Preparation by Sol-Gel Method and Characterizations of $(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ Thin Films

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$(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ (abbreviated as BLT) thin films were prepared by Sol-Gel processing method with the initial materials of bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and tetrabutyl titanate ($(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$). The X-ray diffraction (XRD), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) studies were performed for determining the change of the crystal lattice constant, the surface morphology, the chemical composition of the films, and the chemical bonding energy of the ions in the films. It was found that BLT thin films have high c -axis orientation with monoclinic structure, and the crystal lattice constants of the films are different from those reported in the literature. The a and b values of the lattice remain constant, but the c value reduces with an increasing lanthanum content x . The chemical composition of the films, and chemical bonding energy of bismuth and lanthanum ions in the near surface region are different from those in the inside region of the films. The films are bismuth enriched in the surface region, and the composition in the "bulk" region is agreement with the stoichiometry.

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1. Introduction

In the passed decade, ferroelectric thin films have attracted great attention for the applications in dynamic random-access memories (DRAMs), nonvolatile ferroelectric random-access memories (FeRAMs) and uncooled infrared arrays.¹⁻⁴⁾ For the applications such as nonvolatile memories, ferroelectrics with low coercive field and fatigue-free in the cycle of polarization reverse are desirable,⁵⁾ and from the sustainable development point of view, the thin films without toxicity (such as lead-free materials) are also very important. So, the Aurivillius family $\text{A}_{n-1}\text{Bi}_2\text{B}_n\text{O}_{3n+3}$ ferroelectric materials with perovskite-like structure, which are typical lead-free materials, have attracted great interest in the last years because of their excellent electrical and optical properties.⁶⁾ In the formula $\text{A}_{n-1}\text{Bi}_2\text{B}_n\text{O}_{3n+3}$, A and B are metal ions, and n is an integer. For bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, abbreviated as BTO), $\text{A}=\text{Bi}$, $\text{B}=\text{Ti}$, $n=3$. If $\text{A}=\text{Sr}$, $\text{B}=\text{Ta}$, $n=2$, the formula represents the well-known material $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (abbreviated as SBT or Y1).

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) has a layered perovskite structure consisting of $(\text{Bi}_2\text{O}_2)^{2-}$ layers interleaved with $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2+}$ perovskite-like layers.^{7,8)} The prototypic point group is tetragonal and converts to monoclinic in the ferroelectric phase.⁹⁻¹²⁾ BTO is a ferroelectric material and its spontaneous polarization vector is inclined at a small angle to the a - b plane which leads to two polarization moments: one along the a axis and $P_s = 5.0 \times 10^{-1} \text{ C/m}^2$, the other along the c axis and the $P_s = 4.0 \times 10^{-2} \text{ C/m}^2$, with coercive fields of $5.0 \times 10^6 \text{ V/m}$ and $3.5 \times 10^5 \text{ V/m}$ ^{6,8)} respectively, which are smaller than those of other ferroelectric crystals, such as lead zirconate-titanate (PZT).¹³⁾ The low-coercive field along the c axis makes BTO an attractive gate dielectric in a ferroelectric field-effect transistor (Fe-FET), and it is also expected to be a candidate for the ferroelectric layer of nonvolatile memories.¹⁴⁻¹⁶⁾

Early research results indicated that some rare-earth metal ions, such as La^{3+} , could substitute a few Bi^{3+} ions in the $(\text{Bi}_2\text{O}_2)^{2-}$ layers and other metal ions is hard to enter into $(\text{Bi}_2\text{O}_2)^{2-}$ layers.^{7,8,17)} La^{3+} entering into $(\text{Bi}_2\text{O}_2)^{2-}$ layers could improve the anti-fatigue property of BTO. The general formula of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ changes into $(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ (abbreviated as BLT) when the La^{3+} substitutes Bi^{3+} partially. However, the synthesis and fabrication of $(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ using Sol-Gel method has not been reported in detail in the literature previously. Our group reported the powders and ceramics of $(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ prepared using the Sol-Gel processes.¹⁸⁻²¹⁾ The results show that Sol-Gel processes can be used to prepare nanometer powders and the powders can further be used for preparing the new kinds of BLT ceramics, and the ceramics have better orientation and structure. In this paper, the experimental procedures prepared by Sol-Gel method and the characterizations of the BLT thin films are reported.

2. Sample Preparation and Handling Procedures

BLT thin films were prepared using Sol-Gel process with the initial materials of bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and tetrabutyl titanate ($(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$). Ethyleneglycol ($(\text{CH}_2\text{OH})_2$) was used as a solvent and acetic acid (CH_3COOH) was used as an activator.

Our processing route for preparing $(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ thin films using Sol-Gel method is shown in Fig. 1. In this process, the hydrolysis of tetrabutyl titanate can be completely controlled by adding quantitative acetic acid into tetrabutyl titanate. Two solutions were mixed using the titration process mode, which could make the molecules of the initial materials being completely contacted, and the speed of the hydrolysis and polymerization reaction could be easily controlled.

The precursor solutions were spin coated with the speed of 3000 rounds per second on Si (001) substrates. After every two coatings, the films were heated at a rate of $1^\circ\text{C}/\text{min}$ to the

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Fig. 1 Schematic graphics for preparing BLT films using Sol-Gel method.

temperature of 350°C for 30 min. After coated for four times the coatings were heated, and the BLT thin films were finally annealed in air at 650°C for 60 min.

3. Results and Discussion

3.1 XRD analyses for crystal lattice

The X-ray diffraction (XRD) patterns of the BLT thin films with $x = 0.2, 0.4, 0.6$ were shown in Figs. 2(a), (b), and (c) respectively. As shown in Fig. 2, all of the thin films are highly (00 l) oriented, but the (00 l) diffraction angles increase with an increasing x value. This change influences the crystal lattice constants of the BLT thin films. The formula (1) is the inter-planar spacing d_{hkl} of monoclinic system. It can convert to formula (2) in case of the $\beta = 90^\circ$.¹²⁾

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 + \frac{2hl \cdot \cos \beta}{ac}}} \quad (1)$$

Fig. 2 X-ray diffraction (XRD) patterns of the BLT thin films with $x = 0.2$ (a), 0.4 (b), and 0.6 (c).

Table 1 The crystal lattice constants of the BLT thin films with $x = 0.2, 0.4, 0.6$.

Materials	Lattice Constant			Reference
	a (nm)	b (nm)	c (nm)	
BTO	0.54500	0.54059	3.28320	12)
BLT2	0.54660	0.54174	3.28059	Present Work
BLT4	0.54414	0.54023	3.27164	Present Work
BLT6	0.54510	0.54135	3.25820	Present Work

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}} \quad (2)$$

We calculated the crystal lattice constants of the BLT thin films from the XRD results. Table 1 gives the calculated results.

If La^{3+} is enched into $(\text{Bi}_2\text{O}_2)^{2-}$ layers and substitutes Bi^{3+} in $(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ thin films, it could be considered that the c value of the lattice would reduce because the semi-diameter of La^{3+} is smaller than that of Bi^{3+} . It can be seen from Table 1 that the a and b values of the lattice remain almost constant, whereas the c value reduces gradually with an increasing lanthanum content x . Therefore, we can conclude that the substitution of Bi^{3+} with La^{3+} in $(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ thin films takes place, and La^{3+} enters into $(\text{Bi}_2\text{O}_2)^{2-}$ layers of BLT thin films in our present work.

3.2 AFM analyses for surface roughness

AFM analyses were used to characterize the surface roughness and morphology of the films. Figure 3 shows the $1 \mu\text{m} \times 1 \mu\text{m}$ AFM stereo-images of the BLT thin film with $x = 0.4$ after annealing at 650°C for 1 hour. It can be seen from Fig. 3 that the films are compact and continuous, and the root-mean-square (rms) surface roughness and the average surface roughness of the film measured are 8.843 nm and 7.052 nm respectively.

3.3 XPS analyses for composition and chemical bonding

To identify the film's composition and chemical bonding energy, X-ray photoelectron spectroscopy (XPS) analyses were carried out by the KRATOS 800 spectrometer using $\text{MgK}\alpha$ (1253.6 eV) radiation. Figures 4(a) and (b) give the wide-scan XPS spectra of the surfaces of BLT thin films with $x = 0.6$ before bombardment and after Ar^+ (1.5 keV) bombardment for 40 minutes respectively in the binding energy range of 1000-0 eV. All of the binding energies at various peaks in Fig. 4 were calibrated using the binding energy of C_{1s} (284.8 eV). As shown in Fig. 4, the BLT thin films contain Bi, La, Ti, O and C elements in the surface and the inside ("bulk") regions. No impurity element was detected in the spectrum up to 1000 eV except for carbon which may be caused by pumping oil.

In order to further verify the compositional depth profile revealed from XPS, an Ar^+ (1.5 keV) beam was used to bombard the surface of the film for 5, 10, 20, 30, and 40 minutes respectively. As shown in Fig. 4(b), the elements of the film were not changed after the bombardment, but the

Fig. 3 AFM images of the BLT film after annealed at 600°C for 1 hour (a) Stereo-image; and (b) Plane image.

Fig. 4 Wide-scan XPS spectra of the surface of the BLT thin films with $x = 0.6$ before bombardment (a) and after Ar^+ (1.5 keV) bombardment for 40 minutes (b) respectively in the binding energy range of 1000–0 eV using $\text{MgK}\alpha$ (1253.6 eV) radiation.

relative intensity of the peaks was variational. It mainly embodied that the peak of $\text{Ti}_{2p_{3/2}}$ at about 460 eV and the peak of $\text{La}_{3d_{5/2}}$ at about 840 eV are enhanced, on the other

hand, not only the relatively intensity of $\text{Bi}_{4f_{7/2}}$ peak is weakened but also the Bi_{4f} peak converts to double peaks after bombardment.

The detailed analyses of XPS measurements before and after Ar^+ bombardments will be published elsewhere,²²⁾ from which we know that (1) the Ti exists in the form of Ti^{4+} near the surface and in the “bulk” of the films, and the binding energy of $\text{Ti}_{2p_{3/2}}$ is 458.65 eV; (2) the binding energy of $\text{Bi}_{4f_{7/2}}$ and $\text{Bi}_{4f_{5/2}}$ before bombardment is 159.2 eV and 164.6 eV respectively, which is smaller than that reported in Ref. 23). It may be due to the La^{3+} existing in $(\text{Bi}_2\text{O}_2)^{3+}$ layer. The spin-orbit splitting of Bi_{4f} in BLT thin film is 5.4 eV which is equal to those in Ref. 24); (3) the binding energy of $\text{La}_{3d_{5/2}}$ before and after bombardments is in the region of 834.7–835.0 eV, which is close to that (834.9 eV) reported in the literature;²⁵⁾ (4) the chemical composition of the films in the surface region is different from that in the “bulk” region of the films. The films are bismuth enriched in the surface region, and the composition in the “bulk” region is agreement with the stoichiometry.

4. Conclusion

$(\text{Bi}_{4-x}\text{La}_x)\text{Ti}_3\text{O}_{12}$ (abbreviated as BLT) thin films were prepared by Sol-Gel processing methods. XRD, AFM, and XPS studies were performed for determining the change of the crystal lattice constants, the surface morphology, the chemical composition, and the chemical bonding energy of the ions in the films. It was found that BLT thin films have high c -axis orientation with monoclinic structure, and the crystal lattice constants of the films are different from those reported in the literature. The a and b values of the lattice remain almost constant but the c value reduces with an increasing lanthanum content x . The chemical composition of the films in the near surface region are different from those in the inside (“bulk”) region of the films. The films are bismuth enriched in the surface region, and the composition in the “bulk” region is agreement with the stoichiometry.

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