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Influence of deposition temperature on structural and ferroelectric properties of $Bi_4Ti_3O_{12}$ thin films

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ABSTRACT

Bismuth titanate thin films were deposited using in situ layer-by-layer reactive DC magnetron sputtering. Films were deposited on platinized silicon ($Pt/Ti/SiO_2/Si$) substrates at the temperature of 400–500 °C. The study focused on the dependency of structural, morphological and ferroelectric properties on the parameters of material growth. Thin films, which were formed at the temperature of 450–500 °C, have dense columnar structure and flat surface. Hysteresis measurements revealed the ferroelectric nature of some of the studied films, except for the films deposited at the temperature lower than 450 °C. It was demonstrated that the volatility of bismuth oxide is affected by the temperature starting at 475 °C. The highest coercive field and remnant polarization of E_c = 130 kV/cm and of P_r = 73 μC/cm^2 was obtained for film deposited at 450 °C. It appeared that the shape was clearly influenced by a certain extrinsic contribution (other than leakage) which produces an overestimation of the remnant polarization. Based on the results of the current leakage data investigation, it was established that films exhibit the space charge limited conduction.

1. Introduction

Lead-based materials, such as: $PbZr_xTi_{1-x}O_3$ (PZT) and $PbTiO_3$ (PT) ferroelectrics are widely used in micro- and nanotechnologies, including transducers, sensors, actuators, and non-volatile memories (FRAM) [1–5]. Lead zirconate titanate (PZT) currently dominates in the market of piezoelectric materials. Bismuth-based bismuth titanate $Bi_4Ti_3O_{12}$ (BIT) and bismuth ferrate $BiFeO_3$ are the most promising lead-free piezoelectric materials [6–8]. Moreover, due to its low coercive field and leakage current, long retention, minimal tendency to imprint, and little fatigue with a usual platinum electrode, bismuth titanate is a viable candidate for non-volatile random access memory applications [1,2]. Ferroelectric properties of BIT thin films depend on substrate materials (lattice parameters and thermal expansion coefficient), deposition method, film thickness, measurement frequencies, etc. Such deposition conditions as substrate temperature and deposition rate are very important factors in the growing process for BIT thin film formation [9]. A number of different chemical and physical deposition techniques are used for the formation of bismuth titanate films: RF magnetron sputtering [9–11], pulsed laser deposition [21], sol-gel technique [12], chemical vapor deposition [13], polymeric precursor method [14,15], anodic spark deposition [16], and other. The majority of them experienced issues with film density and crystal structure as well as with stoichiometric and ferroelectric properties. It is important to note, however, that the studies on the dependence of BIT films grown by direct current (DC) magnetron sputtering on growing conditions are scarce. Reactive magnetron layer-by-layer deposition method allows to obtain thin films which are covering a large area and are of uniform thickness and stoichiometry; therefore, this variation of magnetron sputtering appears to be one of the most promising methods for the formation of $Bi_4Ti_3O_{12}$ thin films. Some relevant deposition conditions of this method allow forming and controlling BIT structure with useful ferroelectric properties. In this study, structural, morphological and ferroelectric properties of BIT films are examined as a function of the substrate temperature during their growth.

2. Experiment

The bismuth titanate oxide thin films were deposited on platinized silicon substrate by reactive magnetron layer-by-layer deposition in O_2 gas environment (p = 1.33 Pa) at various substrate temperatures. Multilayer system $Pt/Ti/SiO_2/Si$ was used as the substrate with the thickness of Pt, Ti and SiO_2 layer of 200 nm, 50 nm, and 1 μm, respectively. The SiO_2 film on Si (100) substrate

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was grown by thermal oxidation method. The platinum coating, deposited by magnetron sputtering at 150 °C, was used as a buffer layer as well as a metallic electrode between BIT and $Ti/SiO_2/Si$. Although platinized silicon substrates for synthesis of ferroelectric thin films have been used for about two decades, they do not appear to be suitable for absolutely all synthesis methods. Numerous occurrences of bad adhesion of thin films when synthesis was made using vacuum deposition were reported [17,18]. A few nanometres thickness of Ti or Zr seed layer influence growing mechanism and improve the quality of ferroelectric films [17–22]. Ti seed layer of 5 nm thickness was deposited at 650 °C in order achieve island mode growth due to high surface diffusion of Ti adatoms. In the same process, bismuth titanate synthesis began synthesizing at 650 °C temperature and gradually reduced to 400–500 °C. Gas composition was changed to pure oxygen (p = 1.33 Pa). The deposition of bismuth titanate was realized using substrate periodic and parallel to cathodes motion over the magnetrons (layer-by-layer). 3s period of motion was chosen in order to ensure that the thickness of both Bi_2O_3 and TiO_2 layers was approximately of one atomic layer. Three-inch diameter Bi and Ti disc targets (Kurt J. Lesker Company, Bi and Ti of 99.999% purity) were used. In addition, the distance of 65 mm was kept between magnetrons and the substrate. The samples were heated during this magnetron deposition at the temperature from 400 °C to 500 °C. TiO_2 and Bi_2O_3 deposition rates on unheated substrate were 9 nm/min and 7 nm/min respectively. The power of magnetron sputtering and deposition time (30 min) was chosen to form thin films of 0.30 ± 0.01 μm thickness, which was determined using Linnik micro-interferometer. A shadow mask was used to produce a step in the sample. In addition, thickness was tested by SEM cross-section view. Aluminum top electrodes (∼100 nm thickness) were grown by thermal evaporation technique. The top electrodes diameter for fabricated structures was 1.25 mm. The samples were analysed using scanning electron microscope (SEM) (RAITH-e-LiNE, Raith GmbH). The grain size was determined with average grain intercept method using iSolution DT software. The crystallographic structure of thin films was investigated by X-ray diffraction (XRD) (Bruker D8 series diffractometer using monochromatic Cu Kα radiation with Bragg-Brentano geometry. Sawyer and Tower method for polarization-electric field (P-E) loop measurements was used for measuring hysteresis loops. The resistance of 1 kΩ and capacitor of 150nF was used in circuit.

3. Results and discussion

X-ray diffraction spectra of the deposited thin films bellow 450 °C temperature exhibited amorphous phase of slightly distinguished mixture of bismuth and titanium oxide phases; therefore, only significant XRD patterns were analysed. The crystallization process started when the deposition temperature reached 450 °C. The analysis of film deposited at 450 °C (Fig. 1) was identified as orthorhombic crystallographic structure of Aurivillius phase of $Bi_4Ti_3O_{12}$ (PDF card 35–795) [23]. The increase of deposition temperature to 475 °C caused the appearance of another phase, which was identified as cubic structure of pyrochlore $Bi_2Ti_2O_7$ phase. Further increasing of temperature (up to 500 °C) showed that almost no Aurivillius phase was obtained. Pyrochlore phase dominated in thin films. In order to explain such phase transformation, bismuth oxide volatility was investigated. It is known that bismuth oxide volatiles at high temperature [24]. The volatility efficiency, however, depends not only on temperature, but also on substrate type and on other chemical elements of growing thin films. Fig. 2 shows thickness dependence on deposition temperature. Thin films were deposited by the same deposition time (20 min). It appeared that as substrate temperature reached 475 °C, thickness began to drastically decrease and at 500 °C decreased for almost seven times.

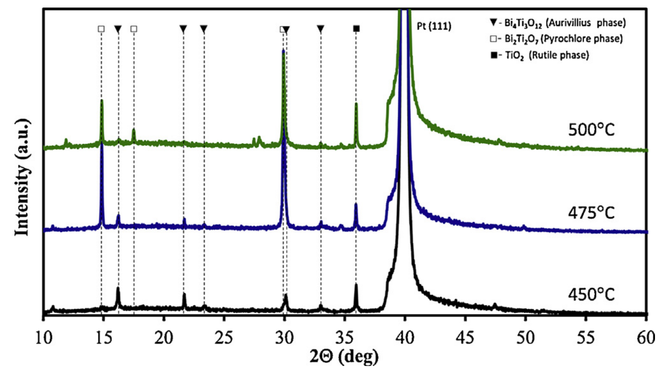

Fig. 1. XRD patterns of BIT films, deposited at 450 °C, 475 °C, and 500 °C.

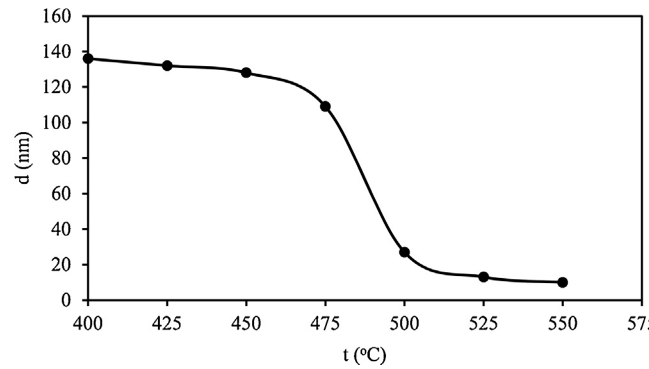

Fig. 2. Bi_2O_3 films thickness dependence on substrate temperature.

These findings correlate with XRD measurements (Fig. 1), which show that pyrochlore phase forms via deficiency of bismuth in BIT thin film.

The morphology of formed bismuth titanate films was investigated by SEM. Fig. 3 displays the SEM images of surface of samples, deposited at 450 °C (a), 475 °C (b), and 500 °C (c) temperatures respectively. It is clear from the figure that dense and plate-like shaped grains structure has formed. Grain size strongly depends on deposition temperature; approximately 94 nm (at 450 °C), ∼133 nm (at 475 °C), and ∼320 nm (at 500 °C) were obtained. According to the results of the XRD analysis, however, the phase of grains was not the same (Fig. 1). It is known that density of grain (or columns) depends on two factors: nucleation centres density and surface migration of adatoms. It appeared that the increase in temperature raised surface migration and agglomeration of adatoms to the centres. The result of this process was the beginning of column growth to width until columns came into contact with each other. Therefore, the grains grow larger. In contrast, due to too low temperature, the surface diffusion of adatoms was limited and nucleation centres density grew. As a result, the grains grew smaller.

It is clear from the cross-section image of film deposited at 450 °C (Fig. 3d), which shows dense columnar growth, that the film is thinner (∼200 nm) than predicted (∼300 nm). It can be explained by denser atoms packing in BIT phase structure rather than in separate oxides and by higher bismuth oxide desorption at high temperatures, which was discussed above. Cross-section image of film deposited at 450 °C was chosen as the ferroelectric properties of this sample were expressed the most, which is discussed more in detail further in this paper.

Fig. 4 demonstrates the dependence of P-E hysteresis loops on applied electric field of thin film, deposited at 450 °C temperature substrate with applied voltage (between 3 V and 10 V at 50 Hz). It is clear from Fig. 4 that BIT thin films have ferroelectric