Bi₄Ti₃O₁₂ Ferroelectric Thin Films: Morphology and Electrical Characteristics

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Abstract. — Bi₄Ti₃O₁₂ thin films have been produced on Pt/TiO₂/SiO₂/Si buffer layers by spin-coating using a mixed bismuth-titanium alkoxide. The crystallization of Bi₄Ti₃O₁₂ is observed at 480 °C. An increase of the average grain size related to an augmentation of the roughness of the films is observed with increasing coatings number. P-E hysteresis loops confirmed the ferroelectric character of the films.

Résumé. — Des couches minces de Bi₄Ti₃O₁₂ ont été préparées par centrifugation à partir d'un alcoxyde mixte de bismuth et de titane sur des substrats Pt/TiO₂/SiO₂/Si. Dès 480 °C, la phase Bi₄Ti₃O₁₂ est cristallisée. Une croissance des grains associée à une augmentation de la rugosité des films a été observée avec le nombre croissant de couches. Les mesures de cycles d'hystérésis ont confirmé le caractère ferroélectrique des films

1. Introduction

Bismuth oxide layer compounds are potentially good candidates for elaboration of ferroelectric thin films for applications to non volatile memories and capacitors of dynamic random-access memories due to their reversible spontaneous polarization and their high dielectric constant [1–3]. Previous studies on the nature of chemical precursors have allowed to choose the use of a mixed bismuth/titanium alkoxide, whose preparation has been detailed elsewhere [4], to obtain the crystallization of pure Bi₄Ti₃O₁₂ phase [4,5]. The present paper deals with the sol-gel spin-coating preparation, microstructural and electrical characterizations of Bi₄Ti₃O₁₂ thin films.

2. Experimental

Hydrolysis, in a glove box fitted out with a dried air generator, of a mixed-solution of 0.203 M bismuth tri-methoxyethanolate and 0.152 M titanium tetra-methoxyethanolate in 2-methoxy-ethanol by a H₂O/CH₃OCH₂CH₂OH (1M H₂O) solution gives either gels for $h > 1$

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($h = [\text{H}_2\text{O}]/[\text{M}(\text{OR})_n]$) or slightly turbid gels presenting a reversible sol-gel transition upon stirring for $h < 1$. These latter conditions are particularly interesting for the deposition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films. In such a case, the viscosity of the gel obtained ($\eta = 1.8 \text{ mm}^2 \text{ s}^{-1}$) and stored in a glove box in dried air conditions, increases progressively with time ($\eta = 2.2 \text{ mm}^2 \text{ s}^{-1}$ for 10 days, $\eta = 2.6 \text{ mm}^2 \text{ s}^{-1}$ for 20 days, $\eta = 3.0 \text{ mm}^2 \text{ s}^{-1}$ for 30 days, $\eta = 3.7 \text{ mm}^2 \text{ s}^{-1}$ for 40 days) to reach a maximum ($\eta = 4.3 \text{ mm}^2 \text{ s}^{-1}$) for 50 days. However, even after 50 days of storage, the viscosity of the gel can easily be decreased down to $\eta = 1.8 \text{ mm}^2 \text{ s}^{-1}$ upon stirring for 5 minutes.

Thin films are obtained by spin-coating stable precursor solutions on $\text{Si}/\text{SiO}_2/\text{TiO}_2/\text{Pt}$ substrates mounted on a Sulzer photoresist spinner and by using appropriate processing conditions: an acceleration of 7 rpm s^{-1} , a rotation speed of 4000 rpm and a rotation time of 30 s. Platinum has been selected as bottom and top electrodes for hysteresis cycle measurements. SiO_2 and TiO_2 layers have been chosen as diffusion barriers between the silicon substrate and the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ coating to avoid the formation of $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_2\text{Ti}_2\text{O}_7$ impurities. These pre-coatings have been realized using the reactive cathodic sputtering process with silicon and titanium targets in low pressure oxygen atmosphere. The coatings are then dried at 300°C to remove organics. Deposition and drying operations are repeated to prepare thicker films. Well-crystallized and pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films are obtained after heating at 700°C for 2 hours.

The crystallization of thin films was followed by X-ray diffraction at various temperatures ranging from 20°C to 800°C , under atmospheric conditions, using a Siemens D5000 diffractometer (θ/θ , $\text{CuK}\alpha$ radiation) fitted out with a high temperature furnace (Anton Paar HTK10, heating sample holder: Pt) and a Elphyse Position Detector (14° aperture). Each diffraction diagram was recorded after an annealing time of 30 minutes at the given temperature in the 2θ range $15\text{--}70^\circ$ (step size: 0.029° , time range: 8 min). The morphology and surface microstructure of the thin films were observed by Scanning Electron Microscopy (SEM) (Hitachi S2500) and atomic force microscopy (AFM) (Digital Instruments Nanoscope II).

AFM is a good tool for atomic scale measurements of surface morphology because of its high lateral (0.01 nm) and its high vertical (1 nm) resolution [6]. AFM measurements were conducted using the constant force mode. A very small tip attached to a cantilever spring ($l = 200 \text{ nm}$) with a force constant of 0.12 N m^{-1} touches the sample surface and the attractive and/or repulsive forces bend the cantilever spring. The deflection of the cantilever is optically detected: a laser beam is specularly reflected from the cantilever surface and the direction of the reflected light beam is sensed with a position sensitive (two elements) photodetector. Three piezoelectric ceramics x , y and z move the tip in the scanning area (x , y) of up to $12 \text{ mm} \times 12 \text{ mm}$. In the constant force mode, the net force between the tip and the sample is used as the feedback parameter in the z feedback circuit which controls the displacement of the sample in the z -direction normal to the surface. The height profil is obtained after each (x , y) scan. The atomic force images are not filtered nor processed. They are just fitted by subtracting a "polynomial plane" which consists of a surface whose cross-section is a second order polynomial in one axis and an horizontal line in the other axis.

Hysteresis cycles were measured using a Sawyer Tower apparatus.

3. Results

After drying at 300°C , amorphous thin films were obtained. These films have to be annealed to enable the crystallization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The crystallization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films prepared with 5, 10 and 15 coatings was followed by X-ray diffraction *versus* temperature. We have

Fig. 1. — X-ray diffraction patterns *versus* temperature of a Bi₄Ti₃O₁₂ thin film prepared with 15 coatings.

Fig. 2. — Scanning electron micrographs of a Bi₄Ti₃O₁₂ thin film prepared with 15 coatings and heat-treated at (a) 500 °C and (b) 700 °C for 2 hours

previously shown that at least five coatings (each coating is about 20–40 nm thick) were needed to obtain dense and well-crystallized Bi₄Ti₃O₁₂ thin films after a heat-treatment of 2 hours at 700 °C [5].

Crystallization of Bi₄Ti₃O₁₂ thin films occurs about 480 °C for thin films prepared respectively with 5, 10 and 15 coatings. The number of coatings does not change the crystallization of Bi₄Ti₃O₁₂ thin films (X-ray diffraction patterns registered at 300 °C, 400 °C, 460 °C, 480 °C, 500 °C, 600 °C and 700 °C for a thin film prepared with 15 coatings are shown in Fig. 1).

Fig. 3 — Three-dimensional images (AFM) of the surface of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films prepared with (a) one coating and (b) 15 coatings and heat-treated at 700°C for 2 hours

Fig. 4 — AFM topographic images of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films prepared with (a) one coating and (b) 15 coatings and heat-treated at 700°C for 2 hours.

Table I. — X-ray pattern data of a Bi₄Ti₃O₁₂ thin film, prepared with 15 coatings, at 700 °C.

<i>h k l</i>	<i>d</i>	<i>2θ</i>	<i>I/I₀</i> (%)
1 1 7	3.0115	29.640	100
0 0 12	2.7459	32.583	61
1 1 13	2.0980	43.080	61
0 0 16	1.9928	45.477	57
2 2 6	1.8175	50.151	48
3 1 7	1.6246	56.605	33

Table II. — Evolution (observed by AFM) of the grain size and mean-roughness (esd are given in parentheses) of Bi₄Ti₃O₁₂ thin films, heat-treated at 700 °C for 2 hours, versus the number of coatings.

Number of coatings	1	5	10	15
Grain size (nm)	< 50	50–80	100–150	100–300
Roughness (nm)	40 (5)	57 (5)	85 (5)	140 (20)

This temperature of 480 °C is the same than those previously observed, using X-ray diffraction *versus* temperature and differential thermal analysis, on the powder of the same gel than the one used to prepare thin films [4]. However, at 300 °C some broad X-ray diffraction peaks ($2\theta = 32.58$ and $2\theta = 50.15$) relative to the Bi₄Ti₃O₁₂ compound are observed. This is certainly due to the presence at this step of Bi₄Ti₃O₁₂ crystalline nanoparticles. Such a phenomenon is currently observed during the crystallization of reactive powders of oxide materials (e.g. ZrO₂, TiO₂) synthesized by sol-gel technology. At 700 °C well-crystallized and randomly oriented Bi₄Ti₃O₁₂ thin films on Si/SiO₂/TiO₂/Pt substrates are obtained. Table I lists the X-ray pattern data of the thin film at 700 °C. The temperature of 700 °C which allows a good

Fig. 5. — Hysteresis loop of a 0.1 μm-thick Bi₄Ti₃O₁₂ thin film (prepared with 10 coatings) heat-treated at 700 °C for 2 hours.

crystallization of the thin films is also useful to increase grain size of the films in order to get a good ferroelectric response. SEM observations have shown the grain size increase observed between 500 °C, 600 °C and 700 °C for an annealing time of 2 hours on a film prepared with 15 coatings. The grain size average increases from about 40 nm at 500 °C to 100 nm at 600 °C and to 200 nm at 700 °C (micrographs of thin films heat-treated respectively at 500 °C and 700 °C are shown in Fig. 2). Crack-free thin films are obtained after heating at these temperatures. However the grain size increase observed *versus* temperature is associated with the appearance at 700 °C of porosity at the surface of thin films.

An AFM study has been performed on thin films prepared with one, 5, 10 and 15 coatings and heat-treated at 700 °C for 2 hours in order to characterize the surface morphology of the thin films and particularly for the film prepared with one coating which is not easily observable by SEM (blurred grain boundaries are observed). The surface morphologies and images of thin films prepared with one and 15 coatings and heat-treated at 700 °C for 2 hours are shown respectively in Figures 3 and 4.

AFM observations show that, as the number of coatings increases, the grain size increases and the film becomes rougher (see Tab. II). A roughness (mean-roughness R_a) of about 40 nm, 60 nm, 85 nm and 140 nm is measured respectively for films prepared with one, 5, 10 and 15 coatings. This roughness increase is directly associated to the grain size augmentation: for one coating grains less than 50 nm are observed, for 5, 10 and 15 coatings grains respectively in the 50–80 nm, 100–150 nm and 100–300 nm ranges are obtained.

Preliminary polarization-electric field hysteresis loops, measured on thin films with $\epsilon' \approx 150$ and $\tan \delta \approx 2 \times 10^{-3}$ under 2 volts (100 Hz, 2 ms pulse), have qualitatively confirmed the ferroelectric behavior of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films as shown in Figure 5 (thin film prepared with 10 coatings and heat-treated at 700 °C)

As previously stated, a high annealing temperature (700 °C) of thin films seems useful to get a ferroelectric response. So a study of the correlation morphology $\leftrightarrow$ ferroelectric properties is now in progress. Other substrates as MgO or SrTiO_3 have to be used to check the possible orientation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films.

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