Phase stability and electrical properties of $(Bi_{0.925}La_{0.075})_2Ti_2O_7$ thin films by chemical solution deposition

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The phase of $Bi_4Ti_3O_{12}$ has been studied by many people. Recently, these materials of thin films have attracted attention and have made great progresses, especially in the field of semiconductor appliances. Consequently, there has been tremendous interest in using high dielectric constant materials for storage capacitors in dynamic random access memory (DRAM) applications and as gate insulators to increase the transconductance of metal-oxide semiconductor field effect transistors (MOSFET). Therefore, it is very important to research $Bi_2Ti_2O_7$ thin films for their applications.

According to the phase diagram of the Bi_2O_3—TiO_2 system [1], there are several phases, including $Bi_2Ti_4O_{11}$, $Bi_2Ti_2O_7$, $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$, *et al.*, in the Bi—T—O system. Among them, $Bi_4Ti_3O_{12}$ is a typical ferroelectric material with useful properties for optical memory, piezoelectric and electric-optic devices. $Bi_2Ti_2O_7$ is considered to be a promising alternative gate insulating material in advanced metal-oxide-semiconductor (MOS) transistors, due to its relatively high permittivity and significantly low leakage current [2]. The $Bi_2Ti_2O_7$ crystal has a cubic structure with a lattice parameter of $a = 20.68$ Å [3]. Lately, a lot of attention has been paid to the $Bi_2Ti_2O_7$ thin films [4–6]. It has been used successfully as a buffer layer to improve the electrical properties of ferroelectrics PZT [7] and $Bi_4Ti_3O_{12}$ [8–10] thin films.

Though it has the above advantages, $Bi_2Ti_2O_7$ thin films can be easily transformed into other phases, and its phase becomes unstable at high temperature [9–12]. Wang *et al.* [9] reported that $Bi_2Ti_2O_7$ is an unstable phase during $Bi_4Ti_3O_{12}$ formation. The X-ray diffraction patterns shown that the film is a mixed-phase structure, which includes $Bi_2Ti_2O_7$ and $Bi_4Ti_3O_{12}$ phases, as annealed at 600 °C for 15 min. A similar result was found in $Bi_4Ti_3O_{12}$ films with a $Bi_2Ti_2O_7$ buffer layer where the $Bi_2Ti_2O_7$ phase disappears from the XRD pattern, as annealed at above 600 °C. Jiang *et al.* [12] reported that the $Bi_2Ti_2O_7$ phase structure can be stabilized by ionic modification in ceramics. Many references [13–16] have reported the preparation and properties of lanthanum-substituted $Bi_4Ti_3O_{12}$ thin films. However, we have not see a report about La-modified $Bi_2Ti_2O_7$ thin films. In this paper, we report the preparation, phase stability and electrical properties of $(Bi_{0.925}La_{0.075})_2Ti_2O_7$ thin films on P-Si (100) substrates by chemical solution deposition (CSD) technique.

The precursor solutions were prepared using the following steps. Bismuth nitrate and appropriate lanthanum nitrate were initially dissolved in acetic acid glacial. After the mixtures were completely dissolved and cooled to the room temperature, tetrabutyl titanate was added to achieve (Bi + La):Ti ratio of 1:1 with constant stirring. To keep the solution stable longer, an amount of acetylacetone was added to the solution. Then, the solution was diluted with ethylene glycol monomethyl to adjust its viscosity and surface tension, and filtered through a 0.2 μm syringe filter to remove dust and other suspended particles. Finally we obtained a $(Bi_{0.925}La_{0.075})_2Ti_2O_7$ precursor solution of 0.1 M. The wet films were coated onto the P-Si (100) substrates by spin coating and then heated at 350 °C for 10 min at a heating rate of 15 °C/min to remove solvents and other organic substances. The deposition and heat-treatment procedure were repeated to prepare thicker films. The multilayered films were finally annealed at various temperatures to make them crystallize.

The structural properties of the BLT films were studied by means of X-ray diffraction (XRD) using a Rigaku D-MAX/RA X-ray diffractometer. Gold dots of 0.3 mm diameter on the BLT film as top electrodes and Au film was sputtered on the back of the silicon substrate as a bottom electrode to form a metal-film-semiconductor-metal (MFSM) configuration. The insulating properties of the films were measured by using a PA-meter/DC Voltage Source (HP4140B) and capacitance-voltage (C-V) characteristics by an impedance analyzer (HP4192).

Fig. 1 shows the XRD patterns of $(Bi_{0.925}La_{0.075})_2$-Ti_2O_7 thin films annealed at different temperature for 30 min. From the patterns, we can see that only one

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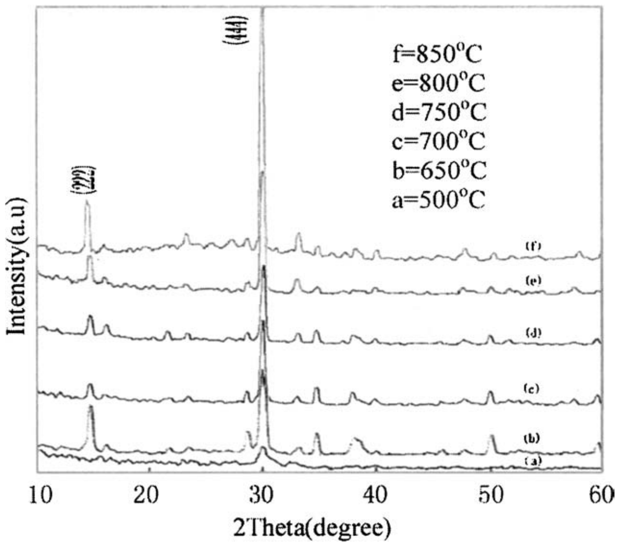

Figure 1 XRD patterns of $(Bi_{0.925}La_{0.075})_2Ti_2O_7$ thin films at different annealed temperatures.

weak peak emerges at 500 °C, indicating the quite poor crystallization of the film. As the annealing temperature increases to 650 °C, the film has began to crystallize. The peaks are indexed according to the standard power diffraction data of $Bi_2Ti_2O_7$. But the (444) peak is still weak at 650 °C. To examine the effect of growth temperature on phase stability, a series of BLT ($x = 0.075$) films was prepared over the temperature range of 700 to 850 °C. A single phase $(Bi_{0.925}La_{0.075})_2Ti_2O_7$ film was observed over this temperature range.

The d values and intensities of the peaks agree very well with those given in JCPDS data cards for $Bi_2Ti_2O_7$. The (444) and (222) diffraction peaks of the films in the XRD patterns are sharp and intense, suggesting that the films had strong (111) orientation and had good crystallization. The cubic structure lattice constant of $a \approx 20.66$ Å was calculated using the (444) peak in the XRD pattern, and this value is consistent with the value given in the reference [5]. The ratio of (111) orientation of the film can be calculated by the following formula [17]:

$$P_0 = \frac{\sum_i I^i(111)}{\sum_i I^i(hkl)} \quad (1)$$

The value of P_0 is 90%, at the annealed temperature of 850 °C. The full width at half-maximum (FWHM) of (444) diffraction peaks of all films was very small. The FWHM value of (c) (d) (e) (f) curves in Fig. 1 is 0.80 °, 0.75 °, 0.75 °, and 0.75 ° respectively. The above results indicate that the substitution of La is effective for the chemical stability of the $Bi_2Ti_2O_7$ phase at a higher annealing temperature. A possible explanation of the chemical stability has been sought from the viewpoint of the charge compensating. The oxygen ions near the Bi ions are unstable due to the volatility of the Bi ions. Considering that the lanthanum ionic radius of 1.06 Å in the Shannon's scale is compatible with that of Bi^{3+} (1.02 Å), we deposited $(Bi_{1-x}La_x)_2Ti_2O_7$ films, where some of the Bi ions in the $Bi_2Ti_2O_7$ films are substituted with La ions in order to eliminate the oxygen vacancies and obtain charge neutrality. Hence we deduced that the chemical stability of $Bi_2Ti_2O_7$ could be improved, if some Bi ions were substituted with the La ions.

The electrical properties of BLT ($x = 0.075$) films annealed at 750 °C for 30 min were studied. The I–V characteristics were measured on a 421 nm-thick BLT ($x = 0.075$) thin film in the MFSM capacitor. The film exhibits a resistivity in the range of 10^{13}–10^{12} Ωcm when a dc bias of 0–5 V applied to the capacitor. Fig. 2 shows the change of leakage current density of a 421 nm-thick BLT film with electric field. When the applied electric field was no more than 20 kV/cm, the index of leakage current density was −9. It became −8 as the applied electric field was between 20–70 kV/cm. The leakage current density was 9.3×10^{-7} A/cm^2 at an applied electric field of 130 kV/cm. The results indicate that the BLT film can be applied in a large range of electric field. The data mentioned above indicate that

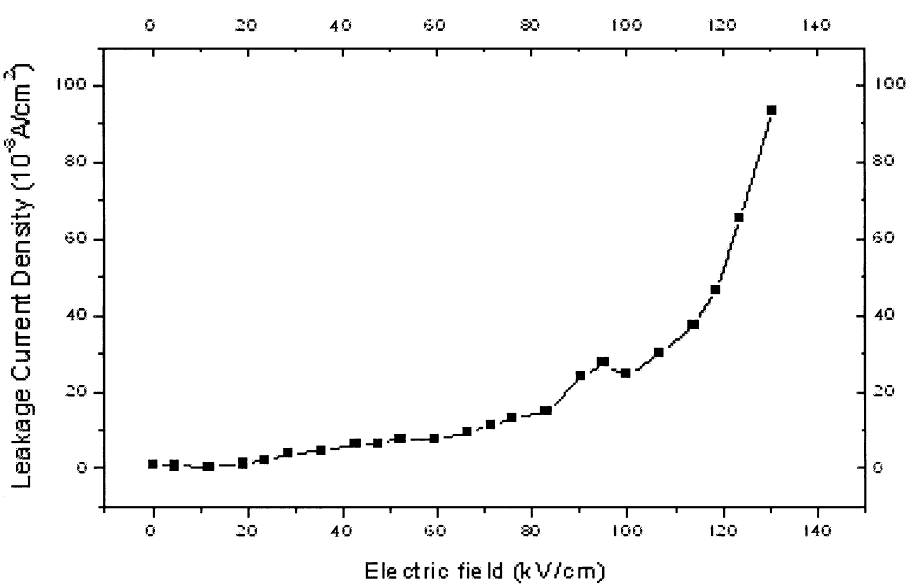

Figure 2 Change of leakage current density of $(Bi_{0.925}La_{0.075})_2Ti_2O_7$ film as a function of electric field.

the BLT films directly deposited on the Si (100) substrates by using CSD technique have good insulating properties.

The C-V measurements were carried out on the BLT ($x = 0.075$) film at 100 kHz. There are accumulation, depletion, and inversion regions in the C-V characteristic curve. In the accumulation region, holes in the semiconductor will accumulate at the silicon surface and the capacitance will be due solely to the insulating BLT film layer. The dielectric constant of BLT film was obtained by measuring the accumulation capacitance (C_{max}) of the Au/BLT/Si/Au capacitor. The dielectric constant is obtained by the following formula:

$$\varepsilon = \frac{d \cdot C_{max}}{\varepsilon_0 \cdot s} \quad (2)$$

where d is the thickness of the BLT film, ε_0 and ε are the permittivity of free space and the dielectric constant of the film, respectively, and s is the area of the electrode. The calculated value of dielectric constant is 79 at the applied electric field of 70 kV/cm, which is higher than that of SiO_2 (3.9). For this reason, the BLT thin films are under consideration as potential replacements for SiO_2 as the gate dielectric materials for MOS technology.

La-modified $Bi_2Ti_2O_7$ thin films with (111) orientation were successfully prepared on (100) Si substrates by chemical solution deposition technique. The influence of La^{3+} substituted for Bi^{3+} on phase stability and electric properties have been studied. It is found that the crystalline temperature of the BLT film was higher than the $Bi_2Ti_2O_7$ film without La modification. Good crystallization and (111) orientation of the BLT ($x = 0.075$) film were obtained at high annealed temperature (850 °C). The ratio of (111) orientation is 90%. The stability of $Bi_2Ti_2O_7$ phase was increased due to eliminating the oxygen vacancies and obtaining charge neutrality by La-modification. The film has good insulating property and has a relatively high dielectric constant. These results show that the BLT films are suitable for new insulating gate materials in dynamic random access memory. There is plenty of room for improvement by varying the amounts of the La substitute.

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