CHIN.PHYS.LETT. Vol. 18, No. 11 (2001) 1513

# Highly Conductive Nb-Doped $BaTiO_3$ Epitaxial Thin Films Grown by Laser Molecular Beam Epitaxy

YAN Lei(颜雷), LÜ Hui-Bin(吕惠宾), CHEN Zheng-Hao(陈正豪)*
DAI Shou-Yu(戴守愚), TAN Guo-Tai(谈国太), YANG Guo-Zhen(杨国桢)
*Laboratory of Optical Physics, Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080*

(Received 8 June 2001)

*The n-type conductive $BaNb_{0.3}Ti_{0.7}O_3$ thin films were grown on $SrTiO_3$(001) substrates by computer-controlled laser molecular beam epitaxy. The $BaNb_{0.3}Ti_{0.7}O_3$ films with (001) orientation are epitaxially grown on $SrTiO_3$ substrates, as confirmed by x-ray diffraction techniques. The root-mean-square surface roughness of the deposited thin films is measured to be 0.24 nm by atomic force microscopy. The resistivity, carrier concentration and mobility of the $BaNb_{0.3}Ti_{0.7}O_3$ thin film are $5.9\times10^{-4}\,\Omega\cdot cm$, $1.8\times10^{21}cm^{-3}$ and $10.7\,cm^2\cdot V^{-1}\cdot s^{-1}$ at room temperature, respectively, which are the best values in Nb-doped $BaTiO_3$ thin films reported so far to our knowledge.*

*PACS: 72. 80. Ga, 73. 61. Le, 74. 62. Dh, 81. 15. Fg*

A lot of studies have been focused on $BaTiO_3$ (BTO) thin films because of their remarkable ferroelectric, electric-optical, nonlinear optical and dielectric properties.[1−5] In particular, when Sr replaces Ba as a solid solution, the dielectric constant of BTO increases dramatically.[6] $BaTiO_3$/$SrTiO_3$ (BTO/STO) superlattices show a large dielectric constant and large optical nonlinearity.[6,7] Although the dielectric, nonlinear optic and ferroelectric properties of $BaTiO_3$ have been extensively studied, there have been only a few studies of the semiconductive and conductive BTO thin films. Gilbert *et al.*[8] and Ardakani *et al.*[9] independently reported semiconductive La-doped BTO thin films. Daisuke *et al.* reported on Nb-doped semiconductive BTO thin films with low resistivity by metal–organic chemical vapour deposition (MOCVD).[10] However, the reported La or Nb content is so low that the resistivity of the thin films is much too high to use as the oxide thin-film electrodes, which could be widely used in the heterostructure devices.

In this letter, the high conductive epitaxially Nb-doped BTO (Nb:BTO) thin films with good crystallinity and atomic smooth surface were grown by laser molecular beam epitaxy (LMBE). The resistivity, carrier concentration and mobility are the best results to our knowledge. The samples of Nb:BTO thin films investigated in this letter were grown by a computer-controlled LMBE system.[11] The base pressure of the epitaxy chamber was $1\times10^{-8}$ Pa. The output of a Lambda Physik LEXTRA 200 excimer laser (308 nm, 20 ns, 2 Hz) was used as the laser source with an energy density of about $1.5\,J\cdot cm^{-2}$. A piece of single-crystal STO and a piece of sintered Nb:BTO (with the doping content of 30 at.%) were used as the targets. Before deposition, the STO(001) substrates were annealed at 660°C for 20−30 min in an oxygen atmosphere ($1\times10^{-4}$ Pa) to clean the surface. Subsequently, 20 unit cells of a homoepitaxied STO layer were grown on the substrate to reduce the defect density and to smooth the surface. In order to decrease the infection of the oxygen vacancy, the oxygen pressure changed into $1\times10^{-4}$Pa. Monitored by reflection high-energy electron diffraction (RHEED) intensity oscillations, Nb:BTO thin films were deposited. The deposition rate was about 0.01 nm/pulse.

*In situ* RHEED patterns and intensity oscillations and *ex situ* x-ray diffraction (XRD) and atomic force microscopy (AFM) were used to investigate the crystallinity and surface morphology of $BaNb_{0.3}Ti_{0.7}O_3$ thin films. The Hall coefficient and the resistivity dependence on the temperature measurements were performed to measure the conductive properties.

During the deposition of both STO and Nb:BTO films, fine streak RHEED patterns and undamping RHEED intensity oscillations were observed. The typical RHEED pattern and its intensity oscillations during the epitaxial growth of $BaNb_{0.3}Ti_{0.7}O_3$ films are shown in Figs. 1 and 2, respectively. The results of the RHEED observation indicate that the Nb:BTO thin film with a smooth surface was two-dimensional epitaxial growth on the STO(001) substrate. The surface morphology of the $BaNb_{0.3}Ti_{0.7}O_3$ thin film was further examined by AFM. Figure 3 shows the AFM images of the $BaNb_{0.3}Ti_{0.7}O_3$ thin film. Figure 3(a) is a three-dimensional image and Fig. 3(b) is an image within a $2\times2\,\mu m^2$ area surface. The root-mean-square surface roughness within the area was 0.24 nm. The crystallinity and crystallographic orientation of the Nb:BTO thin films were investigated by XRD. Figure 4 shows the $\theta\sim2\theta$ XRD scan curve of the $BaNb_{0.3}Ti_{0.7}O_3$. Except for the STO(00l) and

*To whom correspondence should be addressed.
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Nb:BTO(00l) peaks, there are no diffraction peaks from impurity phases or randomly oriented grains, which means that the thin film is of single phase and orientation $BaNb_{0.3}Ti_{0.7}O_3$. As shown in the inset in Fig. 4, the XRD $\theta$ rocking curve displays a full width at half maximum (FWHM) of 0.665° for the (002) peak of the Nb:BTO thin film. The narrow peaks in Fig. 4 indicate that the thin film has a very high degree of crystallinity. The lattice constants of the $BaNb_{0.3}Ti_{0.7}O_3$ thin film and STO substrate calculated from XRD results are 0.41 and 0.39 nm, respectively. The lattice expansion of Nb:BTO may result from two factors. Firstly, the radius of $Nb^{5+}$ (0.064 nm) is greater than that of $Ti^{4+}$ (0.061 nm).[12] Thus the partial substitution of $Ti^{4+}$ by $Nb^{5+}$ makes the crystal lattice expand. Secondly, the change from the covalent Ti–O bond to the ionic Nb–O may be responsible for a part of the lattice expansion.

The property of the resistance versus temperature ($R - T$) of the $BaNb_{0.3}Ti_{0.7}O_3$ thin film is shown in Fig. 5. The result shows that the $BaNb_{0.3}Ti_{0.7}O_3$ thin film has a metallic conductive property.

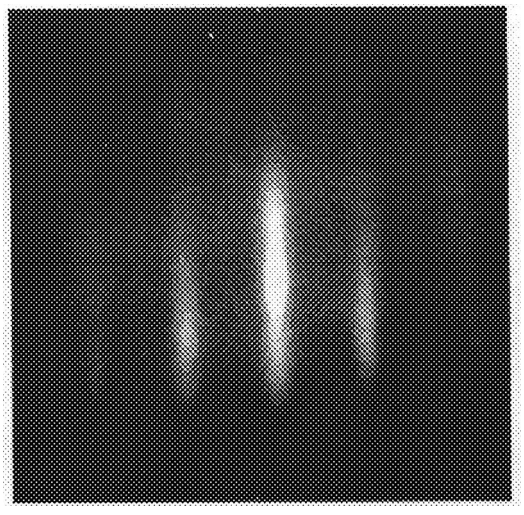


**Fig. 1.** RHEED pattern observed during the epitaxial growth of Nb:BTO.

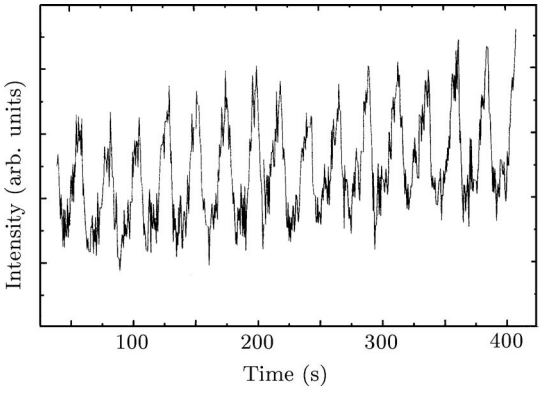



**Fig. 2.** RHEED intensity oscillations observed during the epitaxial growth of Nb:BTO thin film.

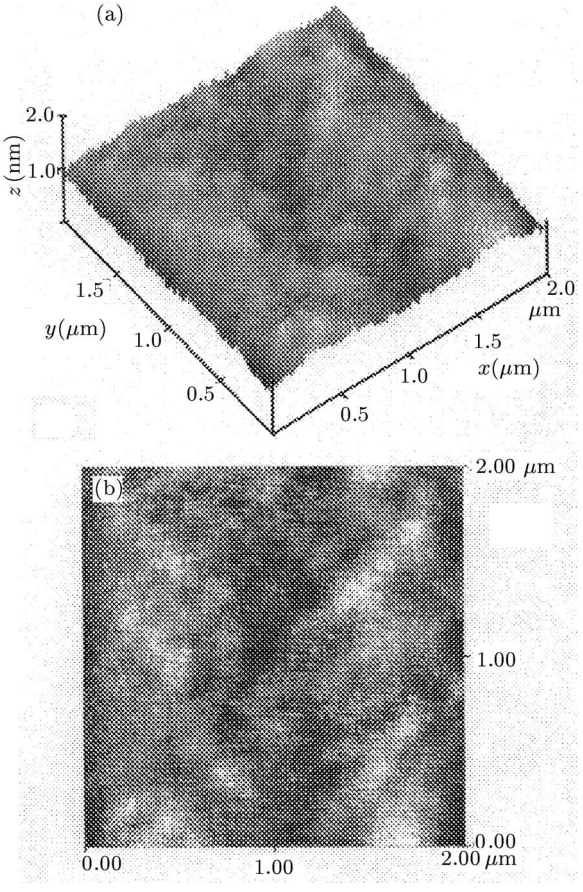



**Fig. 3.** (a) Three-dimensional AFM image of $BaNb_{0.3}Ti_{0.7}O_3$ thin film and (b) the AFM image ($2 \times 2\mu m^2$) of its surface.

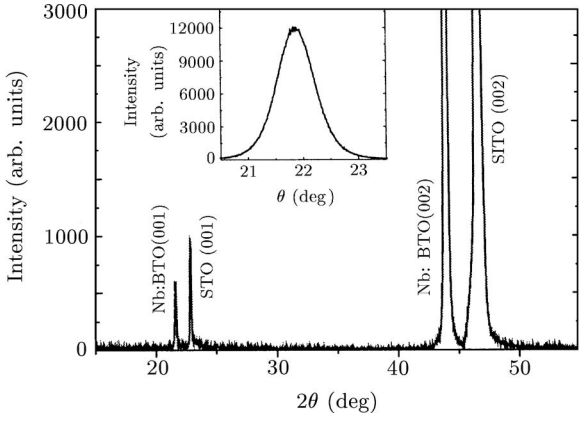



**Fig. 4.** XRD $\theta - 2\theta$ scan of the $BaNb_{0.3}Ti_{0.7}O_3$ thin film. The inset shows the $\omega$ rocking curve for the (002) peak of the film.

The resistivity $\rho$ of the $BaNb_{0.3}Ti_{0.7}O_3$ thin film at room temperature was measured to be $5.9 \times 10^{-4}\,\Omega\cdot$cm by the Van der Pauw method, while the concentration $n$ and mobility $k$ of the negatively charged carriers were measured to be $1.8 \times 10^{21}\,cm^{-3}$ and

$10.7\,cm^2 \cdot V^{-1} \cdot s^{-1}$, respectively. This value of resistivity was two orders of magnitude lower than that of Nagano *et al.*[10] for a Nb:BTO thin film by MOCVD processing. Their values of typical resistivity $\rho$, concentration $n$ and mobility $k$ for 5.7 atom % Nb content Nb:BTO thin films are $2.83 \times 10^{-4}\,\Omega \cdot cm$, $7 \times 10^{20}\,cm^{-3}$ and $0.1\,cm^2 \cdot V^{-1} \cdot s^{-1}$, respectively.

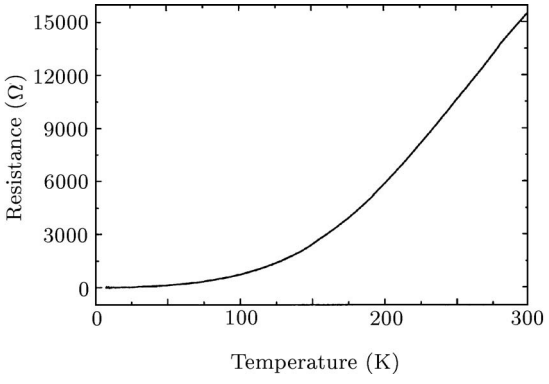



**Fig. 5.** Resistance versus temperature curves of $BaNb_{0.3}Ti_{0.7}O_3$ at the $O_2$ pressure of $1 \times 10^{-4}$ Pa.

The good conductivity of Nb:BTO thin films can be attributed to two factors. The first is the good crystallinity resulting from the careful control of the epitaxy process, which is confirmed by RHEED, XRD and AFM measurements. The second is the highly effective substitution of $Nb^{5+}$ for $Ti^{4+}$. It is well known that there is no mobile carrier in the undoped BTO film, which makes it insulated. However, some free electrons are introduced into the film when $Nb^{5+}$ is substituted for $Ti^{4+}$. Then, the doped BTO film becomes conductive. As discussed in Ref. [12], Nb tends to be well oxidized and to be stabilized as $Nb_2O_5$.[5,12]

In conclusion, highly conductive Nb-doped BTO thin films with good crystallinity and smooth surfaces were epitaxially grown on STO(001) substrates using the LMBE system. The high n-type conductive Nb:BTO thin films can be substituted for the expensive single-crystal $SrNb_xTi_{1-x}O_3$ as oxide electrodes. It can also be used to fabricate some fascinating devices with multi-layer structures, such as conductor/insulator/conductor junctions and heterostructures.[11,12]

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