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Magnetic, ferroelectric and leakage current properties of gadolinium doped bismuth ferrite thin films by sol–gel method

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ABSTRACT

$Bi_{0.9}Gd_{0.1}FeO_3$ (BGFO) thin films were fabricated on Pt(111)/Ti/SiO_2/Si(100) substrates by using the sol–gel technology. The effects of annealing temperature (400–700 °C) on microstructure and multiferroic properties of thin films were investigated. The X-ray diffraction analysis showed that the BGFO thin films had an orthorhombic structure. The thin films showed ferroelectric and ferromagnetic properties with remanent polarization ($2P_r$) of 10 μC/cm^2, remnant magnetization ($2M_r$) of 2.4 emu/g and saturation magnetization (M_s) of 5.3 emu/g. A small leakage current density (J) was 4.64×10^{-8} A/cm^2 under applied field 100 kV/cm. It was found that more than one conduction mechanism is involved in the electric field range used in these experiments. The leakage current mechanisms were controlled by Poole–Frenkel emission in the low electric field region and by Schottky emission from the Pt electrode in the high field region.

1. Introduction

Bismuth ferrite $BiFeO_3$ (BFO) is a well-known multiferroic material, has been given considerable attention recently, owing to its high phase transition temperature, good multiferroic properties, and G-type antiferromagnetic behavior to make it appealing for applications in ferroelectric nonvolatile memories and high temperature electronic devices [1–7]. Recently, it was reported that lanthanide-substituted $BiFeO_3$, $(Bi_{1-x}Ln_x)FeO_3$ (Ln=La, Nd and Eu) could improve its ferroelectric and electrical properties [8–15]. The reason is that the enhanced ferroelectric properties of these films can be attributed to the suppressed formation of impure phases and oxygen vacancies, which is caused by the substitution of stable rare-earth ions for the volatile Bi ions. In addition, the studies of the leakage currents in multiferroic thin films are also important for most electrical applications. The leakage current in thin films often become nonohmic under applied voltage. The reason for this is complex and depends on the nature of the contact, the film composition and its internal structure.

$BiFeO_3$ thin film has been prepared by different deposition techniques such as r.f. sputtering, pulsed laser deposition [16,17], liquid phase deposition [18,19], molecular beam epitaxy and sol–gel process. To prepare bismuth titanate thin film with precise stoichiometric ratio and homogenous composition distribution, chemical solution methods such as sol–gel technology can be used to give flexible and precise control over the stoichiometry. In addition, the sol–gel method has drawn a considerable amount of attention in the scientific and technological fields because of their considerable advantages of generally low temperature processing conditions, easy composition control and homogeneity, easy fabrication of thin films with large area and low cost.

In the present work, the characteristics of leakage current in the $Bi_{0.9}Gd_{0.1}FeO_3$ (BGFO) thin films were investigated. Various conduction models, including the space-charge-limited emission, Poole–Frenkel emission, and Schottky emission, have been proposed and discussed. The crystalline structure, surface morphology, ferroelectric and magnetic properties of the BGFO thin films were also studied.

2. Experimental

The precursor solutions of $Bi_{0.9}Gd_{0.1}FeO_3$ with a general chemical formula were prepared by the sol–gel method. Bismuth acetate, $Bi(OOCCH_3)_3$ (Alfa, 99.99%+ purity), gadolinium isopropoxide, $Gd[OCH(CH_3)_2]_5$ (Alfa, 99.9%+ purity) and iron acetate, $Fe(CO_2CH_3)_2$ (Alfa, 99.9%+ purity) were used as source materials and 2-methoxyethanol was used as solvent. The gravimetrically

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assayed bismuth acetate and gadolinium isopropoxide reagents were dissolved in the 2-methoxyethanol, to obtain sol compositions. The solutions were refluxed at 60 °C for 0.5 h under one atmosphere pressure. After the addition of iron acetate, the solutions were further refluxed at 80 °C for 2 h to promote solution homogeneity; a stock solution of ~1 M concentration was obtained. The obtained solution had a golden color. Inductively coupled plasma mass spectrometry (ICP-MS: Agilent 7500ce) was used to confirm that the deviation from stoichiometry was within approximately ±1%.

The stock solutions were spin-coated onto $Pt/Ti/SiO_2/Si(100)$ substrates at a spin rate of 2500 rpm for 30 s using a commercial photoresist spinner. These substrates were prepared by DC sputtering about 0.1 μm of platinum onto the oxidized silicon substrates. After each coating step, the gel films were pyrolyzed at 300 °C for 2 min by the hot plate before final annealing. The average thickness of a single-coated as-fired layer, measured by α-step surface profiler, was found to be about 0.1 μm. The desired thin film thickness of approximately 0.7 μm was achieved by repeating the spin-coating and annealing cycles. After multi-coating, the BGFO thin films were annealed at 400 °C, 500 °C, 600 °C and 700 °C for 2 min by RTA at a heating rate of 1200 °C/min in the oxygen atmosphere. In this study, the BGFO thin film annealed at 700 °C has the better ferroelectric and leakage current properties. So the experimental result analysis shall be focused on the BGFO thin film annealed at 700 °C.

The crystalline structure of the thin film was analyzed by X-ray diffraction (XRD: Rigaku PC-2200) with Cu-Kα radiation and operating an accelerating voltage and an emission current of 40 kV and 20 mA, respectively. The XRD diffraction patterns were obtained over the 2θ (θ is a Bragg's angle) range from 10° to 60°. The morphology of the thin film was observed on a field scanning electron microscopy (FE-SEM: JEOL JSM-6700F) with an operating voltage of 3 kV. Top electrodes with an area of 7.85×10^{-3} cm^2 were prepared by DC sputtering platinum through a mask onto the surfaces of the thin films. Measurements of the ferroelectric hysteresis loops were carried out using a Sawyer-Tower circuit in a metal–ferroelectric–metal (MFM) configuration. The leakage current was measured using an HP-4156A semiconductor parameter analyzer in a MFM configuration. The magnetic hysteresis loops of the thin films were analyzed at room temperature by a vibrating sample magnetometer (EV7, ADE, USA).

3. Results and discussion

The XRD diffraction patterns of the BGFO thin films annealed at temperatures ranging from 400 °C to 700 °C are shown in Fig. 1. The XRD peaks are quite similar to those of the standard diffraction pattern data of $BiFeO_3$ (BFO) in the JCPDS card. The results (see Fig. 1) show a randomly oriented perovskite phase structure, but there is also a presence of minor $Bi_2Fe_4O_9$ phase structure in all samples at annealing temperatures more than 400 °C. It is obvious that the $Bi_2Fe_4O_9$ phase structure is reduced to the least at annealing temperature 700 °C. In addition, it can be seen that the intensities of (010), (012) and (020) peaks are relatively broad and weak at high annealing temperature 700 °C. The thin film annealed at 700 °C shows the better (110) orientation compared with those annealed at other temperatures, which indicates crystalline enhancement of the thin film. In this study, the oxygen content in thin film was carried out by the Secondary Ion Mass Spectrometry (SIMS) measurement. The elements ratios in the BFO and BGFO thin films are Bi:Gd:Fe:O=0.86:0.12:1:2.92 and Bi:Fe:O=0.8:1:2.8, respectively. From the measured result, it shows that the BGFO thin film has a more oxygen content. Therefore, Gd doping can reduce the oxygen vacancies.

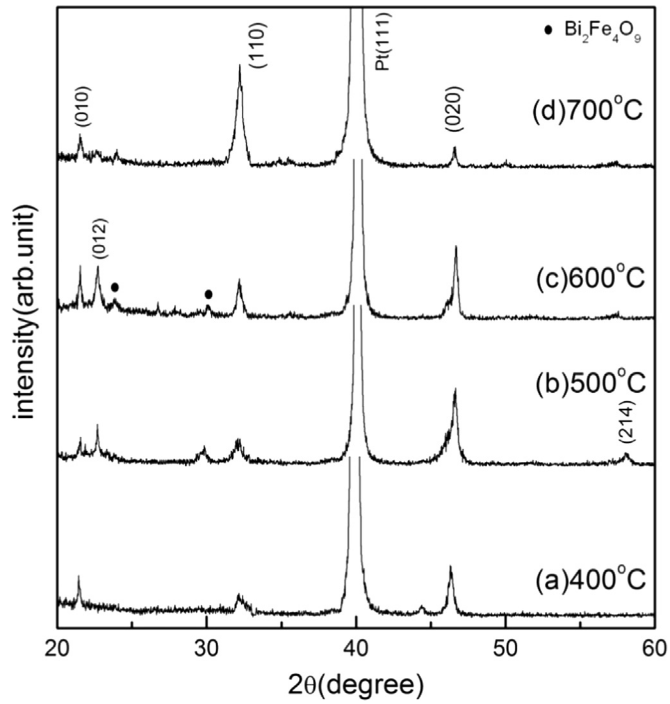

Fig. 1. XRD patterns of the BGFO thin films with various annealing temperatures.

The AFM images of the BFO and BGFO thin films deposited on the Pt coated silicon substrates are shown in Fig. 2. From Fig. 2(a), the BFO thin film shows a plate-like crystal, however, the BGFO thin film has a particle growth morphology. It shows that the Gd ions in the BFO thin film will affect the grain growth mechanism. In this study, the Gd^{3+} and Bi^{3+} ions radius are 93.8 Å and 103 Å, respectively. The BGFO thin films have no plate-like crystal owing to that the BGFO thin film with the $(Bi_2O_2)^{2+}$ layers in the *ab*-plane, which result the grain sizes of the BGFO thin film about 30 nm larger than the BFO thin film about 20 nm.

The polarization hysteresis (P–E) loop of the BGFO thin films were measured at 10 kHz by using the Sawyer-Tower circuit and a HP 54502A digitizing oscilloscope. A ferroelectric hysteresis loop measured at different applied electric fields and room temperature for the BGFO thin film annealed at 700 °C is shown in Fig. 3. This is a slim loop similar to that typically shown by a ferroelectric relaxor. In addition, a remnant polarization $2P_r$ of 20 μC/cm^2 and a coercive field $2E_c$ of 96 kV/cm were obtained at 10 V. Coercive field in the ferroelectric materials is thought to be related to pinning effects of space charge. In this study, we use a doping Gd element in BFO thin film to reduce the leakage current. From the ferroelectric hysteresis loop measurement result, we can obtain a low coercive field $2E_c$, which maybe Gd doping can reduce the oxygen vacancies.

Fig. 4 presents the magnetic hysteresis loop of the BGFO thin film annealed at 700 °C. Magnetic hysteresis loop of the BGFO thin film was measured at room temperature with applied magnetic field parallel to the plane of the samples. From the magnetic hysteresis loop, a well-developed M–H loop can be observed in the BGFO thin film, indicating the presence of an ordered magnetic structure. In addition, the BGFO thin film exhibits a remnant magnetization ($2M_r$) of 2.4 emu/g and a saturation magnetization (M_s) of 5.3 emu/g, respectively. In this study, the BGFO thin films have coexistence of electric and magnetic orders within a single multifunctional material, which shows the BGFO thin films with a great potential for many applications.

The ferroelectric, magnetic and leakage current properties of the BGFO thin film with various annealing temperatures (400–