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Microstructure Patterns by Switching Spectroscopy Piezo-response Force Microscopy of Lead Free Perovskite-type Polycrystalline Thin Films

G. Herrera-Pérez[1], O. Solis-Canto[2], J. Holguin-Momaca[3], S. Olive-Mendez[3], E. Guerrero-Lestarjette[2], G. Tapia-Padilla[1], A. Reyes-Rojas[3], L. E. Fuentes-Cobas[3]

[1.] CONACYT Research Fellow. Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes 120, Chihuahua, Chih., Mexico.
[2.] Laboratorio Nacional de Nanotecnología (NanoTech). Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes 120, Chihuahua, Chih., Mexico.
[3.] Physics of Materials Department. Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes 120, Chihuahua, Chih., Mexico.

The purpose of this work is to perform DC-based manipulations as a nanolithography tool to fabricate nanostructured patterns on lead free ferroelectric thin films (TF) with stoichiometry $Ba_{1-x}Ca_xTi_{0.9}Zr_{0.1}O_3$ (denoted in this work as BCZT), where x = 0.1, 0.15 and 0.2. To establish the evidence of ferroelectricity in BCZT, one has to probe the local domain configurations and demonstrate the switching of the polarization [1]. For this material, the switching corresponds positively and negatively to the polarized regions [2], and as an example, we use the CIMAV logo as template, Fig 1a.

Polarization switching in polycrystalline BCZT bulk and thin films on Pt-coated substrates was studied by switching spectroscopy piezo-response force microscopy (SS-PFM) in dual AC resonance tracking (DART) mode. Fig. 1b and 1c show the switching domains before and after of the hysteresis loop measurement in the region marked with a blue circle on the PFM amplitude micrographs for the BCZT-TF with x=1. In these micrographs, the white region was polarized downward, whereas, the orange dotted region was polarized upward, confirming the 180º phase difference between the two domain configurations. The out-of-plane piezo-response was determined as a function of an applied voltage, and the PFM hysteresis loops, both in amplitude and phase are shown in Fig. 2a and 2b, respectively. Figure 2a exhibits a butterfly shape, whereas Fig. 2b reveals a sharp 180º inversion at the coercive voltages with a clear hysteresis. These results confirm the ferroelectric nature of BCZT-TF. The piezoelectric response d_{33} was determined by analyzing the local amplitude measurements "off-state" through the following equation $(V - V_1)\, d_{33} = D - D_1$ [3]; shown in Fig. 2c. BCZT-TF shows a $d_{33} = 2.2\ pmV^{-1}$ at the maximum voltage of 50 V and the coercive voltage was around 12.2 V.

To complement the characterization of these electro-ceramics, Fig. 3a and 3b show a comparison between the X-ray diffraction (XRD) for the target prepared modified Pechini method [4] and sintered at 1200 ºC for 5 h; and the grazing incidence XRD for BCZT-TF (obtained by radio frequency magnetron sputtering system), respectively. The Rietveld refinement for the XRD results suggest a perovskite-type structure with tetragonal phase (*P4mm* space group), that is compatible with the ferro (Fig. 3c) - piezo electrical response. In summary, the polarization switching behavior in the ferroelectric BCZT-TF as a relevant tool to optimize the image of polarization reversal as a lithography technique to store nanostructured patterns was shown [5].

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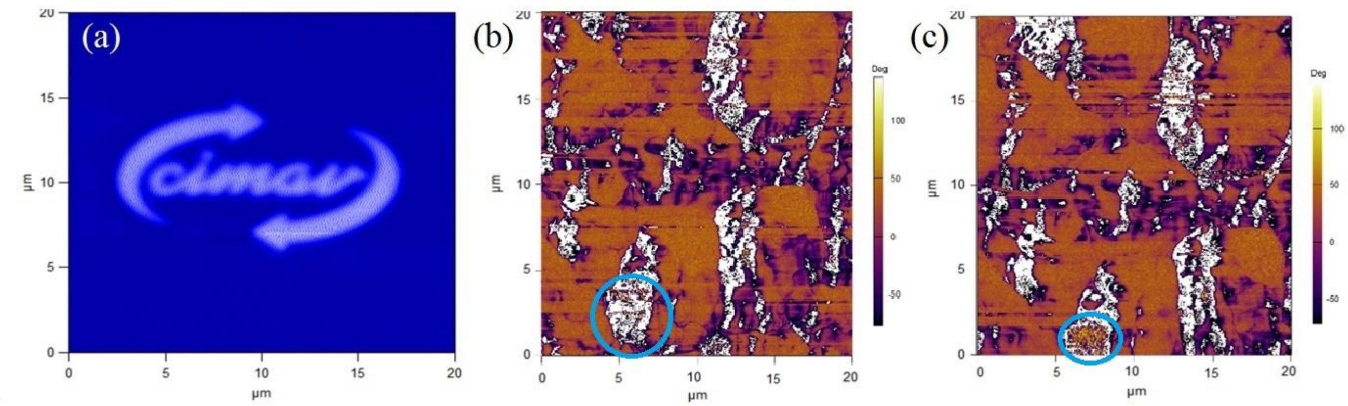

Figure 1. (a) PFM base lithography using CIMAV logo as template. Schematic of DART technique before (b) and after (c) make the hysteresis loop in the region marked with a blue circle.

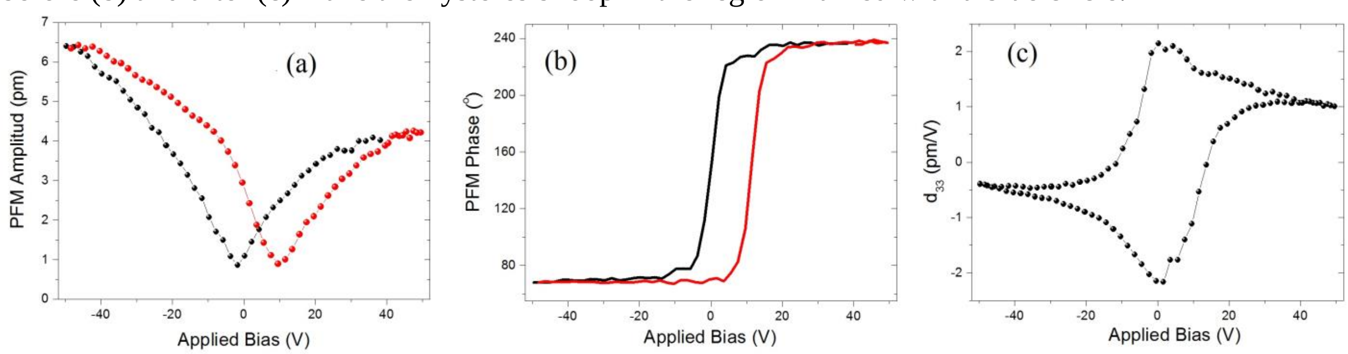

Figure 2. Local hysteresis loops measured by (a) PFM amplitude, (b) PFM phase, and (c) piezo-response (d_{33}) versus bias voltage for the BCZT-TF with x=1.

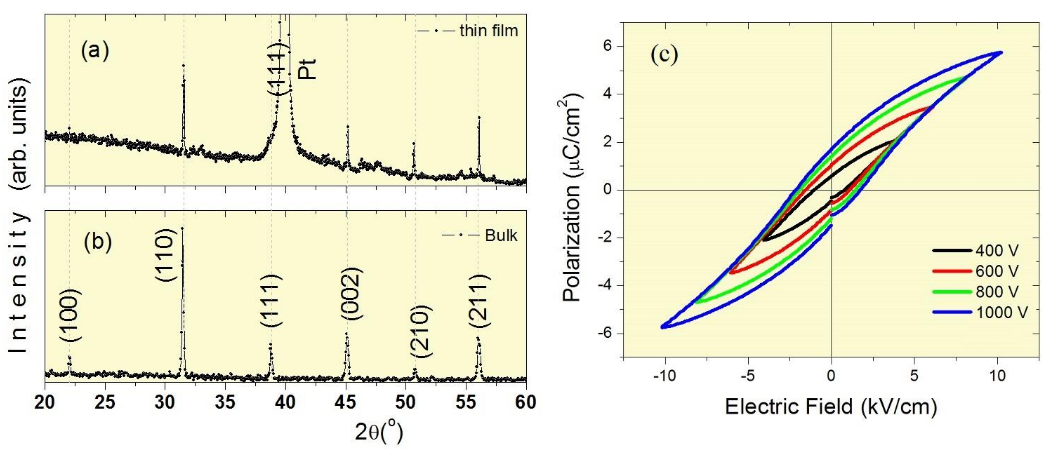

Figure 3. (a and b) Comparison between XRD patterns for BCZT-TF and bulk, respectively. (c) Macroscopic polarization-electric field hysteresis loops at different voltages for the BCZT target.