 522 K, the data are fitted by  $\rho \sim T^{3/2}$  and above 522 K by  $\rho \sim T^5$ . The fact that the fit is good implies that the charge carriers are conduction band electrons above 300 K and the scattering is from acoustical and longitudinal optical phonons.

The occurrence of bound small polaron states is confirmed by valence band measurements. The photoemission spectra of  $BaNb_xTi_{1-x}O_3$  are displayed in Fig. 4, after background subtraction and renormalization. The most striking feature is the appearance of states around 2 eV below  $E_F$ within the band gap of BaTiO<sub>3</sub>. The intensity of the states increases as Nb concentration increases from x=0.1 to x =0.2, but decreases dramatically in the spectrum of thin films with x=0.5. Patino and Stashans<sup>13</sup> have calculated the influence of Nb doping on the electronic properties of BaTiO<sub>3</sub>. Their calculation shows the existence of metastable states within the band gap of BaTiO<sub>3</sub> and the extra electrons from Nb doping tend to transfer from the metastable states to the conduction band of BaTiO<sub>3</sub>. But the position of the metastable states is quite different in different phases of BaTiO<sub>3</sub>. In tetragonal phase, the state is at 2 eV below the conduction



FIG. 4. Valence-band spectra of  $BaNb_xTi_{1-x}O_3$  thin films (x=0.1, 0.2, and 0.5).

band, while in cubic phase it is at 0.3 eV below the conduction band. Therefore, it is reasonable to assume that electrons from Nb doping could remain at the metastable state in tetragonal phase by taking into account other factors such as disorder caused by impurity and oxygen vacancies, while they are more likely to transfer to conduction band when BaTiO<sub>3</sub> is in cubic phase. As mentioned above, thin films with x=0.1, 0.5, and 0.2 are in tetragonal, cubic, and transitional phases, respectively. Therefore, the difference in phase may account for the variation of the intensity within the band gap in thin films with different Nb concentrations. From the position of the state  $E_B$ , we can estimate the polaron binding energy  $E_P$ . According to discussions from Fujimori,<sup>24</sup>  $E_B$  and  $E_P$  are related by the following formula:

$$E_P = E_B - (\pi^2/2)(\hbar^2/m_b r_p^2), \qquad (3)$$

where  $m_b$  is the conduction band mass and  $r_p$  is polaron radius. Using typical values  $m_b \approx 3.5m_0$  (Ref. 25) (where  $m_0$ is the electron rest mass) and  $r_p=2.7$  Å,<sup>24</sup> we get  $E_p$ =0.5 eV. Hence the activation energy,  $E_a \approx E_p/2=0.25$  eV, is in reasonable agreement with the values obtained from the resistivity measurements.

### **IV. CONCLUSION**

In summary, we have shown that the resistivity of  $BaNb_xTi_{1-x}O_3$  epitaxial thin films deposited under low oxygen pressure monotonously decreases with Nb concentration. Room temperature resistivities of the thin films we produced

range from  $10^1$  to  $10^{-4} \Omega$  cm. The temperature dependence of the resistivities shows that thin films with *x* less than 0.2 exhibit semiconducting behavior while thin films with *x* larger than 0.2 exhibit metallic behavior. The resistivity data we obtained are in good agreement with small polaron model. The existence of localized states within band gap in the valence spectra confirms that the charge carriers in asdeposited thin films are mainly small polarons.

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