Grazing incidence X-ray diffraction and atomic force microscopy analysis of BaBi$_2$Ta$_2$O$_9$ thin films

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Abstract

Thin films of BaBi$_2$Ta$_2$O$_9$ (BBT) composition were prepared through the metal organic decomposition method. The crystallinity, phase formation, crystallite size and morphology of the thin films were measured as a function of the type of substrate, stoichiometry of solution and process variables such as thickness and temperature. The thin films were investigated by grazing incidence X-ray diffractometry and atomic force microscopy (AFM) techniques. For the sample without excess of bismuth, diffraction peaks other than that of the BBT phase were observed. A well crystallized BBT single phase was observed for films prepared from a solution with 10% excess of bismuth, deposited on Si$_x$Pt substrate, with a thickness up to 150 nm and sintered at temperatures of 700 $^\circ$C. The thin BBT phase films heat-treated at 600 $^\circ$C presented a diffraction pattern characteristic of samples with lower degree of crystallinity whereas for the thin films heat-treated at 800 $^\circ$C, we observed the presence of other phases than the BBT. For the thin film deposited on the Si$_x$Pt substrate, we observe that the peaks corresponding to the BBT phase are broader than that observed on the samples deposited on the Pt and Si$_x$Pt substrates. No variation of average crystallite size was observed as the excess of Bi increased from 10 to 20%. AFM images for the samples showed that the increasing the amount of bismuth promotes grain growth. The average surface roughness measured was in the range of 16–22 nm showing that the bismuth amount had no or little effect on the roughness of films.

Keywords: BaBi$_2$Ta$_2$O$_9$; Thin films; X-ray grazing incidence; Crystallization

1. Introduction

In recent years, there has been considerable interest in the ferroelectric Aurivillius compounds, since such materials are widely used in technical devices [1]. The Aurivillius family of bismuth layered structure compounds, which were first reported 50 years ago, can be described by the general formula (Bi$_2$O$_5$)$_{2+}$($A_{m-1}B_mO_{3m+1}$)$^{2-}$ where $A$=Ba, Pb, Sr, Bi, K or Na; $m=2, 4$ or $5$ and $B$=Ti, Nb, or Ta [1–3]. Spontaneous polarization in these types of materials can be ascribed both to the displacement of the B cations, in the center position of the octahedrons in the perovskite structure, as well as a tilting of the BO$_6$ octahedra [4].

The two oxides A$B_mB_2$$O_6$ ($A$=Ba; $B$=Nb or Ta) are members of the ($M_2O_5$)$_{2+}$($A_{m-1}B_mO_{3m+1}$)$_{2-}$ family of compounds with $m=2$, and were first reported by Aurivillius in 1949 [2] who determined the structure. Subbarao [3] recognized these materials as possible ferroelectrics. The Curie temperatures, $T_c$, for these compounds are 210 and 110 $^\circ$C for $B$=Nb and Ta, respectively. Both BaBi$_2$Nb$_2$O$_9$ and BaBi$_2$Ta$_2$O$_9$ (BBT) exhibit a broader temperature dependent phase transition [2]. These materials may be good candidates for nonvolatile or volatile memory applications [5].

Currently, Pb$Zr_x$Ti$_{1-x}$O$_3$ (PZT) has been considered to be the promising material for ferroelectric random access memory (FRAM) applications [6]. However, one of the major disadvantages in using PZT films for FRAM applications is its high dielectric constant. Additionally, PZT films are known to suffer from significant...
polarization loss with increasing switching cycles (fatigue) on Pt electrodes [7]. In contrast, bismuth layered structure ferroelectric oxides such as BBT and SrBi$_2$Ta$_2$O$_9$–SrBi$_2$Nb$_2$O$_9$, solid solutions exhibit a low dielectric constant (~300 at 10 kHz), almost no fatigue on Pt electrodes, and very low leakage currents (~10$^{-8}$ A/cm$^2$ at 100 kV/cm) [8,9].

The metalorganic decomposition (MOD) process like almost all chemical methods is well known in the area of processing thin films because of easier composition control, better homogeneity, low processing temperature (compatible with Si processing), easier fabrication of large area thin films, and low cost [10]. In the MOD process the as grown films are amorphous and post deposition annealing of the films is carried out in an oxygen atmosphere.

This paper describes the structural characterization of (BBT) thin films prepared by the MOD process in terms of crystallinity, phase formation, morphology and grain size. The effect of Bi excess content, annealing temperature, type of substrate where the film was deposited and film thickness were analyzed.

2. Experimental

Thin films of BBT were fabricated using barium acetate (Ba(OOCCH$_3$)$_2$), bismuth 2-ethylhexanoate (Bi(C$_9$H$_{15}$COO)$_3$) and tantalum ethoxide (Ta(OC$_5$H$_7$)$_3$) as precursors. Acetic acid, 2-ethylhexanoic acid and 2-methoxyethanol were selected as solvents. Bismuth 2-ethylhexanoate and barium acetate precursors were dissolved in 2-ethylhexanoic acid and acetic acid, respectively, under room temperature conditions. These solutions were then added to the solution of tantalum ethoxide in 2-methoxyethanol. The viscosity of the solution was controlled by varying the 2-methoxyethanol content. Addition of 2-methoxyethanol also improved the wetness and uniformity of coating the substrate. The precursors films were coated onto various substrates by spin coating operated at 6000 rpm for 40 s. Platinum-coated silicon, platinum, silica glass and bare silicon substrates were used in the study. Particulates were removed from the solution by filtering through 0.2-$\mu$m syringe filters. After spinning onto various substrates, films were kept on a hot plate at 350 °C in air for 10 min. After each coating this step was repeated to ensure complete removal of volatile matter.

Grazing incidence X-ray diffraction (GIXRD) measurements of thin films were performed using an automatic Rigaku Rotaflex diffractometer model RINT2000, equipped with a special thin film attachment. Cu K$_\alpha$ radiation (50 kV/100 mA, 1.5405 Å), a divergence slit of 2 mm, a reception slit equal to 0.6 mm and a plane graphite monochromator were used during the measurements. The angle of the incident X-ray beam was fixed at 2°. The scanning range ($\theta$) was 20–90° with a step size of 0.02° and a step time of 3 s.

The identification of crystalline phases was accomplished using the ICDD-PDF files. For comparison, an X-ray diffraction (XRD) measurement of a BBT powder sample was collected using a 0/20 set-up, 0.02° step size and 3 s step time.

The surface morphology of the films was analyzed by Digital instrument’s Dimension 3000 atomic force microscopy (AFM) using tapping mode with amplitude modulation.

3. Results and discussion

Fig. 1 presents the XRD pattern of BBT powder sample. As can be observed, the XRD pattern presented in Fig. 1 was well indexed as being the BBT phase.
according to the data recently published by Paiva-Santos et al. [11]. According to this work, the crystal structure of the BBT compound was found to be tetragonal (space group I4/mmm, number 139) and \(Z=2\), isomorphic of the \(\text{Bi}_2\text{BaNb}_2\text{O}_6\) reported by Blake et al. in Ref. [12]. The unit cell parameters are \(a=3.9332\) Å and \(c=25.505\) Å. The most important diffraction peaks were identified according to Ref. [11].

3.1. Effect of excess of Bi content on the formation of the BBT phase

Previous work showed that the BBT thin films properties are strongly dependent on the excess Bi content [13]. Fig. 2 shows the GIXRD of BBT thin films heat-treated at 700 °C during 1 h as function of excess of Bi.

For all thin films, XRD peaks relative to the Pt phase were observed. Although the thin films XRD experiments were made on a grazing incident angle (2°) configuration, the diffraction peaks corresponding to the Pt substrate were observed because Pt was also deposited on the surface of the samples to be used as a top electrode for the electrical measurements purposes [13]. This observation is valid for all thin film XRD patterns presented in this work.

For the sample without excess of bismuth, diffraction peaks other than that of the BBT phase were observed.
Fig. 4. X-ray pattern of BBT+10% Bi in excess, deposited on Si/Pt substrate, heat-treated at 700 °C for 1 h with different film thickness.

These peaks were characterized as being due to the Bi$_2$O$_3$ or/and Ba$_x$Ta$_{1-x}$O$_{6}$ crystalline phases [14].

For the thin films containing excess of Bi, the BBT phase is easily observed and only one peak with a small intensity due to the Bi$_2$O$_3$ crystalline phase was observed at approximately 31.1° for the sample containing 15% excess of Bi.

It is known that lead and bismuth present a high vapor pressure and that these metals vaporize easily with the increasing of temperature. Therefore, the addition of bismuth excess is to compensate the lost due to vaporization. This fact can be observed in Fig. 5, where at temperatures higher than 700 °C, a Ba$_7$Ta$_9$O$_{16}$ phase appears which can be attributed to the bismuth deficiency.

3.2. Effect of different substrates on the formation of the BBT phase

The effect of substrate on the formation of the BBT phase was examined for four different types of substrates: Si/Pt (Pt-coated Si substrate), Pt (only Pt), Si$^{++}$ (bare silicon) and amorphous SiO$_2$ (silica). All the films were heat treated at the same temperature for

Fig. 5. X-ray patterns of thin films containing 10% of Bi in excess, deposited on Pt/Si substrate and heat treated at different temperatures of 600, 700 and 800 °C for 1 h.
1 h and they present approximately the same thickness. The results are compared on Fig. 3.

If we take the X-ray pattern of the BBT+10% Bi in excess as the reference sample, we can observe that the peaks corresponding at the BBT phase on the X-ray pattern of the thin film deposited on the Pt substrate are less intense and a smaller peak located approximately 31.10° corresponding to the Bi$_3$O$_3$ or/and Ba$_3$Ta$_6$O$_{16}$ crystalline phases can be observed. Concerning the thin film deposited on the Si substrate, we can observe that although the peaks corresponding to the BBT phase are also observed, they are broader than that observed.

Fig. 6. AFM micrographies of thin films with (a) 0; (b) 5; (c) 10; (d) 15 and (e) 20% excess bismuth content, thermally annealed at 700 °C.
on the samples deposited on the Pt and Si/Pt substrates. The broadness in the peaks of BBT phase, in this case, could be attributed to the native silicon oxide; even all substrates were cleaned with a diluted HF solution just before deposition. The peak of Si substrate could be observed and due to the fact that the diffraction peaks are broader, the existence of others crystalline phases in this sample could not be disregarded. Finally, we observe that the thin film deposited on the silica substrate is practically amorphous. Only a smaller peak corresponding to the most intense peak of the BBT phase is observed.

3.3. Effect of film thickness on the formation of the BBT phase

Fig. 4 shows the X-ray pattern of BBT + 10% Bi in excess thin films, deposited on Si/Pt substrate, heat-treated at 700 °C for 1 h with different film thickness.

For the thin film with the thickness equal to 50 nm, the diffracted peaks, corresponding to the BBT phase, are lower in intensity than in 150 nm films, which could be attributed to the amount of material, as the 50 nm films are three times thinner than 150 nm films. The thin film of 150 nm of thickness shows high intensity peaks for the BBT phase. As the film thickness increases to 250 and 350 nm, the degree of crystallinity decreases, the more intense peak of the BBT phase became larger and the diffraction peaks of the Bi₂O₃ phase can be observed.

The effect of substrate type, as well as, the film thickness on the BBT phase crystallization could be explained based on the role that the reaction between platinum and bismuth and a possible PtBi phase formation, as small islands (spots) on top of substrate surface. These spots favor the heterogeneous nucleation of BBT phase, contributing to the lowering of crystallization temperature as observed in Fig. 5. Further investigation will be carried out to confirm this hypothesis.

3.4. Effect of heat treatment temperature on the formation of the BBT phase

Fig. 5 presents the X-ray patterns of thin films containing 10% of Bi in excess, deposited on Pt/Si substrate and heat treated at different temperatures of 600, 700 and 800 °C during 1 h.

As is shown in Fig. 5, the thin film heat-treated at 600 °C presents a diffraction pattern characteristic of sample with lower degree of crystallinity. If the diffraction peaks of the Pt phase are not considered, only two other peaks of small intensity are observed. These two peaks probably belong to the BBT phase. As we discussed before, the thin film heat-treated at 700 °C was one that presented the better X-ray pattern when compared to the X-ray pattern of the BBT powder sample.

Concerning the thin film heat-treated at 800 °C, we can observe the presence of others phases than the BBT. These phases were characterized as being probably the Bi₂O₃ or/and Ba₅Ta₆O₁₆ crystalline phases.

3.5. Average grain size from X-ray analysis and AFM images

From the width of the determined line profiles, more information may be gained, and the average crystallite size can be determined using the Scherrer equation [15]:

\[
D = \frac{K\lambda}{B\cos \theta_B}
\]

where \( K \) is a factor \( \sim 0.9–1.0 \), \( \lambda \) is the wavelength of the radiation used, and \( B \) the broadening profile. The broadening \( B \) has to be corrected for instrumental broadening due to slit sizes and X-ray source characteristics. To determine the instrumental broadening, a reference X-ray diffractogram from powder Si was recorded. The silicon powder with grain size approximately 5 μm was used to avoid broadening of the line profiles. Moreover, the grains should not be strained. The broadening of half-height peak widths due to slit sizes and X-ray source characteristics was calculated and was equal to 0.14° (26).

The average crystallite size was calculated using \( \{110\} \) reflection approximately 32.08° for samples that present well crystallized BBT phase (BBT + 10% Bi in excess sample deposited on a Si/Pt substrate, BBT + 10% Bi in excess sample deposited on a Pt substrate, BBT + 15% Bi in excess sample deposited on a Si/Pt and BBT + 20% Bi in excess sample deposited on a Si/Pt substrate). The calculation showed that the line broadening \( (B) \) of \( \{110\} \) reflection approximately 32.08° for all samples was approximately 0.42 (rad) and the crystallite size is 29 ± 1 nm. This result shows that the average crystallite size is not affected by the increasing of the Bi amount from 10 to 20%.

The AFM images for the samples with bismuth excess ranging from 0 to 20% are shown Fig. 6. We can observe that increasing the amount of bismuth promotes grain growth, as can be seen when we compared the microographies of Fig. 6a and e for example. On the other hand, the average surface roughness measured is in the range of 16–22 nm showing that the bismuth amount had no or little effect in the roughness of films.

4. Conclusion

The BBT phase crystallization is strongly dependent on the Bi content, substrate type, film thickness and annealing temperature.

BBT thin films deposited onto Pt recovered Si substrates, prepared by MOD method with 10% excess bismuth content, thermally annealed at 700 °C with thickness lower than 350 nm, revealed a good crystalli-
zation, without the presence of secondary phases and with a grain size in order of 30 nm.

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