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Microstructure and ferroelectric properties of dysprosium-doped bismuth titanate thin films

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Abstract

$Bi_4Ti_3O_{12}$ (BIT) ferroelectric thin films with Dy^{3+} substitution ($Bi_{4-x}Dy_xTi_3O_{12}$, $x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively) were grown on Pt(111)/Ti/SiO_2/Si(100) substrates using sol–gel method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) revealed that after annealing at 710 °C for 10 min, all $Bi_{4-x}Dy_xTi_3O_{12}$ films became polycrystallites. Among all the deposited thin films, the $Bi_{3.4}Dy_{0.6}Ti_3O_{12}$ specimen exhibits improved ferroelectric properties with the largest average remanent polarization (2Pr) of 53.06 μC/cm^2 under applied field of 400 kV/cm and fatigue free characteristics (16% loss of 2Pr after 1.5×10^{10} switching cycles), indicating that it is suitable for non-volatile ferroelectric random access memories applications.
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Keywords: Sol–gel; Substitution; Ferroelectric thin films

1. Introduction

Since La^{3+}-substituted BIT (BLT) films showing excellent ferroelectric properties were prepared by pulsed laser deposition [1], the effect of substituting Bi^{3+} ions with other lanthanide metals (e.g., Nd, Sm) was reported [2–4]. Recently, Dy^{3+}-substituted BIT thin films, $Bi_{4-x}Dy_xTi_3O_{12}$ thin films have emerged as good candidates for NvFeRAM applications due to its good fatigue endurance and large polarization. Kim et al. [5] reported that the remnant polarization (2Pr) of $Bi_{3.4}Dy_{0.6}Ti_3O_{12}$ thin film deposited on Pt/TiO_2/SiO_2/Si(100) substrates by sol–gel method is about 39 μC/cm^2. Obviously, there is a considerable improvement in 2Pr of rare earth ions substituted bismuth titanate thin films prepared by sol–gel method. Generally, the effect of annealing temperature on the microstructure and ferroelectric properties was focused for $Bi_{4-x}Dy_xTi_3O_{12}$ thin films. Few studies are on the effect of Dy contents on microstructure and ferroelectric properties of $Bi_{4-x}Dy_xTi_3O_{12}$ thin films. It is imperative to know whether the change of Dy content in $Bi_{4-x}Dy_xTi_3O_{12}$ thin films can improve ferroelectric properties, such as 2Pr and fatigue endurance. For this purpose, the ferroelectric properties of $Bi_{4-x}Dy_xTi_3O_{12}$ thin films crystallized by sol–gel with various Dy contents ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively) on Pt(111)/Ti/SiO_2/Si(100) substrates annealed at 710 °C in air ambient will be presented in this work.

2. Experimental details

$Bi_{4-x}Dy_xTi_3O_{12}$ ferroelectric thin films with various Dy contents ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively) were deposited on Pt(111)/Ti/SiO_2/Si(100) substrates by sol–gel, using a repeated coating/drying cycle. Each differently doped film was prepared with five identical samples. Bismuth nitrate [$Bi(NO_3)_3\cdot5H_2O$], dysprosium nitrate [$Dy(NO_3)_3\cdot5H_2O$], and titanium butoxide [$Ti(OC_4H_9)_4$] were used as starting materials for Bi, Dy and Ti, respectively. Bismuth nitrate (10 mol% excess) and dysprosium nitrate were dissolved at 40 °C in glacial acetic acid [CH_3COOH]. 10% excess of bismuth nitrate was added to compensate for possible bismuth loss during the high temperature process. Separately, in a beaker, titanium

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butoxide was dissolved in glacial acetic acid, and acetylacetone [$CH_3COCH_2COCH_3$] was used as chelating agent. The titanium solution was added to the bismuth–dysprosium solution with continuous stirring, and the final mixture was stirred for an additional 30 min. The concentration of $Bi_{4-x}Dy_xTi_3O_{12}$ in the final solution was adjusted to approximately 0.1 M. The preparation of the films consisted in spin coating the Pt(111)/Ti/SiO_2/Si(100) substrates with the stock solution at 3000 rpm for 30 s. The samples were then fully dried in a rapid thermal processor (RTP-500) at 180 °C for 3 min followed by another 3 min at 400 °C to remove residual organic compounds. The coating and preheating process was repeated several times to obtain the desired film thickness. Finally, the coated $Bi_{4-x}Dy_xTi_3O_{12}$ films were annealed for 10 min in air by a rapid thermal annealing process at 710 °C. Phase identification, crystalline orientation, and degree of crystallinity of the prepared films were studied by a Rigaku D/max-rA X-ray diffractometer with Cu Kα radiation using normal θ–2θ scanning method. SEM (JSM-5600LV) was used to determine the prepared film's thickness and surface morphology. The thickness of the $Bi_{4-x}Dy_xTi_3O_{12}$ films is about 400 nm, through a cross-sectional view of SEM. The derived thin films are smooth, crack-free, uniform, dense, and adhered well on the substrates. For electrical measurements, the top Au electrodes with diameters of 0.2 mm were sputtered on the $Bi_{4-x}Dy_xTi_3O_{12}$ thin films by DC sputtering. The ferroelectric measurements were performed using a Radiant technology precision workstation ferroelectric tester.

3. Results and discussion

As the pyrolyzed $Bi_{4-x}Dy_xTi_3O_{12}$ thin films (~400 °C) were found to be amorphous in nature. The post-deposition annealing of the films was carried out in atmosphere to promote crystallinity. The crystallinity of deposited $Bi_{4-x}Dy_xTi_3O_{12}$ thin films on Pt(111)/Ti/SiO_2/Si(100) was examined using XRD analysis. Fig. 1 shows the XRD patterns of $Bi_{4-x}Dy_xTi_3O_{12}$ with different Dy contents (x=0, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively) annealed at 710 °C. All the diffraction peaks were identified and indexed using the standard XRD data of BIT powder. The films were deposited with the same procedure and of the same thickness. As shown in Fig. 1, all films deposited under the same conditions were crystallized with layered perovskite phase, predominantly with (117) and (00*l*) grains, and without observable pyrochlore phase.

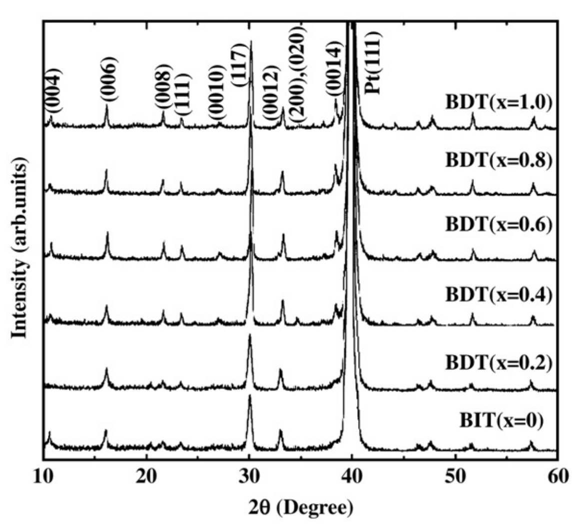

Fig. 1. XRD patterns of $Bi_{4-x}Dy_xTi_3O_{12}$ with various Dy contents (x=0, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively) crystallized in air at 710 °C.

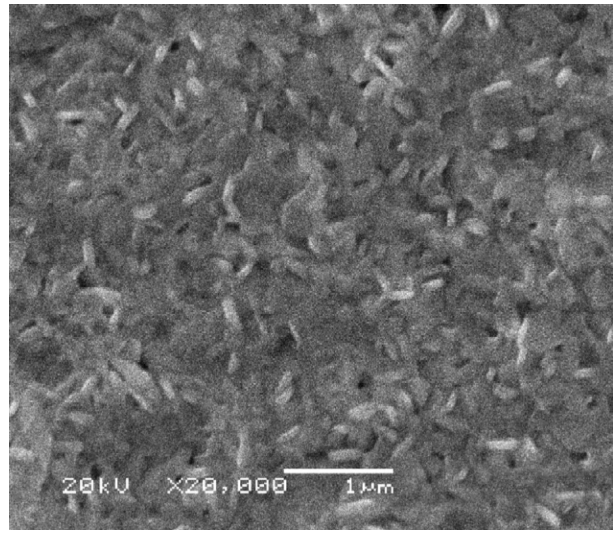

Fig. 2. The surface morphology of the $Bi_{3.4}Dy_{0.6}Ti_3O_{12}$ film crystallized in air at 710 °C.

The surface morphology of the $Bi_{3.4}Dy_{0.6}Ti_3O_{12}$ film crystallized in air at 710 °C is shown in Fig. 2. It can be found from Fig. 2 that the film has rod-like grains and plate-like grains and shows smooth and dense microstructure. It has been reported that, for La^{3+}-doped BIT films, the rod-like grains are presented in (117) preferentially oriented films, while the plate-like grains may correspond to the (00*l*)-preferred orientation [6–8]. The mixed rod-like and plate-like grains found in the present deposited $Bi_{4-x}Dy_xTi_3O_{12}$ films are consistent with the XRD results shown in Fig. 1 where mixed (00*l*) and (117) orientations have been observed.

Table 1 lists the remanent polarization (2Pr) of each sample. Under 400 kV/cm electric field, the average 2Pr values of the differently doped thin films with an x value of 0, 0.2, 0.4, 0.6, 0.8, and 1.0, respectively, are 13.28 μC/cm^2, 36.53 μC/cm^2, 38.10 μC/cm^2, 53.06 μC/cm^2, 39.09 μC/cm^2 and 40.22 μC/cm^2, respectively. From Table 1 we can find that the 2Pr values of all $Bi_{4-x}Dy_xTi_3O_{12}$ thin films are remarkably larger than the 2Pr value of the BIT thin film prepared under the same condition. This fact indicated the remarkable enhancement of remanent polarization in BIT thin films by Dy^{3+} substitution. It is notable that when x is 0.6, the average remanent

Table 1
The 2Pr values of each sample for differently doped films (μC/cm^2)

2Pr	x					
	0	0.2	0.4	0.6	0.8	1.0
Sample 1	13.44	36.91	37.82	53.26	39.30	40.80
Sample 2	13.24	36.93	38.23	53.12	38.76	39.92
Sample 3	13.52	36.25	38.32	52.89	38.97	40.56
Sample 4	12.96	36.31	37.96	52.78	39.58	39.87
Sample 5	13.25	36.26	38.15	53.25	38.82	39.96
Average	13.28± 0.24	36.53± 0.40	38.10± 0.17	53.06± 0.76	39.09± 0.76	40.22± 0.84

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