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Synthesis, microstructure, and electronic band structure properties of nanocrystalline neodymium-doped bismuth titanate ferroelectric films fabricated by the sol–gel method

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ABSTRACT

$Bi_{4-x}Nd_xTi_3O_{12}$ (BNT) films with different Nd contents (from 0 to 1 with 0.25 intervals) are prepared by the sol–gel process. The Nd substitution effects on the preferred orientation, surface morphology, phonon modes, emission bands, andelectronic band structures of the BNT films are investigated by microscopy, Raman scattering, photoluminescence, and spectroscopic ellipsometry (SE) at room temperature. X-ray diffraction indicates that the films are polycrystalline with the pure perovskite phase. Ten Raman active modes and one silicon substrate mode can be observed. The A_{1g}[Bi] at about 59 cm^{-1} is unchanged whereas the B_{1g} and A_{1g}[Ti] phonon modes shift towards higher frequencies. Photoluminescence shows that the intensities of the two peaks increase with Nd concentration except the $Bi_3NdTi_3O_{12}$ film, due to the smallest grain size and oxygen vacancy defects. Good optical functions of the BNT films are achieved due to the SE suggesting potential applications in ferroelectric-based optoelectronic devices.

1. Introduction

Bismuth layered perovskite type ferroelectric oxides have received much attention as prospection materials to replace lead-based materials such as $Pb(Zr_{1-x},Ti)O_3$ in microelectronic nonvolatile memories, ferroelectric random access memories, and pyroelectric detectors [1–3]. $Bi_4Ti_3O_{12}$ (BTO) which is currently regarded as one of the most promising candidate materials has the general formula of $(Bi_2O_2)^{2+}[A_{m-1}B_mO_{3m+1}]^{2-}$ with $m=3$ consisting of three perovskite-like units $(Bi_2Ti_3O_{10})^{2-}$ sandwiched between the bismuth oxide $(Bi_2O_2)^{2+}$ layers [4]. It is well known that the ferroelectric properties arise from the perovskite block, $(Bi_2Ti_3O_{10})^{2-}$. However, BTO is known to suffer from high leakage current due to defects, leading to polarization fatigue and small remnant polarization due to defects such as Bi vacancies accompanied by oxygen vacancies [5].

Recent studies have revealed that Bi^{3+} ions in $Bi_4Ti_3O_{12}$ structure can be substituted by trivalent lanthanide ions to improve the ferroelectric properties by substituting Bi with La at the A-site [6]. The role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen vacancies acting as space charges. In 1999, Park et al. showed that a fatigue-free La-doped bismuth titanate film (BLT) on Pt electrodes exhibited significant advantages in electrical properties such as the larger remnant polarization ($2P_r \approx 24\ \mu C\ cm^{-2}$), smaller coercive field (E_c), lower dielectric loss, higher fatigue resistivity, and lower deposition temperature ($\leq 750\ ^\circ C$) in comparison with undoped Bi-layered ferroelectrics [2].

The value of remnant polarization in Bi-layered oxides determines the structural distortion in the perovskite block and is governed by the size difference between Bi and the dopant ion. It is also possible to dope bismuth titanate with other lanthanide elements such as Nd, Sm, and Pr. Although the effects of dopants on the ferroelectric properties and electrical conduction have been widely studied, the detailed microstructure and optical properties and their relationship with the electronic band structures have not been fully clarified. Pure and neodymium-substituted BTO bulk and films with the layered perovskite structure have attracted much attention for their optical applications such as nonvolatile memory devices, nonlinear electro-optical devices, and electro-optical waveguide modulator due to their excellent functional

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properties. In the past few years, their structural, ferroelectric, dielectric, and ultraviolet detection properties have been extensively investigated but the physical parameters of the ferroelectric materials pertaining to optoelectronic devices have not be established. A systematic investigation of the optical properties of the materials is very important to their potential use as an optical waveguide or/and electro-optical active materials.

There are many techniques to determine the optical characteristics of the films. For example, spectroscopic ellipsometry (SE) which is sensitive to ultrathin films and surfaces is a nondestructive and powerful technique to investigate the optical characteristics of materials [7,8]. It is useful to measure the thickness and dielectric functions of a multilayered system. Unlike other experimental methods, ellipsometry does not need the Kramers–KrÖnig transformation (KKT) to derive the optical constants because two independent angles can be monitored simultaneously [9–14]. In this work, the degree of orientation, surface morphology, phonon modes, and optical properties of ferroelectric BNT films with different Nd contents are systematically studied. The effects of the Nd concentration on the microstructure and electronic band structures of the BNT films are investigated and discussed in details.

2. Experimental details

The ferroelectric BNT ($Bi_{4-x}Nd_xTi_3O_{12}$) thin films were deposited directly on *p*-type Si(100) substrates by the sol–gel method. The crystal structure of BNT was formed by neodymium substituting for Bi in the perovskite units in which the Nd-substitution ranges from 0 to 1 with 0.25 intervals. The five synthesized samples, $Bi_4Ti_3O_{12}$, $Bi_{3.75}Nd_{0.25}Ti_3O_{12}$, $Bi_{3.50}Nd_{0.50}Ti_3O_{12}$, $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$, and $Bi_3NdTi_3O_{12}$, are labeled BNT0.00, BNT0.25, BNT0.50, BNT0.75, and BNT1.00, respectively. Analytically pure bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, 99%), neodymium nitrate ($Nd(NO_3)_3{\cdot}6H_2O$, 98%), and titanium butoxide ($Ti[O(CH_2)_3CH_3]_4$, 98%) were the starting materials and an excess of 8 mol% Bi precursor was added to compensate for Bi evaporation during annealing. The detailed processes are described in the following. Firstly, Bi $(NO_3)_3{\cdot}5H_2O$ and Nd $(NO_3)_3{\cdot}6H_2O$ with the required molar ratio were mixed in a solution of ethylene glycol monomethyl ether ($C_3H_8O_2$, 99.0%), heated glacial acetic acid (CH_3COOH, 99.5%) and acetylacetone where ethylene glycol monomethyl ether was the solvent, glacial acetic acid used as cosolvents, and acetylacetone as the stabilizer of the solution at the same time, keeping the volume ratio of 2:1 for ethylene glycol monomethyl ether and glacial acetic acid. Secondly, an appropriate amount of $Ti[O(CH_2)_3CH_3]_4$ was added to the solution and the concentration was adjusted to 0.05 M. Subsequently, the precursor solutions were stabilized for about 20 days before spin coating onto Si substrates to enhance hydrolysis and polymerization. Before deposition of the BNT films, the silicon wafers were cut into chips with dimensions of 1 cm × 1 cm and cleaned by the standard RCA process. Thirdly, the BNT films with different Nd contents were deposited by spin coating of the 0.05 M solution onto the Si substrate at 4000 rpm for 20 s. At last, the layered thin films were dried at 180 °C for 200 s, pyrolyzed at 380 °C for 240 s to remove residual organic compounds, and annealed at 750 °C for 1 h in ambient air. The deposition and annealing procedures were repeated six times to obtain the desired thickness.

The crystalline structure of the BNT films was determined by X-ray diffraction (XRD) using Cu Kα radiation (Rigaku, RINT2000, Japan). In the XRD measurement, a vertical goniometer and continuous scanning mode (θ–2θ) were selected a scanning rate of 10° min^{-1} and interval of 0.02°. The surface morphology was investigated by atomic force microscopy (AFM) (Digital Instruments Dimension 3100, Veeco). The roughness of the BNT films was characterized in the contact mode on areas of 5 × 5 μm^2. The surface and cross-sectional microstructures of the films were examined by scanning electron microscopy (SEM) (Jeol JSM-5610, Japan). Raman scattering was carried out on a Jobin-Yvon LabRAM HR 800 UV micro-Raman spectrometer with the 325 nm He–Cd laser. The photoluminescence (PL) spectra were acquired on the same instrument. Ellipsometry was carried out in the photon energy range of 200–1400 nm with a spectral resolution of 5 nm on the near-infrared ultraviolet (NIR-UV) SE (SC630UVN by Shanghai Sanco Instrument, Co., Ltd.). The incident angle was 70° corresponding to the experimental optimization near the Brewster angle of the Si(100) substrate. The work was performed at room temperature (RT) and no mathematical smoothing was performed for the experimental data.

3. Results and discussion

3.1. Microstructure

According to the XRD patterns (Fig. 1) of the BNT films with different Nd contents, all the films are polycrystalline with a strong (117) diffraction peak. The position (2θ) is at about 30.1°. Besides this salient feature, there are several weaker diffraction peaks of (111), (200), (008), (208), etc., and no impurity phases are observed, confirming that the films have a pure anatase structure. Polycrystalline grains with different orientations are formed in the films and Nd atoms are successfully incorporated into the BNT host lattice. The diffraction patterns are fitted by Gaussian analysis to extract the peak positions and full-width at half-maximum (FWHM) (see Table 1). It should be pointed out that the *a* and *b* axes cannot be distinguished because the crystals have a polydomain and $a \approx b$ [15]. Based on the (200) and (117) diffraction peaks, the lattice constant $a(b)$ of the Nd-doped films increases from 5.394 to 5.413 Å with increasing Nd concentration, whereas the lattice constant *c* decreases from 32.966 to 32.863 Å except for the BNT1.00 film which value is 32.879 Å (see Table 1). The deviations of the lattice constant suggest that there are different lattice distortions in the BNT films. The average gain size *r* can be calculated to be about 28 nm from the (117) diffraction peak according to the Scherrer equation $r = \kappa\lambda/\beta\cos\theta$; here, $\kappa \approx 1$ is the shape factor, $\lambda = 1.540$ Å is the average wavelength of Cu Kα radiation, β is the full-width at half-maximum, and θ is the diffraction angle. The gain size of about 22.9 nm of the BNT1.00 film is the smallest, corresponding to the largest value of the full-width at half-maximum (FWHM). It demonstrates that the crystal

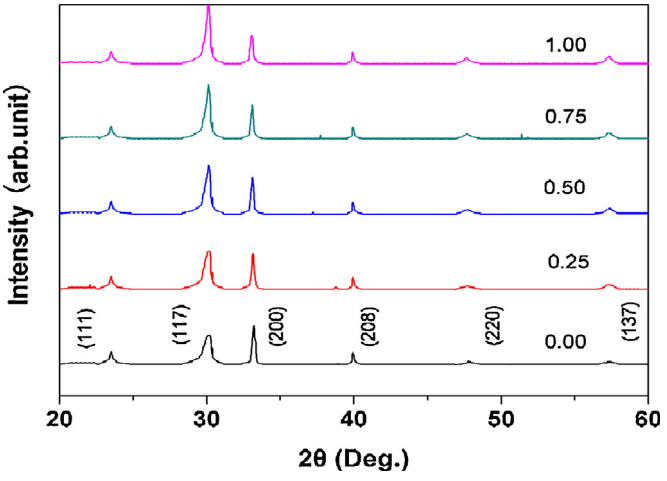

Fig. 1. The XRD patterns of BNT films with different Nd compositions.