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# Ferroelectric behavior of bismuth titanate thin films grown via magnetron sputtering

C.M. Bedoya-Hincapié[a,b], E. Restrepo-Parra[c,*], J.J. Olaya-Flórez[a], J.E. Alfonso[a], F.J. Flores-Ruiz[d], F.J. Espinoza-Beltrán[d]

[a]*Universidad Nacional de Colombia, sede Bogotá, Bogotá, Colombia*
[b]*Universidad Santo Tomás, Bogotá, Colombia*
[c]*Universidad Nacional de Colombia, sede Manizales, Manizales, Colombia*
[d]*CINVESTAV Unidad Querétaro, Lib. Norponiente 2000, Real de Juriquilla, 76230 Querétaro, Qro., Mexico*

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**Abstract**

Bismuth titanate ($Bi_xTi_yO_z$) thin films were grown using the r.f. magnetron sputtering technique on (100) silicon substrates. In the process, annealing was performed in both oxygen and dry air atmospheres at 600 °C for 30 and 120 min. The structure of the thin films was characterized through X-ray diffraction (XRD), and the ferroelectric response was determined with measurements of piezoelectric force microscopy (PFM). $Bi_4Ti_3O_{12}$ with a predominant orthorhombic phase was obtained in the annealed thin films. All the annealed films exhibited the characteristic hysteresis and butterfly loops of ferroelectric materials. Thermal annealing of $Bi_xTi_yO_z$ films in an atmosphere of air for 30 min resulted in the highest $d_{33}$ value of $78 \pm 14$ pm/V, which decreased to $64 \pm 26$ pm/V for 120 min. On the other hand, annealing in an oxygen atmosphere produced $Bi_xTi_yO_z$ films with more uniform $d_{33}$ values, $54 \pm 3$ pm/V and $42 \pm 6$ pm/V for 30 and 120 min, respectively. Ferroelectric coefficient values decreased with the increase of annealing time in an oxidant atmosphere, which can be explained by the vacancies present. These results are consistent with the experimental measurements carried out in other investigations.


*Keywords:* Ferroelectricity; Thin films; Bismuth titanate; PFM; Piezoelectric coefficient

## 1. Introduction

Lead-free materials have received considerable attention in recent decades due to interest in the reduction of environmental impact by using appropriate materials to replace harmful ones. For this purpose, bismuth-based film materials have been considered. For instance, bismuth layer-structured ferroelectric (BLSF) ceramics are compounds of great technological interest due to their application as a piezoelectric material with high Curie temperature ($T_c$), low temperature coefficients of dielectric constants, low aging rate, and strong anisotropic characters [1]. The most representative compound is bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT), which belongs to the Aurivillius family, with a general formula of $(Bi_2O_2)[A_{m-1}(B)_mO_{3m+1}]$, which consists of $(Bi_2Ti_3O_{10})^{2-}$ layers sandwiched between bismuth oxide $(Bi_2O_2)^{2+}$ layers [2–4]. The BIT phase has been studied intensively due to its ferroelectric and piezoelectric properties over a wide temperature range close to 948 K which makes it suitable for applications in standard electronic devices (ceramic capacitors, piezoelectric transducers, sensors, etc.) or new ones such as nonvolatile ferroelectric random memories (NvFRAM) [5]. The ferroelectricity in BIT arises from a tetragonal structure (*I4/mmm*) turning into a lower symmetry structure such as an orthorhombic ($B_2cb$) [6] or monoclinic one (*Pc*) [7]. Although the monoclinic distortion in the lattice is reported to be too small to differentiate these two types [8], in terms of ferroelectricity, the space group *Pc* allows, besides the polarization component in the *a*(*b*) direction, another smaller contribution in *c*, while in

*Corresponding author. Tel./fax: +57 6 8879495.
*E-mail address:* erestrepopa@unal.edu.co (E. Restrepo-Parra).

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*B2cb* only a polarization in *a*(*b*) appears. Experimentally, thermal processes in $Bi_xTi_yO_z$ thin films can induce dipole defects resulting from vacancies in the thin film, which could cause ferroelectric domain wall pinning [9–12] and also a common failure phenomenon called imprint [13,14], which can be noticed by a large voltage shift and deformation in the hysteresis loops [15,16]. So it is important to study the effects of vacancies in ferroelectric properties of thin films under different conditions of annealing parameters. Few studies have been carried out so far on the annealing atmosphere and determining the time for crystallization of the BIT ferroelectric phase. Simões et al. [17] have carried out the study of BIT thin films' growth through the polymeric precursor method and annealing in static air and oxygen atmospheres. A decrease in the ferroelectric behavior was evidenced in oxygen atmosphere as a consequence of the vacancies concentration, favoring the imprint phenomenon and reducing the piezoelectric coefficient dramatically. Nevertheless, reports about the effect of the annealing atmosphere on the ferroelectric properties of BIT films grown via the magnetron sputtering technique have not yet been discussed at the nanosize level.

Therefore, in this paper the effect of oxygen and dry air atmospheres during annealing treatment of BIT films on the structure and ferroelectric behavior is reported. The thin films were structurally characterized through X-ray diffraction (XRD), and their ferroelectric properties were analyzed using piezoresponse force microscopy (PFM).

## 2. Experimental details

BIT thin films were grown via an r.f. sputtering system, a model CIT-Alcatel HS 2000 with a balanced magnetron of 4 in. diameter, described in a previous paper [18], using a $Bi_4Ti_3O_{12}$ target of high purity (99.999%) and Si (100) wafer as a substrate. The substrates were ultrasonically cleaned in acetone solution for 15 min. The thin films were deposited at 350 °C for 45 min, with a target power supply of 150 W and 20 sccm argon flux. The thin films were crystallized through thermal annealing as a BIT phase that appears in the range 500–700 °C. A Linderberg Beng M furnace was employed in dry air (19.9% $O_2$) atmosphere and oxygen atmosphere with 20 sccm flux at 600 °C for 30 and 120 min. The crystalline structure of the films was characterized with a Rigaku X-ray difractometer (XRD) using incident geometry with Cu-Kα radiation ($\lambda = 1.5405$ Å) in the $2\theta$ range 10–70° with steps of 0.02°. The ferroelectrical domain structure of the films was studied via contact resonance piezoresponse force microscopy (CR-PFM) and switching spectroscopy PFM in order to obtain the local hysteresis loops. Contact resonance condition is attained when the amplitude of oscillation (converse piezoelectric effect) of the tip-sample contact area is amplified by a factor of 10 to 100 times due to the resonant vibration of the cantilever in contact with the sample. The amplification factor is proportional to the Q-value of the corresponding resonance peak of the cantilever. The CR-PFM was carried out with Nanoscope IV Dimension 3100 equipment from Digital Instruments – Bruker with the addition of a high frequency lock-in amplifier SR844 Stanford Research Systems. An AC bias excitation at a resonance frequency of the AFM probe was applied to the conductive tip while the thin film's base was electrically grounded. CR-PFM measurements were performed with a modulation amplitude of 3 V at frequencies in the range from 352 to 378 kHz. The AFM probes used for these measurements were BudgetSensors Cr/Pt coated silicon probes with 450 μm length and 0.2 N/m spring constant as nominal parameters.

On the other hand, in the switching spectroscopy PFM (SS-PFM) measurements, a signal composed of DC squared pulses (half of the time with a DC bias and half with null bias) with a triangular envelope applied to the tip. This signal was superposed on an AC signal at a resonance frequency of the cantilever in order to produce the contact resonance effect. Modulation AC amplitude of 2 V and a frequency from 311 to 314 kHz, and a DC amplitude of the triangular envelope in the range from −21 to +21 V were used. The AFM probes used for these measurements were Rocky Mountain Nanotechnology RMN-12Pt400B platinum probes with 400 μm length and a 0.3 N/m spring constant as nominal parameters. The employed resonance frequencies are more sensitive for detecting the out-of-plane contribution; these are flexural modes of the cantilever. The local loops were obtained from the average of 20 loops in order to reduce the noise effect. In order to obtain $d_{33}$ values in pm/V units, the PFM amplitude values (given in V) were compared with the vertical variations of height (given in pm) of the tip-sample surface as measured by the AFM system.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the annealed thin films at 600 °C. They exhibited a polycrystalline structure as a result of the numerous XRD peaks. The XRD peaks correspond to a mixture of standard crystal data of $Bi_4Ti_3O_{12}$ indexed as monoclinic (*Pc*), orthorhombic *(B2cb*), and tetragonal

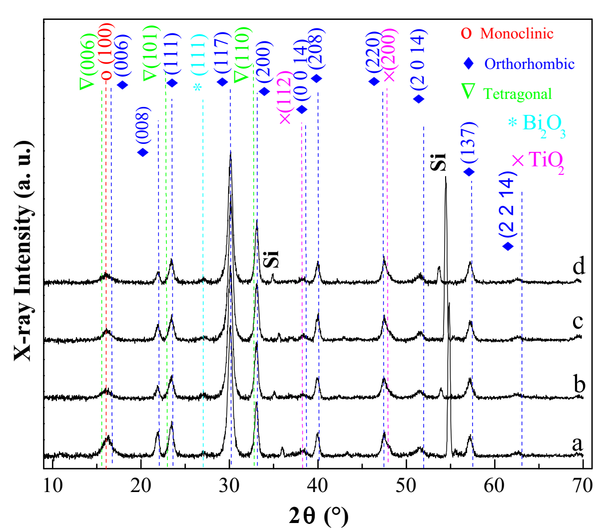


Fig. 1. XRD patterns of annealed $Bi_4Ti_3O_{12}$ thin films: (a) 30 min-air, (b) 30 min $O_2$, (c) 120 min-air and (d) 120 min-$O_2$.

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