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Antiferroelectric-like behavior in polycrystalline $Pb(Zr_{0.2}Ti_{0.8})O_3$-$BiFeO_3$ multilayers prepared by sol-gel method

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$Pb(Zr_{0.2}Ti_{0.8})O_3$-$BiFeO_3$ (PZT-BFO) multilayer structures were realized by sol-gel on Pt/Si substrate and their electrical properties were investigated using top Pt, Au and Cu electrodes. All multilayers start and end with PZT films. The polarization-voltage and current-voltage hysteresis loops resemble to those encountered in case of antiferroelectric (AFE) films, although component materials are both ferroelectric (FE). The AFE-like behavior is more clearly visible in the case of three-layer structures of PZT-BFO-PZT type, and it is not dependent of the metal used as top electrode. After fatigue cycling the polarization hysteresis apparently changes from characteristic AFE double-loop to FE single loop, although the four switching current peaks characteristic for an AFE behavior are still present in the current hysteresis. These results suggest the presence of an AFE interfacial coupling between the PZT and BFO layers.

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1. Introduction

Ferroelectric multilayers and super-lattices are subject to intensive studies because offer the possibility to obtain structures with superior properties compared to the component materials. Significant enhancement of the polarization or dielectric constant were obtained by combining materials with perovskite structure and different properties, such as $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, $Pb(Zr,Ti)O_3$, $SrTiO_3$ and others [1-6]. Another important aspect is that the physical properties of multilayers or super-lattices can be tuned by changing the thickness of the component layers or by adjusting the strain and charge conditions at the separation interface between the component films [7].

A controversial problem is the presence of antiferroelectric (AFE)-like behavior in multilayers of ferroelectric (FE) materials. It is thought that the fingerprint for an AFE behavior is the presence of the double-loop in the polarization-voltage (P-V) hysteresis, similar to the double loop shown by the $PbZrO_3$ films, which is the prototype of AFE materials [8]. However, there are experimental reports showing that it is possible to obtain double-loop hysteresis even in the case of FE materials [9]. It was explained that, more generally, a double-loop is characteristic for a field-induced transition from a state characterized by zero net polarization (e.g. paraelectric state), to a state with non-zero net polarization [10]. Double-loops were reported in the case of some FE ceramics, also [11-13]. This were explained by the model of ”pinched” hysteresis, saying that part of the polarization cannot switch due to internal constraints (charged defects, internal stress, etc.), thus the polarization at low fields is smaller than normal. These constraints can be removed by raising the temperature or by repeated cycling, after which the hysteresis turns to a normal FE shape. A model was developed to explain this behavior [14].

There are several reports about the experimental observation of double-loop-like hysteresis in the case of FE multilayers [15-18]. The explanations are divided between “pinched” hysteresis due to domain pinning on charged interface defects, and AFE coupling between component layers. There are also some theoretical works predicting that an AFE behavior is possible if there is an antiferroelectric coupling at the interface and the thickness ratio is in a certain range of values [19-21]. Therefore, the problem of the AFE-like behavior in the case of FE multilayers is far from being solved.

A possible cause can be the fact that the reports show either only the hysteresis loops, or only the capacitance-voltage (C-V) characteristics. The behavior of the current hysteresis was never discussed. We remind that an AFE-like behavior is characterized by the simultaneous presence of: double hysteresis loop; four peaks in the current hysteresis, two peaks of opposite sign for each polarity; and four peaks in the C-V characteristics [22]. Only two current peaks of opposite sign are observed in the current hysteresis, and two peaks in the C-V characteristic, in the case of a FE-like behavior.

Someone can argue that the hysteresis loop (D~V, with D, the electric displacement), the C-V characteristic (C~V), and the current-voltage hysteresis (I~V, I is the current) are related and cannot bring supplemental information as long as they have the same source, namely D. For example:

$$C = \frac{\varepsilon A}{d} = \frac{A}{d}\frac{\partial D}{\partial E} \tag{1}$$

where A is the area of the electrodes and d is the thickness of the ferroelectric capacitor. It results that the C-V characteristic can be obtained by simply differentiating the hysteresis loop and vice-versa, the hysteresis loop can be obtained by integrating the C-V characteristic. On the other hand, the density of the displacive current is given by:

$$j = \frac{\partial D}{\partial t} = \frac{\partial D}{\partial E}\frac{dE}{dt} \tag{2}$$

Equation (2) shows that the current-voltage hysteresis can be also obtained by differentiating the hysteresis loop if dE/dt, the variation rate of the applied field, it is known. This is constant in the case of a triangular-shape ac signal. The above observations are valid for an ideal ferroelectric crystal, with no structural defects and no leakage. In real crystals they are not valid. In most cases the C-V characteristic is not coincident with the derivative of the hysteresis loop and the leakage current adds to the displacive one, inflating the hysteresis loop. Regarding the current-voltage hysteresis, its showing is important not only as evidence for the presence of ferroelectricity but also for discerning between AFE behavior and "pinched" hysteresis. This will be detailed in the **Discussions** section.

In this paper we are presenting experimental results suggesting the presence of AFE-like behavior in multilayers made from $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) and $BiFeO_3$ (BFO) materials. Both are ferroelectrics and with large values of spontaneous polarization, around 100 μC/cm^2 as recently reported [23,24].

2. Experiment and results

The multilayers were deposited by sol-gel method on standard Pt/Si substrates. The BFO sol was prepared using hydrated bismuth nitrate ($Bi(NO_3)_5{*}5H_2O$), iron (III) nitrate ($Fe(NO_3)3{*}9H_2O$), acetic anhydride and thriethanolamine. The PZT sol was prepared by using lead acetate, titanium iso-propoxide and zirconium n-butoxide. 2-metoxiethanol was used as solvent. The Bi and Pb losses during the thermal annealing were compensated by adding 10 % molar Bi and 5 % molar Pb excess respectively, in precursor solutions. All the multilayers start and end with PZT films. The general formula is $(PZT\text{-}BFO)_{(n-1)/2}$+PZT, where *n* is the total number of layers. This means that the 3-layer structure has one PZT-BFO pair plus a top PZT layer, 5-layer structure has 2 PZT-BFO pairs plus top PZT layer, and so on. The top PZT layer was deposited to ensure the symmetry of the structure. Crystallization annealing was performed after each layer deposition. The PZT films were crystallized by rapid thermal annealing (RTA) at 650 ^{0}C/15 min, while the BFO layer were crystallized by RTA at 600 ^{0}C/10 min. From SEM photographs (not shown) the thickness of an individual layer was estimated to about 50 nm. The X-ray diffraction (XRD) analysis performed on the 3-layers structure had revealed the presence of the characteristic peaks for PZT and BFO, as shown in Fig. 1. This fact suggests that the repeated crystallization treatments do not change the multilayer structure into a PZT-BFO solid-solution through the inter-diffusion of the component elements. Top Au, Cu and Pt electrodes of 0.2 mm^2 were deposited by radio-frequency sputtering for electrical measurements. A TF2000 ferroelectric thin film analyzer was used for hysteresis measurements, while the capacitance-voltage (C-V) characteristics were raised using Agilent 4263B LCR meter.

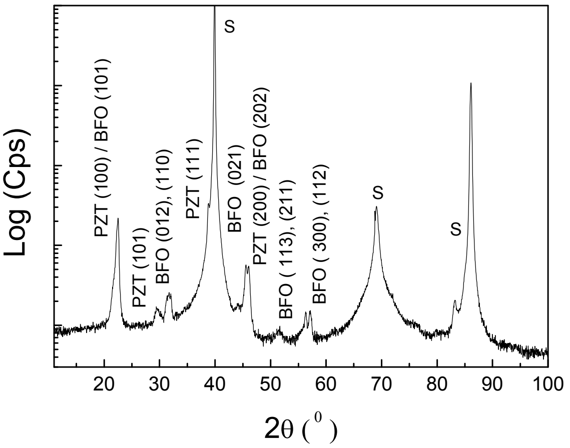

Fig. 1 The XRD spectra for a 3-layer PZT-BFO structure. "S" stands for substrate.

The results of the hysteresis measurements performed on the multilayers are shown in Fig. 2a, polarization-voltage (P-V), and 2b, current-voltage (I-V), respectively. The P-V hysteresis in the case of the 3-layer structure clearly shows a double loop similar to antiferroelectric materials like $PbZrO_3$. This is confirmed by the current hysteresis, which shows two switching peaks of opposite sign for each polarity of the applied voltage, also similar to those encountered in the case of $PbZrO_3$ [22]. For the 5 and 7 layers structures the AFE behavior is not visible in the P-V hysteresis, but it is visible in the I-V hysteresis by the presence of 4 (four) characteristic switching peaks. It has to be noticed that the peaks occur at about the same voltages for all multilayers, although they become broader and show the tendency to merge in two peaks of opposite sign as the number of layers increases. This can explain why the hysteresis loop has a FE-like shape for the structures with 5 and 7 layers. This appearance may be deceiving when only the P-V hysteresis is analyzed, without considering the I-V hysteresis, and can lead to erroneous conclusions.

Further-on we will focus on the 3-layer structure. Fig. 3a shows the hysteresis loops recorded for the three metals used as top contacts. The double loop hysteresis occurs in all cases, suggesting that the AFE-like behavior is not induced by extrinsic effects taking place at the metal-PZT interface but is an intrinsic property of the PZT-BFO stack. Fig. 3b shows capacitance-voltage (C-V) characteristic for a 3-layer structure with top Au contacts. Again, the AFE behavior it is suggested by the presence of the 4 (four) capacitance peaks when the dc voltage is swept up and down.

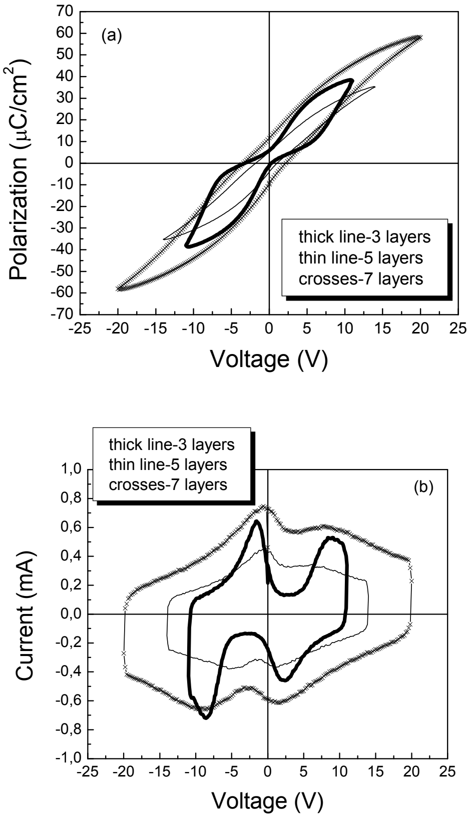

Fig. 2 The hysteresis polarization-voltage (a) and current-voltage (b) loops for PZT-BFO multilayers. The frequency of the triangular voltage was 1000 Hz, measurements performed in the dynamic mode on Au top contacts.

Finally, the stability of the AFE behavior during repeated cycling of polarization was tested by performing a short fatigue treatment up to 10^5 cycles, with a frequency of 1000 Hz and amplitude of 8 volts. Apparently, at the end of the fatigue experiment the hysteresis loop turns to a FE-like shape, although the multiple current peaks are still visible in the current hysteresis. We remind that the hysteresis loop is obtained by integrating the total current flowing through the multilayer, including the leakage current. This one may be sensitive to the potential non-uniformities in the multilayer, associated with the presence of interfaces. The potential non-uniformities (barriers) can change during repeated cycling, due to re-arrangement of the charged defects. This will lead to changes in the voltage dependence of the leakage current, with impact on the shape of the hysteresis loop [25]. Therefore, the FE-like shape after repeated cycling can be deceiving, suggesting ferroelectric behavior when the multilayer is still antiferroelectric. Similar results were obtained in case of structures with 5 and 7 layers, although the apparent change from AFE to FE behavior occurs after a smaller number of fatigue cycles.

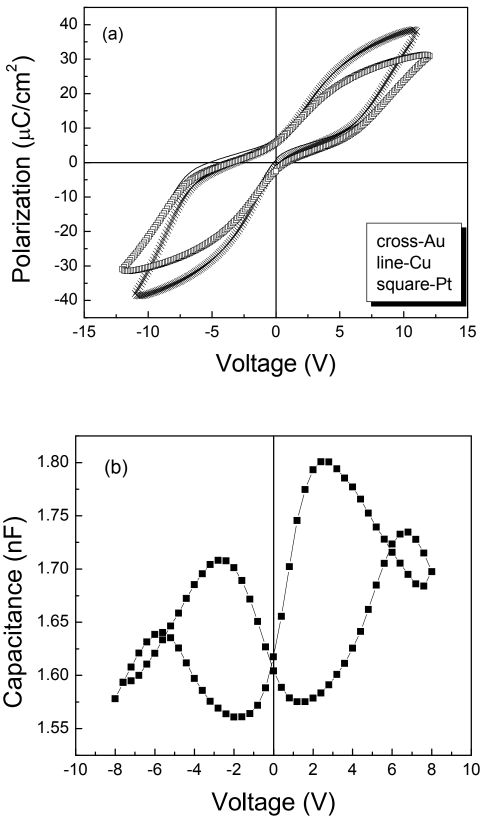

Fig. 3 a) The polarization-voltage hysteresis loops obtained in the case of 3-layer PZT-BFO structure with Au, Pt and Cu top electrodes; b) Capacitance-voltage characteristic for a 3-layer structure with top Au contacts.

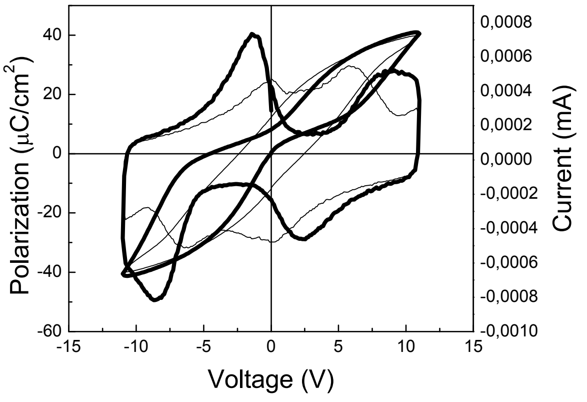

Fig. 4 The hysteresis polarization-voltage and current-voltage loops obtained at the beginning (thick line) and at the end (thin line) of a fatigue treatment up to 10^5 cycles. Measurement performed on 3-layer PZT-BFO structure with top Au contacts; the fatigue signal had a frequency of 1000 Hz and amplitude of 8 V.

3. Discussions

The presence of the AFE-like behavior supports the conclusion that the multilayers are not transforming into PZT-BFO solid solutions during crystallization annealing, because only FE behavior was reported in this case [26,27]. As mentioned in the introduction, there are two possible explanation for the double-loop observed in the present PZT-BFO multilayers: the model of "pinched" hysteresis; the presence of an AFE coupling at the PZT-BFO interface. We will discuss these possibilities.

Model of "pinched" hysteresis is based on the assumption that the charged defects in the material are producing local internal fields which can block the polarization reversal, thus leading to different values of the coercive field [14]. Simplifying this, we may consider the case of two different values for the coercive field. Schematically, the hysteresis loop will look like the one presented in Fig. 5. Assuming that in the initial state the polarization is fully oriented in one direction, for example positive, first will switch the volume of the sample with lower coercive field when the applied voltage starts to decrease towards negative values. This is equivalent to a drop in the polarization value because the flowing charge has opposite sign to the one already integrated on the reference capacitor in the Sawyer-Tower circuit. When the applied voltage reaches the value corresponding to the higher coercive field, then the rest of the polarization will switch. Now all the polarization will be oriented on the negative direction. The similar process will take place when the voltage is changed from negative to positive. The result will be a "pinched" hysteresis, a hysteresis constricted at low values of the applied field. After several switching cycles (aging) the constriction disappear, the two peaks merge in one peak, and the loop turns to a standard FE behavior with a single value for the coercive field. This happens most probably due to a redistribution of the charged defects, leading to a homogeneous distribution of the internal field. Eventually, the internal field is seen as a shift of the loop on the voltage axis. What it is important to note in this case of "pinched" hysteresis is that the current peaks corresponding to polarization switching have the same sign. Therefore, if there will be more values for the coercive field then we will have successive switching peaks, but all having the same sign. If there is a continuous distribution of values for the coercive field then we will see the envelope of these successive switching peaks, like in the case of a slim hysteresis loop. This corresponds to a gradual switching of the polarization.

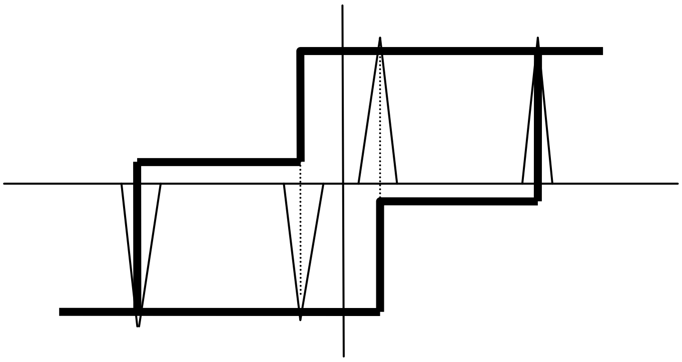

Fig. 5 Schematic of a hysteresis loop in case of a system showing "pinched" hysteresis. The triangles simulate the current peaks associated to polarization switching when the applied electric field reaches the value corresponding to coercive field. It is important to notice that the current peaks have the same sign for one polarity.

In the case of an AFE-like loop the successive current peaks corresponding to polarization switching have opposite sign, like in the schematic shown in Fig. 6. In this case there could be two volumes of the sample, with opposite orientations of the polarization, switching independently one from the other like in the case of a true AFE material. This can happen when the cause leading to the two volumes with opposite orientations of polarization is not aging with repeated cycling. A possible cause can be an AFE coupling at the interface, for example a difference in the polarization value of the neighboring layers. A split in 180 ^{0} domains it is possible in the layer with higher polarization because the system has the tendency to cancel the polarization difference and to bring to zero the net polarization charge at the interface. It is not very difficult to show that, in the layer with higher polarization value, an internal field opposed to the polarization direction will appear. This can induce the arrangement of opposite ferroelectric domains. This problem was analyzed in many papers, thus we will not detail it further more [28-30].

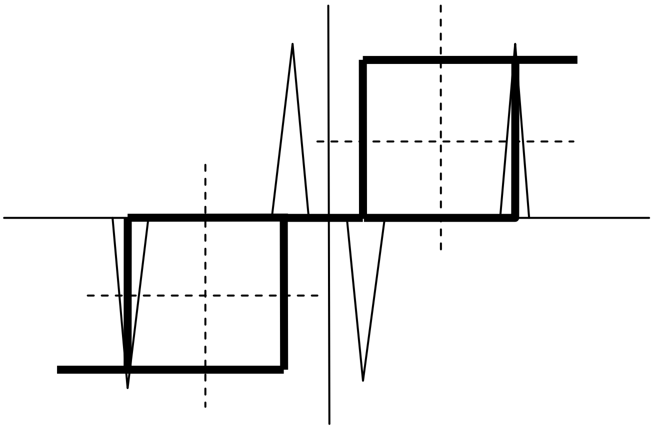

Fig. 6 Schematic of a hysteresis loop in case of a system showing AFE-like hysteresis. The triangles simulate the current peaks associated to polarization switching when the applied electric field reaches the value corresponding to coercive field. It is important to notice that the current peaks have the opposite sign for one polarity.

In the present case, the material with higher polarization is PZT. The remnant polarization measured at room temperature on single composition films is about 15 μC/cm^2 in PZT, compared to only 8 μC/cm^2 in BFO. Beside this, the BFO film is leakier compared to PZT. Therefore, we can assume that opposite 180 ^{0} domains occur in PZT layers, generating a kind of two "dipole sub-lattices" with opposite orientations of polarization, analogue to what is present in a true ferroelectric material like $PbZrO_3$. The observed double loop can be explained based on the schematic shown in Fig. 7. When the applied field is parallel to the polarization direction in one "sub-lattice", then switching will take place in the "sub-lattice" with opposite orientation until all polarization is parallel to the field. When the electric field is removed the system will turn back to the arrangement of 180 ^{0} domains presented in Fig. 7. Changing the direction of the applied field means that the other "sub-lattice" will switch. Always one "sub-lattice" will be parallel to the field and the other anti-parallel, thus only the last one will switch. During the switching cycles the charged defect may re-arrange, leading to some changes in the distribution of the local electric fields, including the interface regions. This can smear the double-loop behavior, as shown in Fig. 4, but the origin of the AFE-like behavior remains and is visible in the sign of successive switching peaks which still alternates from negative to positive even after 10^5 cycles. This is not possible in the case of a "pinched" hysteresis.

Regarding the polarization in the BFO layer, according to Fig. 7 it will switch only for one direction of the applied field. This will lead to a higher polarization for one direction compared to the other, visible as a shift of the hysteresis loop along the polarization axis. A closer analysis of the hysteresis loops presented in Fig. 3a shows that, indeed, the loops are shifted up, along the positive direction on the polarization axis.

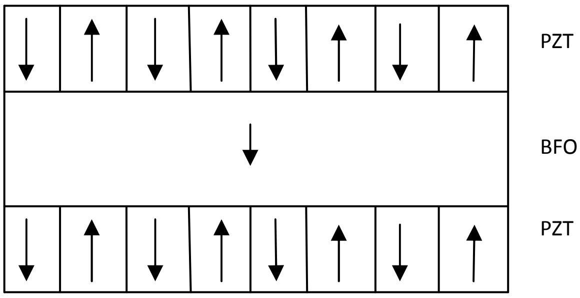

Fig. 7 Schematic of the domain arrangement in the PZT-BFO multilayer.

It has to be also noticed that theoretical models considering AFE coupling predicts AFE-like behavior for bilayers with components of equal thickness [19]. In our case the layers have a thickness of about 50 nm each, value similar to that of 40 nm reported in Ref. 15 and 16.

4. Conclusions

In conclusion, we have shown the presence of AFE-like behavior in multilayers made from PZT and BFO ferroelectric materials. The experimental results support the idea that the AFE behavior is related to AFE coupling at the PZT-BFO interface. The model of "pinched" hysteresis cannot explain the I-V hysteresis results, which are specific for AFE-like behavior. The reported results open the possibility to engineer multilayer structures with completely different macroscopic properties compared to the component layers, similar to metamaterials [31].

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