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Covering vertical aligned carbon nanotubes with a multiferroic compound

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Abstract: This work highlights the possible use of vertically-aligned multiwall carbon nanotubes (VA-MWCNTs) as bottom electrodes for microelectronics, for example for memory applications. As a proof of concept BiFeO₃ (BFO) films were fabricated in-situ deposited on the surface of VA-MWCNTs by RF (Radio Frequency) magnetron sputtering. For in situ deposition temperature of 400 °C and deposition time up to 2 h, BFO films cover the MWCNTs and no damage occurs either in the film or MWCNTs. In spite of the macroscopic lossy polarization behaviour, the ferroelectric nature, domain structure and switching of these conformal BFO films was verified by piezo force microscopy. G type

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antiferromagnetic ordering with week ferromagnetic ordering loop was proved for BFO films on VA-MWCNTs having a coercive field of 700 Oe.

Keywords: carbon nanotubes, ferroics, multiferroics, bismuth ferrite, sputtering, thin films

1. Introduction

Carbon nanotubes (CNTs) are currently being considered to be integrated in various microelectronic applications due to their unique set of properties, including ballistic electron transport and a huge current- carrying capacity and one dimensional (1D) geometry, which make them of great interest for future microelectronics [1]. There are various fields in microelectronics in which CNTs are displaying promising applications. CNTs used for Field Effect Transistors (FETs) depict 20 times less switching resistance and 200 times more current handling capacity [2] besides the further miniaturization of devices they permit. MWCNTs are predicted as the material for the next generation of interconnectors due to its metallic behaviour and high current density [3]. Nantero Inc. demonstrated the use of MWCNTs sandwich between two metallic electrodes to form resistive Nanotube based / Non-volatile random access memory (NRAM) cells. The memory works based on the principle of change in the resistance that occurs due to the interaction between CNTs [4]. In addition, there are various fields of energy related microelectronics where CNTs electrodes can be applied [5]. CNTs are seen as possible alternative to the expensive indium tin oxide (ITO) substrates used in solar cells [6] or as channel material in FETs [1, 7].

One among other applications is the use of CNTs integrated with high dielectrics and ferroelectrics materials for memory devices. Jang *et al.* [8] demonstrated the use of CNTs coated with Si_3N_4 for the development of ultra large integration (ULSE) memories. Later,

based on a similar idea Kawasaki *et al.* [9] in 2008, employed CNTs as bottom electrodes for the development of pin shaped 3D capacitors for Ferroelectric Random Access Memories (FeRAM) with $\text{Pb}_{1-x}\text{Zr}_x\text{TiO}_3$ (PZT), using a liquid source misted chemical deposition (LSMCD). The damage of CNTs lattice and contaminations from the silicon substrate was reported in this work. Later, these same researchers used pulse laser deposition technique to coat CNTs with ferroelectrics, as $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and PZT [10-12] and ferromagnetic as $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ [13]. In the above studies the working principle was based on the coverage of individual tubes. Other than memory applications, VA-MWCNTs were also coated with SrTiO_3 (STO) by pulse laser deposition, in order to reduce the work function of CNTs so that electron field emission can be controlled for FET applications. Here the main purpose was the coverage of a carpet type layer of CNTs, instead of individual CNTs. However, in this work synthesis and phase formation was not addressed [7]. Recently, Zang *et al.* [14] have used CNTs as a top electrode for photovoltaic heterojunctions (CNT/BiFeO₃ (BFO)/Pt) so that the effective surface of the top electrode increases due of the high aspect ratio of CNTs and enhance the exciton dissociations and carrier transportation process. They found enhanced photovoltaic properties.

Recently special attention has been paid to materials, designated as multiferroics that possess two or more ferroic properties, as ferroelectricity, ferroelasticity and ferromagnetism. The possibility of combining and controlling two different physical phenomena in a single material is indeed considered the epitome of functionally. Multiferroics are because of that very promising from the technological point of view for modern electronics, as memory elements, sensors, and spintronics. Bismuth ferrite (BiFeO_3 , BFO) is one of the few single phase multiferroic materials. BFO has a rhombohedral distorted perovskite structure with space group of $R3c$ and displays ferroelectricity below 820 - 830 °C and antiferromagnetism below 370 °C [15]. BFO has a very large intrinsic polarization (theoretically predicted to be

as high as $90 - 100 \mu\text{C}/\text{cm}^2$) [16] and room – temperature multiferroism. This predicted high switching polarization is indeed higher than the one of the most commercialised ferroelectric material for memory applications (PZT based compositions). So besides the multiferroic properties and due to the large remanent polarization BFO is a promising material for applications in which polarization switching will be required (as memory applications). Indeed BFO is the ferroelectric material of Fujitsu 256Mbit FRAMs [17]. However, it is challenging to obtain monophasic BFO that is almost always accompanied with second phases, such as $\text{Bi}_{25}\text{FeO}_{39}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ [18]. In addition high dielectric losses, leakage current and tendency to fatigue are the main hurdles to overcome of BFO for any kind of electronic applications.

Due to the technological importance of nanostructured materials, efforts have been made to fabricate nanostructures of BFO [19, 20]. Template-assisted methods have been adopted to grow BFO-nanorods arrays on substrates. Researchers used Anodic Aluminum Oxide (AAO) Template Assisted Growth [21, 22] and template free strategy to fabricate 1D BiFeO_3 structures [23-25]. BFO 1D nanostructures have been also produced for 3D memory cells by depositing BFO on ZnO nanorods by RF sputtering using LaNiO_3 as a buffer layer at 450°C ; these nanostructures depict piezoelectric coefficient of 32.93 pmV^{-1} and a polarization of $133 \mu\text{C}/\text{cm}^2$ [26].

However, in spite of the above studies, there is no report on the fabrication and characterization BFO films on VA-MWCNTs. In this work BFO is sputtered on the top of VA-MWCNTs. Due to the high crystallization temperature of ferroelectrics ($> 650^\circ\text{C}$) and the need of oxygen atmosphere, that favour the decomposition of CNTs (the lattice of carbon skeleton CNTs starts to oxidize above 420°C [27]) the pressure / temperature window to process BFO on MWCNTs is predicted to be narrow. Indeed the crystallization temperature of BFO is similar to the oxidation temperature of CNTs. Because it is a challenge to grow

complex oxides (like ferroelectrics) on the surface of CNTs, the effect of the deposition parameters on the phase formation and morphology of the films is investigated in this work. The macroscopic and local electrical and magnetic properties of BFO films on MWCNTs are quantified.

2. Experimental

Bismuth oxide (Bi_2O_3 assay 99.5 %, Riedel-deHaën) and iron oxide (Fe_2O_3 Merck assay 99 %) powders were used as precursors for the synthesis of BiFeO_3 targets. The powders were mixed according to the BFO stoichiometry in a ball miller for 24 h using ethanol as media. The mixed powders were dried in an oven at 100 °C for 24 h followed by a calcination step at 720 °C for 3 h. The BFO calcined powders were then ball milled for 24 h to obtain a finer particle size distribution. Next, these powders were uniaxially pressed in a 60 cm diameter mould with an applied pressure of 1.5 MPa and finally heat treated at 800 °C for 4 h to obtain a dense ceramic target for sputtering.

VA-MWCNTs grown on Si substrates with diameter and length of 5-20 nm and 1-2 mm, respectively, were used as sputtering substrates (CVD Materials Corporation, USA). BFO deposition was carried out in a RF sputtering unit (CRIOLAB - Equipamento Criogénico e de Laboratório Lda) at different temperatures and exposure times in an atmosphere of argon/oxygen with a flow rate of 15 and 5 sccm, respectively, and working pressure of 7×10^{-4} Torr. The deposition was carried out at 60 W and working distance of 100 mm.

The phase formation of BFO was studied using X-ray powder diffraction (XRD, Philips X'Pert, Cu-K α source). The BFO morphology, chemistry and interface to the VA-MWCNTs were characterized by scanning electron microscopy (SEM, Hitachi S70, 25 kV) and transmission electron microscopy (TEM, JEOL2200FS, 200 kV, or FEI Titan, 300 kV).

The dielectric responses of BFO, CNTs and BFO/CNTs composites were measured using a precision LCR (inductor capacitor resistor) meter (Model HP4284A, 1-1000 kHz) connected to a PC via a GPIB card and working in the frequency range from 1 kHz to 1 MHz. P-V loops were measured in a ferroelectric test system (aixACCT, TF ANALYZER 1000 Measurement System). Topography analysis and local piezoelectric response was measured using a MFP-3D Asylum Research Atomic Force Microscope, equipped with Zurich Instruments (HF2LI) external lock-in amplifiers and a Tektronix (AGF320) function generator. The measurements were carried out using a soft cantilever XSC11 platinum coated with spring constant of 0.1-0.4 N/m and resonance frequency of 15 kHz. Raman spectrum was carried out in a HR 800, Jobin Yvon spectrometer, using the excitation line of 532 nm. Cryogenic VSM was used to measure the magnetic behaviour of the sample up to 10 T at room temperature.

3. Results and discussion

XRD patterns of BFO targets and films deposited on VA- MWCNTs synthesised in-situ at 400 °C and 600 °C are illustrated in Fig. 1. The BFO target depicts almost pure BFO rhombohedral phase with minor amounts of secondary phases ($\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_{40}$). The diffraction peaks from the planes (012), (104), (110), (113), (006), (202) and (211) are indexed to the R3c crystal symmetry. At 350 °C the deposited BFO is amorphous as seen by XRD. BFO deposited on VA-MWCNTs at 400 °C for 1 and 2 h is almost monophasic, with trace amounts of Bi_2O_3 (Fig. 1). To note that Bi_2O_3 does not have significant effect on the magnetic properties, while increasing the conductivity of the film [28]. Moreover, its amount can be reduced by changing the oxygen partial pressure [29]. As the growth temperature increases from 400 °C to 600 °C, formation of the non-perovskite phase $\text{Bi}_2\text{Fe}_4\text{O}_9$ takes place (Fig. 1). Indeed there is a very narrow temperature window in which pure monophasic BFO can be obtained, depending on processing parameters [30] and purity of the reagents [31].

Secondary phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{25}\text{FeO}_{40}$ reduce significantly the electrical response, therefore they should be avoided. In addition, BFO sputtered on VA-MWCNTs at room temperature and later annealed at 500 °C (ex-situ) in air and in flowing nitrogen depicts Bi_2O_3 as the major phase with small amounts of BFO and $\text{Bi}_2\text{Fe}_4\text{O}_9$, as observed by XRD (Fig. S1). Considering the above, BFO films deposited at 400 °C on VA-MWCNTs were used for further characterization.

The optical micrographs of VA-MWCNTs and BFO on VA-MWCNTs are represented in Fig. 2 (a) and (b), respectively. The complete covering of VA-MWCNTs by the brownish layer of BFO can be seen. In order to check the microscopic morphology the films fabricated at 400 °C with varying time were investigated by SEM (Fig. 3). SEM micrographs of BFO on VA-MWCNTs at 400 °C for deposition times of 1 and 2 h depict uniform coverage on the aligned tubes with rough topography. However, as the deposition time increases (above 2 h) films become porous what may result from the partial or local oxidation of MWCNTs, due to isothermal heating at ~400 °C for prolonged periods of time. Indeed isothermal heating near 400 °C in air results in the oxidation of MWCNTs as reported before [27].

VA-MWCNTs (400 °C - 2 h) covered with BFO were removed from the substrate and observed under HRTEM (Fig. 4). There is a uniform covering of VA-MWCNTs with BFO films with average thickness of 150 nm. Detailed observation of VA-MWCNTs coated with BFO revealed tubes coverage thickness of about 5 - 10 nm in size (Fig. 4 (b)). The inset (marked by a circle in Fig. 4 (b)) depicts VA-MWCNTs lattices with spacing of 0.34 nm and also intact carbon nanotubes; no visual damage after deposition of BFO can be seen from HRTEM (Fig. S2 TEM micrograph of as received VA-MWCNTs). BFO crystalline particles with lattice spacing of 0.27 nm from d110 plan are also specified in the micrograph. EDS (Energy-dispersive X-ray spectroscopy) on coated VA-MWCNTs identifies Bi, Fe and O

elements (Fig. 4 (c)) and the elemental mapping proves the uniform distribution of Bi, Fe and O throughout the BFO layer (Fig. 5). Under the current experimental settings the best conditions for the fabrication of BFO by in-situ rf sputtering on VA-MWCNTs are 400 °C with deposition time between varying between 1 and 2 h for which there is no damage of the morphology of BFO films and MWCNTs.

BFO films on VA-MWCNTs were further characterized by RAMAN spectroscopy (Fig. 6 (a)). VA-MWCNTs used in this work depict two characteristic peaks at 1336 and 1575 cm^{-1} corresponding to D and G band respectively, where the D band is attributed to the breathing vibration of aromatic rings of carbon in the lattice, indicating the defect level of CNTs and G band corresponds to E_{2g} mode where atoms of the carbon unit cell vibrate tangentially to each other [34]. After the BFO deposition the D and G band of MWCNTs shift to high frequency by $\sim 2 \text{ cm}^{-1}$ and the full width half maximum of the peaks also decreases due to less phonons interaction [11]. The shift in Raman peaks gives the information of the stress level of the MWCNTs [32]. In our case, because the observed shift there is quite small stresses developed at the interface are not so strong, as observed for example for MWCNTs covered with PZT by pulse laser deposition [10, 11]. The change in the intensity ratio of D and G bands (I_d/I_g) is 1.0 and 1.2 for the MWCNTs and BFO coated VA-MWCNTs of this study, respectively. The increase in the intensity ratio after BFO deposition, may state that the BFO layer constrain the vibration motion of carbon lattice and results in the increase of D band intensity; other possible reason for this shift can be related with the loss of structure, the conversion of significant number of sp^2 hybridized carbon to sp^3 carbon hybridization during deposition of BFO [33]. From the Raman results one can also conclude that MWCNTs do not deteriorate significantly during the in-situ growth of BFO films at 400 °C corroborating the previous observations.

The group theory predicts 13 Raman active modes $4A_1 + 9E$ for rhombohedral lattice type with $R3c$ space group, as is the case of BFO. Fukumura *et al.* [34] found all the 13 Raman active mode for BFO cubic single crystals [111] at 4 K (A_1 147, 176, 227, 490 cm^{-1} and E 265, 279, 351, 375, 437, 473, 525, 77, 136 cm^{-1}). In the present studies of BFO films on VA-MWCNTs, very weak Raman modes were observed at 121, 245, 458 and 612 cm^{-1} , where 121, 245 and 458 cm^{-1} peaks are from A_1 mode, 245 and 612 cm^{-1} are from E mode (Fig. 6 (b)). The Raman modes observed for BFO on VA-MWCNTs shift towards lower frequency when compared with the Raman mode observed for bulk BFO [35]. As well known in thin films soft modes are very sensitive to strain and nano structuring and generally it results in the shifting of Raman peaks; the shift upwards in the frequency results from compressive stresses while tensile stresses cause downwards shifts [36]. Therefore, the shift of Raman peaks to lower frequency, as here observed, indicates that BFO films on MWCNTs are in tensile state.

The capacitance, losses and P-V loops were measured on BFO - MWCNTs composites and are depicted in Fig. 7. BFO-MWCNTs composites show capacitance of 9 pF and dielectric losses ~ 0.02 at 1 MHz, for an applied voltage of 0.1 V. Lossy P-V loops were observed with polarization values around 1.5 - 2 $\mu\text{C}/\text{cm}^2$ at 50 and 100 Hz respectively. Indeed one main limitation of BFO (bulk, films and nanostructures in general) are the high dielectric losses and low resistivity. It is now well recognised that the lossy polarization behaviour of BFO is mainly extrinsic, i.e. created by space charge, defects, cationic and anionic vacancies, etc. The existence of oxygen vacancies has been related to the reduction of Fe^{3+} species to Fe^{2+} $[\text{Bi}(\text{Fe}^{2+}\text{Fe}^{3+})]\text{O}_{3-d}$ and Bi deficiency ($\text{Bi}_{1-x}\text{FeO}_{3-d}$) due to the high volatility of Bi [37-40]. In the present case the synthesis of BFO carried out in reduced oxygen pressure might have contributed to oxygen vacancies formation [41] and in addition the CNTs and BFO interface and topography might have contributed as well to enhance the

conduction behaviour of BFO. Because lossy hysteresis loops may hinder the ferroelectric behaviour, therefore domain switching and local electrical polarization were studied by PFM.

Topography and PFM phase response of BFO films (on top of VA-MWCNTs) were simultaneously acquired with the application of 5 V at 30 kHz between the tip and the ground electrode (MWCNTs) (Fig. 8 a-b). The rms roughness of the BFO on VA-MWCNTs is 25 nm for $2 \times 2 \mu\text{m}^2$ scan area; this is due to non-uniform surface of VA-MWCNTs. No well-defined grain boundaries can be seen from the topography micrograph for BFO. Nevertheless, the line profile from topography image and piezoresponse depicts most of the response are consisting of mono domains (Fig. 8 (c)). The piezoresponse image is characterized by strong domain contrast: deep bright and dark areas indicate significant out of plane components of polarization. There is a small fraction of regions with poor contrast likely corresponding to domains with polarization directed parallel to the surface. The piezohistogram acquired from the piezoresponse micrograph depicts the bi-modal distribution of the domains for BFO on VA-MWCNTs (Fig. 9 (a)). The deconvolution of the piezohistogram into two peaks was done to emphasise the covered area with positive and negative domains. The out of plan phase response centre is 32° for the positive phase and $\sim 42^\circ$ for negative domains (Fig. S3). From the fitting peaks and area under them it is clearly suggested that most of the domains are oriented along the applied field. There is a very small area which is not covered by the two fitting peaks and is representing the number of domains which do not show out of plane response.

BFO on VA-MWCNTs was further characterized by point poling to investigate its ferroelectric behaviour. The point poling was performed on two areas, where domains are showing the dark contrast (marked by cross in Fig. 9 (b)). The marked area on the left of the micrograph was poled by - 30 V and the marked area on the right of the micrograph was poled by + 30 V each for approximately 30 s. After poling both the areas, the piezoresponse

was acquired with the application of 5 V depicted in Fig. 9 (b) (poled area marked by cross). The piezoresponse from the area poled with -30 V, reveals no significant change in the contrast. However, the area poled with +30 V shows a change in the contrast of the area, which confirms the switching of domains with the application of DC bias.

The above poling results indicate that BFO domains can be switched with the application of an electric field. To further strengthen this claim of ferroelectric nature of the BFO on the surface of MWCNTs switching spectroscopy PFM (Switching spectroscopy, SS-PFM) with frequency of 0.2 Hz and period of individual pulses of 0.5 ms, was carried out. Fig. 10 illustrates ferroelectric hysteresis loop and amplitude loop obtained with the application of ± 30 V DC bias. A square PFM loop was obtained with coercive bias of ± 10 V. In PFM the measurements are local and come from individual grains or adjacent grains, which reflects more or less single crystal properties. It was proved that BFO films on VA-MWCNTs in spite of the low synthesis temperature and lossy polarization macroscopic response exhibit local ferroelectric behaviour where switching of ferroelectric domains is possible under an applied field.

In order to confirm the magnetic nature of these BFO films, the magnetization was measured as the function of applied magnetic field (H) of -10000 Oe to 10000 Oe at 300 K (room temperature, RT) and given in Fig. 11. M-H hysteresis curves of BFO films on VA-MWCNTs at 400 °C for 2 h depict unsaturated hysteresis loops, indicating the R3c structure with antiferromagnetic nature, similar to the one observed for polycrystalline BFO bulk or single crystals [35]. However, a small coercivity ($2H_c$) of 700 Oe was observed for these BFO films (represented as inset of Fig. 11). The weak ferromagnetic behaviour was also observed for nanoparticles and thin films of BFO as reported before [28, 42]. There are two possible explanations for the weak ferromagnetism in BFO films and nano particles: first, strain effects and oxygen vacancies associated with Fe^{+3} ions in BFO and second, size effects

where below 62 nm size the uncompensated spins at the surface of the particle arise [24, 43, 44]. Indeed it is clear from the TEM micrographs of BFO films on VA-MWCNTs that the crystalline particles of BFO around the MWCNTs are smaller than 10-20 nm and the small shift in the Raman peak of MWCNTs after BFO deposition also indicates the existence of strains. Therefore, one can assumed that the weak ferromagnetic behaviour of BFO on VA-MWCNTs may be due to the combined effect of strain and size effects. Similar unsaturated weak ferroelectric loops were also reported for BFO nanotubes synthesised by chemical solution methods [22]. The shift in the hysteresis loops shown in inset of Fig. 11, can be ascribed to the presence of exchange coupling between the ferromagnetic surface and antiferromagnetic cores. The self-orientation of the magnetic domains during the synthesis can also be one of the reasons for the shift in the ferromagnetic loop from the origin.

4. Conclusions:

BFO films on VA-MWCNTs can be successfully deposited by RF sputtering at 400 °C without damaging the morphology of both the tubes and films. SEM and HRTEM studies prove the conformal covering of MWCNTs with BFO. These composite structures (BFO on MWCNTs) present a lossy macroscopic hysteretic response with low polarization values of 1-2 pC/cm². In spite of that locally at the nanometric scale domains can be reversed from one direction to another under the applied field. It is also clear from the M-H curve that BFO films on VA-MWCNTs are antiferromagnetic without any saturation. The small opening of the magnetization loop near zero indicates the presence of a week ferromagnetic nature of these BFO films which might be due to size and/strain effects. The results here presented are a proof that BFO films on aligned MWCNTs can find potential applications in photovoltaics, memories and other microelectronic applications.

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Figure Captions

Fig. 1. XRD spectra of BFO target and BFO films on VA-MWCNTs fabricated in-situ at 400 °C - 1 h, 400 °C - 2 h and 600 °C - 1 h. With the increase in deposition temperature to 600 °C secondary phases are well visible.

Fig. 2. Optical images of (a) dense VA-MWCNTs on Si substrates and (b) BFO sputtered on the surface of VA-MWCNTs, deposited at 400 °C for 2 h. BFO covers uniformly the VA-MWCNTs.

Fig. 3. Top view SEM micrographs of BFO on VA-MWCNTs deposited at 400 °C for (a) 1 h (b), 2 h and (c) 4 h. Dense BFO films on VA-MWCNTs are obtained at 400 °C with a deposition time of 2 h.

Fig. 4. HRTEM micrographs of BFO on MWCNTs deposited at 400 °C for 2 h (a). Magnified view of one of the tubes with a 5 nm BFO thick layer (b). A d spacing of 0.34 nm and 0.27 nm was measured for MWCNTs and BFO, respectively (b). EDS confirms the presence of Bi and Fe.

Fig. 5. SEM elemental maps of MWCNTs coated with BFO at 400 °C for 2 h (a): bismuth (b), iron (c) and oxygen (d) showing a uniform distribution of elements.

Fig. 6. Raman spectra of VA-MWCNTs and BFO on VA-MWCNTs (a); comparison of characteristic peaks of MWCNTs and BFO (b). The shift in Raman peaks states that CNTs and BFO on top of CNTs are under stress.

Fig. 7. Hysterisis loop (a) and dielectric permittivity and losses as a function of frequency (800 Hz to 1 MHz) (b) for BFO films on VA-MWCNTs sputtered at 400 °C for 2 h.

Fig. 8. Topography (a), out of plane piezoresponse (b) and line profile from topography and piezoresponse (c) from BFO films on VA-MWCNTs. The dark and bright contrast from domains of these BFO films is clearly visible.

Fig. 9. Point poling was performed on the area marked by cross, with -30 V on left and +30 V on right: phase response (out of plane) before poling (a) and phase response (out of plane) after point poling for BFO films on MWCNTs (b).

Fig. 10. Phase hysteresis loop (a) and amplitude loop (b) from BFO films on MWCNTs acquired for 30 V.

Fig. 11. Magnetic hysteresis of BFO on VA-MWCNTs at 300 K up to 10000 Oe. BFO on VA-MWCNTs depicts the week ferromagnetic response with $2H_c = 700$ Oe.

Figures

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(b)

(c)

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Fig. S1 XRD of BFO deposited on VA-MWCNTs followed by annealed at 500 °C – 2 h in air shows poor crystallization and domination of secondary phases.

Fig. S2 HRTEM micrograph of as received VA-MWCNTs, with well-defined carbon walls and covered with amorphous carbon layer.

Fig. S3 Phase piezohistogram of BFO on VA MWCNTs.