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Thermal and piezoelectric properties of $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ thin film prepared by metal organic decomposition

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Abstract: $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNT) powder and thin film were prepared by metal organic decomposition (MOD) method. The heat flow curve of BNT powder was measured with a modulated temperature differential scanning calorimeter, and thermal physical parameters such as thermal conductivity coefficient and thermal diffusion coefficient were obtained from the heat flow curve. The phase identification, ferroelectric, and piezoelectric properties of BNT thin film annealed at 700 °C were investigated with X-ray diffractometer, ferroelectric analyzer, and scanning probe microscope. The results show that the thin films consisting of a single phase of bismuth-layered perovskite are polycrystalline, without a preferred orientation. Remnant polarization $2P_r$ is 63.2 μC/cm^2 under 530 kV/cm applied field, and the effective piezoelectric coefficient d_{33} is 30 pm/V.

Key words: bismuth-layered perovskite; metal organic decomposition (MOD); thermal parameter; remnant polarization; effective piezoelectric coefficient

1 Introduction

Micro-electromechanical systems (MEMS) employing ferroelectric thin films have been extensively studied in the past decade, and lead-free ferroelectric thin film materials for MEMS applications are desired for the sake of environmental protection and biocompatibility. $Bi_{4-x}Nd_xTi_3O_{12}$ thin films have great polarization, excellent imprinting and fatigue-free characteristics, and ferroelectric properties of $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNT) thin films can even be comparable with those of conventional lead based ferroelectric thin films [1]. Previous studies in recent years revealed that Bi^{3+} ions in $Bi_4Ti_3O_{12}$ structure could be substituted by trivalent rare earth ions, such as La^{3+}, Nd^{3+}, Eu^{3+}, and Sm^{3+}, for the improvement of ferroelectric properties[2−4], therefore, bismuth titanate-based thin films have been considered to be candidates for the application as lead free ferroelectrics. Thin film materials operating in many structures, especially aerospace components, are inevitably subjected to severe thermal loading which may be produced by aerodynamic heating, laser irradiation, or localized intense fire[5−6]. In order to predict the life and study the failure mechanism for ferroelectric thin film system operating at heating environment, the thermal physical parameters and mechanical physical parameters should be first known. MANSOUR et al[7] provided a method to obtain the thermal conductivity coefficient by measuring the heat capacity of materials with the modulated temperature differential scanning calorimeter (MTDSC), and they presented an equation to calculate the thermal conductivity coefficient. Because the heat capacities of two samples with different thickness are needed for applying the equation, SIMON and GREGORY provided a simplified representation of

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MARCUS and BLAINE's equation to avoid the obvious drawback[8]. However, for BNT ferroelectrics the temperature dependent parameters cannot easily be found, and the physical parameters are all temperature independent in the present investigation. Generally, Bi-layered perovskite thin films are only focused on the ferroelectric and dielectric properties[1−4], and never involved in the piezoelectric performance. Piezoelectric materials, especially in form of thin film, offer a number of advantages in MEMS, such as low hysteresis, high available energy density, high sensitivity with wide dynamic range, and low power requirement, therefore, it is worth considering the impetus for integrating piezoelectric thin films into MEMS devices.

In this work, BNT powder and thin film were prepared by metal organic decomposition (MOD) method. In order to obtain thermal parameters, a modulate temperature differential scanning calorimeter (MTDSC) was used to measure the heat flow curve of BNT powder, and then thermal conductivity coefficient and thermal diffusion coefficient were obtained from the curve in the temperature range of 30−80 °C. Phase identification and crystalline orientation of BNT thin films were investigated with X-ray diffractometer (XRD). The ferroelectric and piezoelectric properties were characterized by using a ferroelectric analyzer and a scanning probe microscopy (SPM) system. It is worth mentioning that this research is useful to simulate the failure behavior of lead-free ferroelectric thin film subjected to severe thermal loading, and guide the design on MEMS based on the lead-free ferroelectric thin film.

2 Methodology

2.1 Thermal parameters

As a reserved patent of TA Instrument Corporation, MTDSC is superimposed a sinusoidal oscillation temperature controlling program to the conventional linear heating program, therefore, it can provide an oscillating heating procedure in testing.

For the heat capacity, during the program heating procedure, there is such an equation as follows[8]:

$$\frac{\mathrm{d}H}{\mathrm{d}t}=mc_p\frac{\mathrm{d}T}{\mathrm{d}t} \tag{1}$$

where m is the mass of the sample, c_p is the constant pressure heat capacity of the material, dH/dt is the rate of heat flow, and dT/dt is the rate of temperature rising. As for thermal conductivity coefficient, theoretically, it can be determined via determination on the heat capacity of the material[8]:

$$k=\rho c_p\omega L^2\left(\frac{c_{\mathrm{app}}}{c_p}\right)^2 \tag{2}$$

where k is the thermal conductivity coefficient, ρ is the density of the material, ω is the testing frequency and L is the thickness of the sample. c_{app}/c_p is the ratio of heat capacity for thin film to thick film, which can be approximately adopted as 0.9 in general according to Simon's research. In this case, we can obtain the thermal conductivity coefficient via measuring the heat capacity of a single sample. A modified formula as follows is adopted for accurate determination[8]:

$$k_{\mathrm{corr}}=\frac{1}{2}[k-2D+(k^2-4Dk)^{\frac{1}{2}}] \tag{3}$$

where D is the coefficient, taken as 0.014 W/(K·m). Thermal diffusion coefficient curve can also be obtained via simple formula $\alpha=k/(\rho c_p)$.

2.2 Piezoelectric coefficient

The measurement of effective piezoelectric coefficient d_{33} was achieved by keeping the SPM tip fixed above the interesting point and applying a DC voltage from −9 V to 9 V while recording the piezoresponse signal. A stiff cantilever was used to get a large indentation force ensuring that the measurement was in the so-called strong-indentation regime and the piezoresponse was dominated by d_{33} of the material[9]. A well-shaped piezoelectric displacement vs applied field (D—E) "butterfly" loop was obtained and the piezoelectric hysteresis loop is calculated from D—E loop according to the follow equation[10]:

$$d_{33}=\frac{D-D_{\mathrm{i}}}{d(E-E_{\mathrm{i}})} \tag{4}$$

where d is the initial thickness of the film before deformation; D and E are the measured values of piezoelectric deformation and electric field for each point in the D—E loop; D_{i} and E_{i} are the piezoelectric deformation and electric field of the intersection of D—E loop, respectively.

3 Experimental

BNT precursor solution was prepared by dissolving bismuth nitrate, neodymium acetate and tetrabutyl titanium in proportion in glacial acetic acid at room temperature, with an appropriate amount of acetylacetone to stabilize the solution. A 10% excess amount of bismuth nitrate was used to compensate for Bi loss during annealing. The final concentration of precursor solution was adjusted as 0.05 mol/L by adding the required amount of glacial acetic acid into the mixed solution. The BNT powder was obtained by baking the precursor solution in an insulation at 120 °C for 12 h.

Appropriate annealing mode, temperature and heat preservation are essential factors for required microstructure properties[11−12]. In order to ascertain the appropriate temperature for heat treatment, the differential thermal analysis (DTA) and thermo-gravimetric analysis (TG) were performed on BNT powder by thermal analysis system (TD-40, Shimadzu, Japan) with a warming up rate of 10 °C/min. In order to measure the heat flow curve between the BNT sample and the reference sample under different temperature and time, the BNT powder was pressed into a circular shaped flake with thickness of about 1 mm, diameter of 15 mm, mass of 1 490 mg, and density of 8.436 kg/m^3 and then the flake sample was put into MTDSC (DSC2910, TA Instrument Corporation, USA). During the measurement, both of the BNT flake sample and the reference sample were kept in an environment where the temperature, pressure and atmosphere were accurately controlled. The temperature variation range was set as 30−80 °C, and the testing frequency was 1.5 Hz.

The BNT precursor solution was spun on Pt/Ti/SiO_2/Si (001) substrate at a rate of 4 000 r/min for 20 s, then the wet film was dried at 210 °C for 300 s and pyrolyzed at 400 °C for 300 s in rapid thermal annealing (RTA) furnace (RTP-500, Qi Xing, China). The coating/ drying cycle procedure was repeated nine times to achieve the desired film thickness (about 324−342 nm [12]) in the previous experiment. The pre-baked films were finally annealed at 700 °C for 400 s to promote crystallization in RTA furnace with a ramping rate of 200 °C/s.

Phase identification and crystalline orientation of thin film were investigated by XRD (D/Max 2500 PC, Rigaku, Japan), and the Cu K_α radiation with wavelength of 1.540 6 Å was adopted at 40 kV and 350 mA; the BNT film was scanned at 4 (°)/min in the range from 5° to 65° and the degree increment was 0.02°. The circular Pt top electrodes with radius of 0.1 mm were deposited on the thin film using a shadow mask by DC magnetron sputtering. P—E hysteresis loop was measured using a ferroelectric analyzer (Precision Workstation, Radiant Technologies, USA) at applied voltage of 18 V. The surface morphology and the piezoelectric properties of BNT thin film were characterized by using a SPM system (SPI4000 & SPA300 HV, Seiko, Japan) with a conductive Rh-coated Si cantilever (SI-DF3, Seiko, with a spring constant of 1.9 N/m and a free resonance frequency of 28 kHz, Japan).

4 Results and discussion

For BNT powder, DTA and TG curves are described in Fig.1(a) while the heat flow curve is shown in Fig. 1(b). In Fig.1(a), the endothermic peak at 43.4 °C indicates the volatilizing of organic solvents. Also, there is a another blunter endothermic peak around 411.1 °C, corresponding to the decomposition of the remaining organic solvents. When the temperature exceeds 411.1 °C, the BNT powder maintains a sustained heat releasing, indicating the decomposition and combustion of organic components of the solution. For TG curve, the mass of the sample dramatically decreases while the temperature rises from 20 to 500 °C, indicating a strong volume contraction of the BNT powder. But there is no evident change about the mass of the sample when the temperature exceeds 600 °C, indicating no more decomposition or volatilization of organic substances occurs, and just only solid phase reactions proceeding in the sample. According to the results of DTA and TG of the BNT powder, the final temperature of the heat treatment is set as 700 °C. After the heat treatment, the organic ingredients can be primarily removed, and the measured thermal parameters are available. In Fig.1(b), the heat flow dH/dt drastically increases with the increasing of temperature from room temperature to about 35 °C, and there is not apparent change above this temperature.

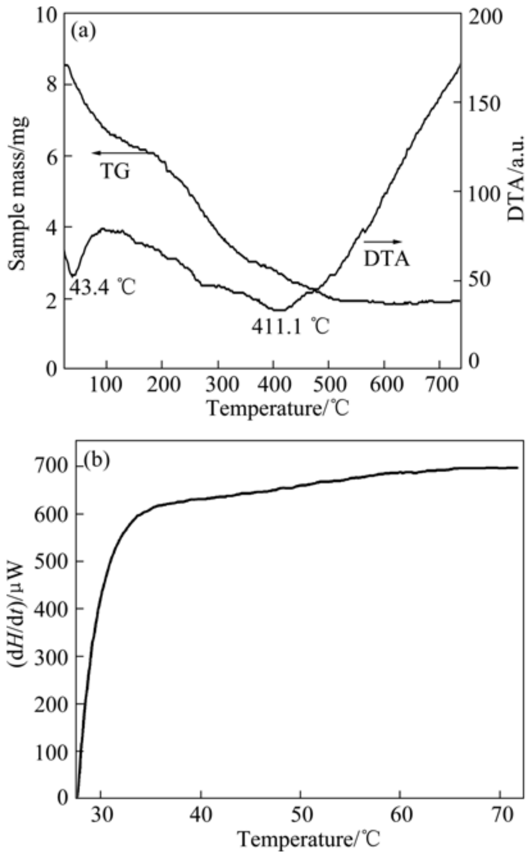

Fig.1 DTA and TG curves (a) and DSC curve (b) of BNT powder

Thermal conductivity coefficient k_{corr} and thermal diffusion coefficient curves can be calculated from the heat flow curves, as shown in Fig.2. The tendency of thermal conductivity coefficient curve is similar with the heat flow curve in Fig.1(b), indicating that the thermal conductivity coefficient is linear with the heat flow. In the thermal diffusion coefficient curve, we can conclude that the value of thermal diffusion coefficient is about 1.2×10^{-6} m^2/s.

For BNT thin film annealed at 700 °C, the XRD pattern and polarization hysteresis loop are given in Fig.3. From Fig.3(a), the BNT thin film consisting of a single

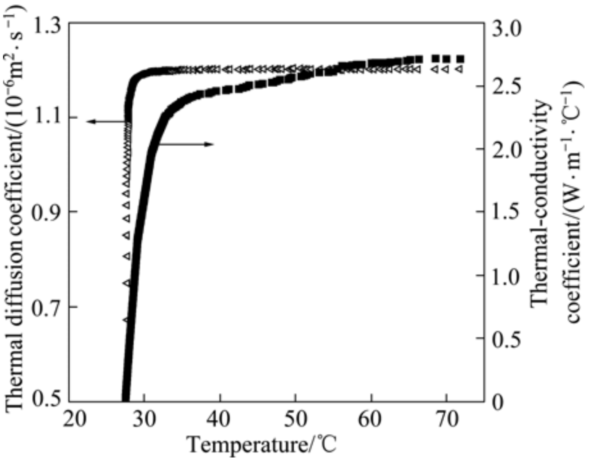

Fig.2 Thermal conductivity and thermal diffusion curves of BNT powder

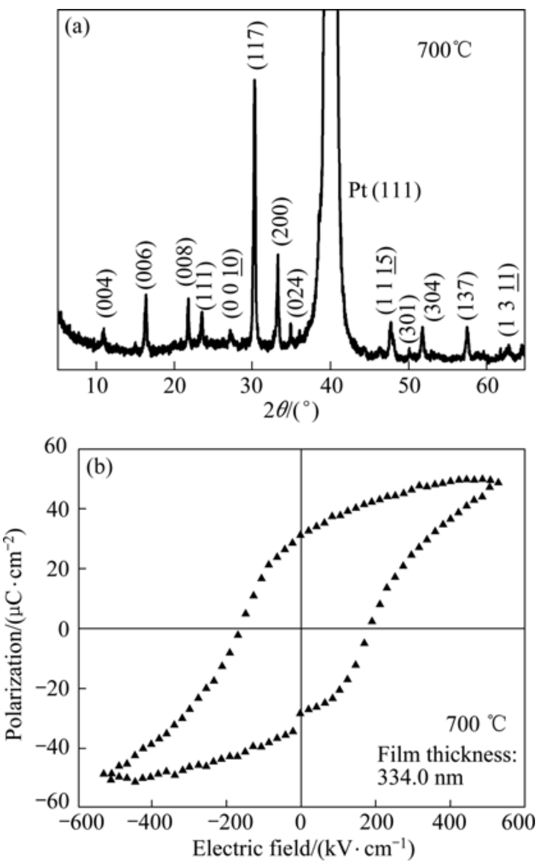

Fig.3 XRD pattern (a) and polarization hysteresis loop (b) of BNT thin film

phase of bismuth-layered perovskite are polycrystalline, without a preferred orientation. This indicates that the film already has a good crystallinity. In Fig.3(b), it can be seen that the remnant polarization $2P_r$ is 63.2 μC/cm^2 under 530 kV/cm electric field. This value is comparable to the value of 64 μC/cm^2 reported on $Bi_{3.5}Nd_{0.5}Ti_3O_{12}$ thin film fabricated by chemical solution deposition[13]. The hysteretic feature makes Pt/BNT/*n*-Si ferroelectric field effect transistors a candidate for nonvolatile memory devices. $Bi_{4-x}Nd_xTi_3O_{12}$ thin film with one kind of component (x=0.85) was only investigated in this work, and BNT thin films with a series of different components will be focused to increase the reliability in future.

Using SPM, the topography for the as-prepared BNT thin film and the local effective piezoresponse versus applied field of the grain marked by an arrow were measured by the atomic force microscopy mode and the conductive Rh-coated Si cantilever, and the results are shown in Fig.4. In Fig.4(a), the grain size is approximately 40−70 nm and the measured root mean

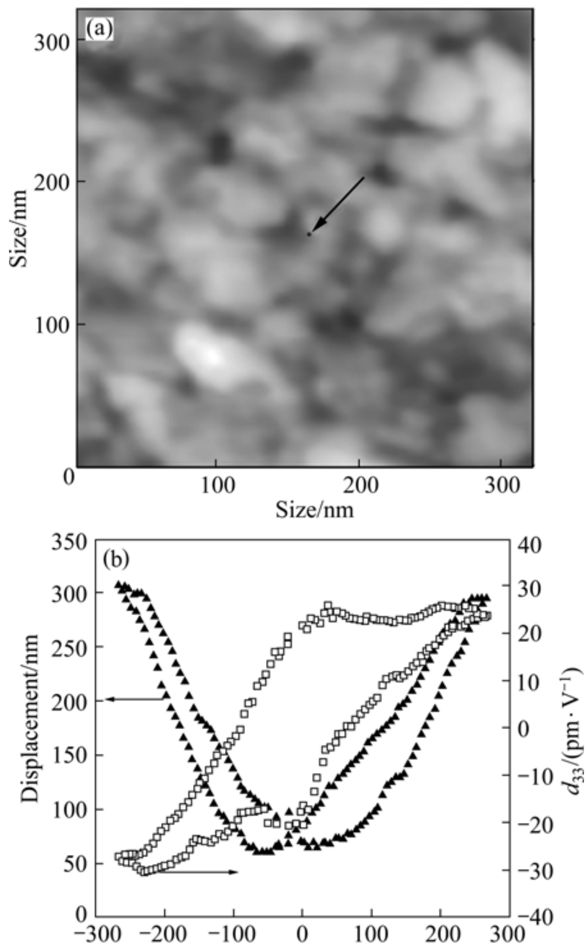

Fig.4 Topography of BNT thin film (a) and local piezoelectric response versus applied field (b) of grain marked by arrow in topography

square value of the surface roughness is 1.599 nm. In Fig.4(b), a typical well-shaped *D*—*E* "butterfly" loop is observed with a displacement maximum of 306 nm appearing at −9 V. So, the electrically induced strain under a bipolar driving field of 267 kV/cm is 0.092%. From the piezoelectric hysteresis loop, the maximum absolute value of effective piezoelectric coefficient d_{33} is about 30 pm/V. This value is comparable to the value of 38 pm/V reported on Nd-doped $Bi_4Ti_3O_{12}$ film fabricated by chemical solution deposition[14] and higher than 16.9 pm/V from Nd-doped $Bi_4Ti_3O_{12}$ film reported by ADACHI et al[15]. Although the obtained value of 30 pm/V is smaller than the reported values of PZT thin films range from 40–110 pm/V[16−18], it is much higher than 17 pm/V from $SrBi_2Ta_2O_9$ film[19], 10–12 pm/V from ZnO films[16], and 3.4–3.9 pm/V from AlN films[20], in comparison with other lead free materials. The improved piezoelectric properties could make Nd-doped $Bi_4Ti_3O_{12}$ thin film a promising candidate for sensors, actuators, and transducers based on lead-free thin film.

5 Conclusions

1) The temperature dependences of thermal conductivity coefficient and thermal diffusion coefficient were obtained in the temperature range of 30−80 °C for BNT powder, and the thermal diffusion coefficient is about 1.2×10^{-6} m^2/s.

2) BNT thin film fabricated by MOD exhibits a polycrystalline film consisting of a single phase of bismuth-layered perovskite without a preferred orientation. The BNT film shows remnant polarization $2P_r$ of 63.2 μC/cm^2 and the effective piezoelectric coefficient d_{33} corresponding to 30 pm/V. Based on these properties, BNT is considered a promising alternate film material to PZT in piezoelectric MEMS applications.

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