Resistive switching phenomena in thin ferroelectric films

N V Andreeva¹, A Petraru², A E Petukhov³ and A V Batueva¹

¹St. Petersburg Electrotechnical University “LETI”, Saint Petersburg, 197376, Russia
²Nanoelektronik, Technische Fakultät, Christian-Albrechts-Universität zu Kiel, D-24143 Kiel, Germany
³Research Park, St. Petersburg State University, Saint Petersburg, Russia

nvandr@gmail.com

Abstract. Switching of the resistance in thin ferroelectric films is a complex phenomenon involving an influence of polarization states, point defects, processes of electron injection from electrodes and peculiarity of polarization charges screening. In order to clarify the mechanism of surface charge screening under ferroelectric polarization switching and its correlation with the local resistive properties in thin ferroelectric films, we studied the changes in the surface potential under dc bias voltage application in SrTiO₃/La₀.⁷Sr₀.₃MnO₃/BaTiO₃ heterostructures using different modes of atomic force microscopy (Kelvin probe, piezoresponse, and conductive) at ambient conditions. It is found that the peculiarity of surface charge screening under polarization reversal gives a strong electrostatic contribution in the measurements of local resistive properties at the ambient conditions and could completely veil the real current distribution over the film surface. Remarkably, scanning tunnelling microscopy measurements under ultra-high vacuum conditions show evidence of oxygen vacancy formation in thin ferroelectric films after poling, revealing an increase of the film thickness due to the chemical expansion.

1. Introduction

Point defects in perovskite thin films could significantly affect their structural, electronic, and ferroelectric (FE) properties. Oxygen vacancies (defects in anion sublattice) are the most intensively studied ones in relation to aging and fatigue phenomena in FE [1-3]. The most common models of fatigue involve the mechanisms of the domain wall motion impeding or local polarization disturbance due to the presence of oxygen vacancies. Several plausible studies demonstrate that the polarization driven oxygen vacancy migration plays a key role in resistive switching effects observed in thin FE films [4-8]. It is claimed that oxygen vacancy migration is the sole reason for the resistive switching in all oxide tunnel junctions, including FE ones [9]. Moreover, oxygen vacancies could enable ionic conductivity in perovskite-based solid solution for solid oxide fuel cells [10]. Related with the structural properties, the presence of oxygen vacancies could induce an increase of volume (chemical expansion) [11] in perovskites, giving a significant impact on resistive properties of FE tunnel junction. Besides this, oxygen vacancies together with injected charges and charges from ambience could be considered as a sources of screening charges of the FE polarization at the surface and could strongly influence both the surface potential and polarization reversal behaviour in thin films [12]. Thus, the functional properties of thin ferroelectric films are governed by the interplay of ferroelectric polarization, peculiarity of surface charge screening, and oxygen vacancies distribution. On this way, a detailed study
of relative contribution of all above-mentioned factors to the resistive and FE properties of thin films opens a way for designing new materials with tailored functionality.

Toward this end, we study surface potential changes, dynamics of local FE properties, and oxygen vacancies migration accompanying the resistive switching effects in SrTiO$_3$/La$_2$O$_3$:Sr$_0.3$MnO$_3$/BaTiO$_3$ (STO/LSMO/BTO) heterostructures with thin FE films. In our previous studies, we experimentally observed that with increasing the thickness of epitaxial FE film in STO/LSMO/BTO structures the current through the structure associated with inelastic, trap-assisted tunnelling was slowly prevailing [13]. We attribute this result to the increase in the oxygen vacancies content in FE films with increasing their thickness. The shift from epitaxial state towards the polycrystalline structure is another way to increase the oxygen vacancy concentration in thin FE film due to the formation of crystallite boundaries. Thus, to elucidate the issues related to oxygen vacancies effect on resistive and ferroelectric properties, we opted for polycrystalline thin ferroelectric films. In order to analyse the nanoscale distribution of electric charges on the FE film surface, we combined Kelvin probe force microscopy (KPFM) and piezoresponse force microscopy (PFM) measurements in ambient conditions, with the resistive properties investigation by conductive atomic force microscopy (cAFM) in ambient conditions and scanning tunnelling microscopy (STM) under ultra-high vacuum (UHV).

2. Materials and methods

12-nm-thick polycrystalline BTO films were prepared on (001) LSMO/STO substrate by pulsed laser deposition (Fig. 1a,b). Gold top 10-15 nm thick electrodes were deposited on the BTO films by thermal evaporation sputtering. The electrodes were patterned using a stencil mask, which area ranged from 2 to 36 $\mu$m$^2$.

FE properties of fabricated heterostructures were measured by means of PFM, while for surface potential distribution noncontact KPFM regime was employed. Both KPFM and PFM measurements were performed under ambient condition using commercially available Pt-coated silicon tips and Veeco SPM instruments. During the PFM imaging, the bottom electrode was grounded, and an ac voltage was applied to the AFM tip. The poling procedure was done by applying dc voltage to the bottom electrode while keeping the grounded AFM tip in contact with the film surface.

In order to investigate the resistive properties of the fabricated heterostructures, I-V curves were measured using conductive AFM Pt-coated probes and tungsten STM tip by applying quasi-static voltage sweeps to the thick electrodes of the structure (in AFM regime) or bare film surface (in STM regime).

The tunnelling AFM and STM measurements were performed under UHV conditions at the resource centre “Physical Methods of Surface Investigation” (RC PMSI) of Research Park of Saint Petersburg State University. The pressure in the UHV chamber was below 3×10$^{-10}$ mbar. Before measurements, samples were heated up to 120$^\circ$ C and exposed for 24 hours in UHV to remove the adsorbed residual gas particles on a sample surface. The electrochemically etched STM tip was annealed in UHV to remove the oxide layer from the tip apex. The I-V curves were obtained in the tunnelling current range from 1 pA to 330 nA at room temperature using an Omicron VT AFM XA scanning probe microscope.

3. Results and discussion

The PFM image of the as-grown 12 nm thick BTO film (Fig. 1d-f) at ambient condition revealed the asymmetry of FE heterostructure, which may be partially attributed to the self-polarization effect [14]. The results of piezoresponse-voltage hysteresis loop measurements justify the existence of an internal bias field varying in the range of 0.1-0.4 V (Fig. 1c). The PFM images obtained after poling procedure showed that the spontaneous polarization had a preferred upward direction, as indicated by predominantly bright contrast of the area polarized with the positive (relatively to the BE) dc bias and areas outside of the polarized square on the film surface (Fig. 1e,f). In the absence of internal bias, positively charged oxygen vacancies should be compensated by negatively charged defects in the cation sublattice or electrons in accordance with the principle of electroneutrality [15]. The existence of internal bias should result in the internal charge redistribution in the film. For these reasons, we assume that in
a pristine state of the BTO film the oxygen vacancies are mostly concentrated at the interface of the structure with the bottom electrode (Fig. 2d), combining negative screening charges and metallic charges of the bottom electrode. While at the film surface, the positive polarization charges are partially screened by chemisorbed water molecules in ambient conditions.

Figure 1. (a) AFM topography image of the 12 nm thick polycrystalline BTO film; (b) a sketch of a STO/LSMO/BTO structure; (c) local piezoresponse-voltage hysteresis loops of the 12 nm thick polycrystalline BTO film measured on bare film surface in spectroscopic PFM regime; (d) AFM topography image of BTO film, the area of a bias voltage application is indicated; (e) PFM amplitude and (f) PFM phase images of the poled area.

Figure 2. (a) AFM topography image for 3 nm thick epitaxial BTO film surface scanned with different applied biases from -3.5 to +3.5 V; (b) PFM signal and (c) current map of the same area (taken under 1.5 V applied between the tip and the bottom electrode).
During the poling procedure, the polarization reversal is accompanied by charge carrier injection in the FE films. Here, we consider a charge carrier injection mainly from the bottom electrode, as the barrier for this interface is significantly lower compared with the barrier “FE film - Pt-coated AFM tip” (Fig. 3f). The injected charged (electrons) and charges from the ambience influence the surface potential of the BTO films. Changes in surface potential could give a critical impact on the study of the local resistive properties of thin FE films by means of conductive AFM (for example, studies of a tunnel electroresistance of FE tunnel junctions). The long-range electrostatic contribution (due to the changes in the surface potential) to the AFM cantilever buckling [16] could induce changes in the image of local current distribution over the FE film surface measured with the conductive AFM probe and could be misunderstood as a change in resistive properties associated with FE polarization switching (Fig. 2).

In order to investigate the surface potential change during the polarization switching in our structures, we applied a series of dc voltage bias to the BTO film by scanning rectangular areas with different biases in the range of -6 - +6 V (indicated with the scale bar in Figure 4a). Subsequently, we acquired the potential distribution and piezoresponse from the same area on the film surface. The application of positive bias does not affect the polarization state (Fig. 4c) of the film, as evidenced from the PFM phase image, but lowers the surface potential (Fig. 4a). The appearance of the bright contrast on the PFM amplitude signal may be attributed to the electrostatic charge effect between the cantilever and the film surface due to changes in internal charges. We consider two possible sources of changes in internal charge concentration for this polarity of the applied bias: electron injection from the AFM tip and oxygen vacancies formation in the FE film. According to I-V curve measurements (Fig. 4f), the level of electron injection from the AFM tip is relatively low at the values of applied positive voltage below 6-7 V. Under these circumstances, we cannot eliminate the formation of oxygen vacancies at the values of positive

![Figure 3](image-url)

**Figure 3.** (a) AFM topography image of nanocrystalline 3 nm thick BTO film, the area of a bias voltage application is indicated; (b) PFM phase images of the poled area; (c) AFM topography line profile obtained from (a); (d) STM topography of nanocrystalline BTO film surface region (1x1 μm², 10 pA, 1.5 V); (e) STM topography of nanocrystalline BTO film surface region showing an expansion of the film volume after scanning with negative (relatively to the BE) voltage; (g) I-V characteristics of nanocrystalline BTO film (obtained from (d) measured with STM at T = 295 K under UHV conditions (voltage sweep is measured relatively to the STM tip).
voltages exceeding the coercive voltage of FE film. Thus, we relate the observed surface potential change mainly to extra charges from the ambience neutralizing the extra amount of oxygen vacancies in the FE film. The application of negative bias voltage to the film below the coercive voltage produces an increase in surface potential without disturbing both PFM amplitude and PFM phase signals. In this case, the low barrier of the structure with the bottom electrode (Fig. 4d) implies electron injection in the FE film. No change in corresponding PFM amplitude image suggests that at the given level of a charge carrier injection, charge compensation does not induce a significant electrostatic contribution to the AFM tip–sample interaction. The maximum change of the surface potential is observed from the negatively biased region (scanned with a voltage of -3 V) and coupled with a polarization reversal. Corresponding change in the electrostatic interaction, visualized in the PFM amplitude image, arose from the compensation of the negative polarization charges on the surface and electrons injected from the bottom electrode by positive charges from ambience. Eventually, as decreasing the negative bias to -6 V, the amplitude of the surface potential decreases gradually. As estimated from the I-V curves (Fig. 3f), starting from approximately -5 V there is a sharp increase in the current through the FE film, influencing the internal charge distribution and screening conditions of the polarization charges. Summarizing the experimental results, we assume that local surface potential reflects the changes in the surface charge screening conditions as response to complex interaction between electron injection, oxygen vacancy formation, and polarization reversal in thin FE films.

Figure 4. (a) KPFM surface potential distribution of the 12 nm thick polycrystalline BTO film surface scanned with different applied biases from -6 to +6 V; (b) PFM amplitude and (c) PFM phase images of the same area; (d) Surface potential line profile obtained from (a), insets show a scheme of an interplay between the polarization state, inner and surface charges distribution for different biases.
For further understanding of the role of oxygen vacancy formation in electrical properties of thin FE films, we study the correlation of the surface morphology with local electrical properties. Due to the fact that chemical expansion is accompanied by the presence of oxygen vacancies in perovskite-structure materials, an increase in the film volume as response to the voltage bias application could indicate oxygen vacancies formation in the film. To ascertain this effect, STO/LSMO/BTO structures with nanocrystalline BTO films with thicknesses in ranging from 3 to 7 nm (the description of the sample fabrication and characterization procedures can be found in [13]) were polarized by applying dc bias voltage applied between the conductive AFM tip and the bottom electrode of the structure at the ambient conditions. The corresponding polarization switching was visualized in the PFM mode. According to the results of PFM phase measurements (Fig. 3b), the positive voltage induces the upward polarization reversal, while the negative voltage – the downward one. Interestingly, the negatively biased regions exhibit an expansion of the film thickness (Fig. 3a). For 3 nm thick nanocrystalline BTO film, the increase in the thickness was equal to 1 nm (Fig. 3c). The same effect could be observed for the most nanocrystalline samples, when the applied voltage was comparable with the coercive voltage or exceeded it.

To eliminate the possible influence of screening charges from the ambience and electrostatic contribution to the “conductive AFM cantilever/FE film” contact on the results of the measurements, complementary studies were carried out under UHV condition in STM regime. Tunnel current as a control parameter for feedback loop in STM ensures a stable “STM probe/FE film” contact, in contrast with AFM feedback loop based on Van-der-Waals interactions. Moreover, STM has a better spatial resolution due to the fact that 90 % of tunnel current flows through the nearest to the sample atom of the STM tip. In case of dielectrics, the resistance of the tunnel barrier, between the film surface and the STM probe, is significantly lower than the resistance of the FE film, so, it could be considered as a series resistor between tip and the sample. Prior to the STM measurements, samples were placed in a UHV chamber for 24 hours to remove the chemisorbed water molecules. The results of STM topographical imaging of BTO film allow us to clearly distinguish nanocrystalline (Fig. 3d) surface structure with better spatial resolution as compared to the AFM measurements (Fig. 3a). Negatively biased regions of the BTO film surface demonstrate the vertical height increase while maintaining the lateral structure of the film (Fig. 3e). This behaviour could suggest that the crystal structure does not change at the volume expansion, being in accordance with the hypothesis about the formation of oxygen vacancies under bias voltage application accompanied by the chemical expansion in perovskite oxides. Unfortunately, the quantification of this effect is not simple and requires taking into account the dependence of the formation energy of oxygen vacancies on the potential landscape in thin FE film [11].

The resistive switching phenomena were observed both in ambient conditions and under UHV on the I-V curves measured on the STO/LSMO/BTO structures with polycrystalline BTO films. The existence of a pinched hysteresis effect is indicated on the experimental I-V curves (Fig. 3f). The change in slope of the I-V curves is associated with switching between different resistive states in BTO films. According to the results of our previous studies, we relate the appearance of the I-V hysteresis with the peculiarity of charge transport in the BTO films with thicknesses greater than the mean free pass of injected electrons [13]. In polycrystalline BTO films, we assume a contribution from inelastic, trap-assisted tunnelling in current through these structures (traps are presented by oxide defects). The questions on temporal stability of the observed resistive states and their changes after bias application go beyond a consideration of this paper. Here, we would just like to mention that pinched hysteresis I-V curves are observed for all studied nano- and polycrystalline BTO films.

4. Conclusions

In summary, we demonstrate that the local surface potential in thin FE films with resistive switching effects is influenced by the peculiarity of surface charge screening. Combined KPFM/PFM and PFM/cAFM measurements give evidence of strong impact of the long-range electrostatic interaction between AFM tip and FE surface on the results of local resistive property measurements by means of conductive AFM at the ambient conditions. Sometimes, the true current distribution over the FE film
surface is completely veiled by electrostatics, driven by changes of surface charge screening conditions under polarization switching. Besides the chemisorbed water, electron injection in FE film together with oxygen vacancies formation could be considered as additional sources of screening charges, in ambient conditions.

The formation of oxygen vacancies in thin FE films under the bias voltage application is indirectly confirmed both by AFM measurements at the ambient conditions and the STM measurements under UHV. An increase in the thickness with retaining the lateral structure in the biased regions of the FE film is associated with a chemical expansion in perovskite oxide materials related to the presence of oxygen vacancies.

Acknowledgements
The research performed at the St. Petersburg Electrotechnical University “LETI” was funded by the grant of the Russian Ministry of Education and Science (Grant No. 16.2873.2017/4.6). The work carried out at the Christian-Albrechts-Universität zu Kiel was financially supported by the DAAD through their fellowship program under the contract number 8.9986.2017 (N.V. Andreeva). The authors are grateful to the resource centre "Physical Methods of Surface Investigation" of Research Park of Saint Petersburg State University for UHV SPM measurements performed at SPM module of the unique scientific facility "Nanolab".

References
[1] Li W, Ma J, Chen K, Su D and Zhu J S 2005 Europhys. Lett. 72 131-6
[2] Erhart P, Träskelin P and Albe K 2013 Phys. Rev. B 88 024107
[3] Ikegami S and Ueda I 1967 J. Phys. Soc. Jpn. 22 725-34
[4] Kim Y-M, Morozovska A, Eliseev E, Oxley M P, Mishra R, Selbach S M, Grande T, Pantelides S T, Kalinin S V and Borisevich A Y 2014 Nat. Mater. 13 1019-25
[5] Kim D J, Lu H, Ryu S, Bark C W, Eom C B, Tsymbal E Y and Gruverman A 2012 Nano Lett. 12 5697-702
[6] Mao H J, Song C, Xiao L R, Gao S, Cui B, Peng J J, Li F and Pan F 2015 Phys. Chem. Phys. 17 10146
[7] Li M, Zhou J, Jing X, Zeng M, Wu S, Gao J, Zhang Z, Gao X, Lu X, Liu J M and Alexe M 2015 Adv. Electron. Mater. 1 1500069
[8] Hu W J and Wang Z, Yu W and Wu T 2016 Nat. Commun. 7 10808
[9] Qin Q H, Äkäslompolo L, Tuomisto N, Yao L, Majumdar S, Vijayakumar J, Casiraghi A, Inkinen S, Chen B, Zugarramurdi L, Puuska M and Dijken S V 2016 Adv. Mater. 28 6852-9
[10] Jeen H, Choi W S, Biegalski M D, Folkman C M, Tung I C, Fong D D, Freeland J W, Shin D, Ohta H, Chisholm M F and Lee H N 2013 Nat. Mater. 12 1057-63
[11] Cazorla C 2017 Phys. Rev. Appl. 7 044025
[12] Kim Y, Bae C, Ryu K, Ko H, Kim Y K, Hong S and Shin H 2009 Appl. Phys. Lett. 94 032907
[13] Andreeva N, Petrov A, Petarau A, Petukhov A and Rybkin A 2019 Mater. Res. Express 6 026427
[14] Khoklin A L, Brooks K G, Taylor D, Hiboux S and Setter N 1998 Integr. Ferroelectr. 22 525-33
[15] Tuller H L and Bishop S R 2011 Ann. Rev. Mater. Res. 41 369-98
[16] Hong S Nanoscale Phenomena in Ferroelectric Thin Films 2004 Boston: Kluwer Academic Publishers