Conductive AFM study of the local current in thin ferroelectric sol-gel PZT films

E V Gushchina¹, N V Zaitseva¹, L A Delimova¹, D S Seregin² and K A Vorotilov²

¹ Ioffe Institute, Saint-Petersburg 194021, Russia
² MIREA-Russian Technological University, Moscow 119454, Russia

E-mail: katgushch@yandex.ru

Abstract. The local current distribution across the grains and their boundaries in ferroelectric PZT films are studied using conductive AFM. The films were formed with various grain structures and different lead excess content by chemical solution deposition. C-AFM measurements have shown the influence of the lead excess and seed sublayer crystallization conditions on the grain-boundary conductivity. PZT films with fixed 0-15 wt% Pb excess demonstrate non-conductive grain boundaries, whereas in films with fixed 30 wt% Pb excess the grain-boundary conductivity is found to be much higher than that of the grains themselves. Conductive grain-boundaries was also found in PZT films without lead excess in crystallized sublayer. A study of the transient current at varied preliminary polarization revealed the current peaks in the current-voltage curves. The appearance conditions and magnitude of these peaks depend on the grain-boundary conductivity. The correlation between the grain-boundary conduction and the current polarization dependences is confirmed.

1. Introduction

Thin-film lead zirconate–titanate Pb(Zr,Ti)O₃ (PZT) continues to be very attractive material for applying in various integrated electronic devices, including the nonvolatile ferroelectric (Fe) random access memory (FeRAM), field-effect transistors, piezoelectric microelectromechanical systems (MEMS), pyroelectric infrared sensors and so on. This is due to its high values of spontaneous polarization, piezo- and pyroelectric coefficients alongside with a relative low crystallization temperature of the perovskite phase [1–3]. Currently, the formation methods of epitaxial PZT layers are incompatible with the semiconductor manufacturing processes, therefore, the real Fe heterostructures exhibit a polycrystalline structure that determines their properties to a significant extent. For example the orientation of perovskite (Pe) grains in direction (100) usually results in the highest values of the piezoelectric coefficients, whereas (111) texture is more preferable for applying in FeRAM devices because of lower elastic stresses during switching [4-5]. The chemical solution deposition technique (sol-gel) yields an amorphous film that undergoes crystallization during the subsequent heat treatment. The formation of crystalline structure in this case is a result of the competition between the heterogeneous and the volume nucleation [5]. As films form on Pt(111), the surface nucleation dominates providing a columnar structure of perovskite (Pe) grains with (111) orientation [5]. To enhance the favorable for MEMS Pe(100) texture, Pb- or Ti-enriched orienting layers are usually used, because their oxide phases have lattice parameters close to those of Pe(100) [6-8]. To compensate lead loss during annealing due to the volatility of its oxide vapors, the initial solutions have some Pb excess [5], however, with its increasing
the heterogeneous nucleation rate enhances. As a result, Pe grain sizes decrease and the texture gradually changes the direction from (111) to (100) [7].

In our previous study of the polarization dependence of the transient current in epitaxial PZT films, we have found pronounced current peaks that are not associated with the domain switching [9]. We have shown that these peaks can appear in the current-voltage curves only in case the directions of the applied bias and polarization coincide, which looks unexpectedly. At the same time in studied polycrystalline MOCVD-prepared PZT films, the current peaks arise just in the opposite case, when the bias is directed against the polarization vector, which is natural, since the current flows along the conductive grain boundaries and is governed by a depolarization field [9]. Thus, the grain-boundary conduction can affect the polarization dependence of the transient current. Recently we have studied the transient current of the polarized sol-gel PZT films, which differed in their grain structure and observed the current peaks in the current-voltage curves [10]. We confirmed the correlation between the emergence of the current peaks and grain-boundary conductivity by the conductive AFM (c-AFM) method. Namely, in films with nonconductive grain-boundaries, where the current flows inside the PZT grains, the current peaks arise only when the direction of the bias and polarization vector coincide. In this paper, we report the c-AFM study of the local current distribution across the grains and their boundaries in sol-gel PZT films in more details.

2. Samples

The PbZr$_{0.48}$Ti$_{0.52}$O$_3$ films were formed on silicon wafers with the Pt(150 nm)/TiO$_2$(10 nm)/SiO$_2$(300 nm)/Si structure using the sol-gel technique [11]. The PZT film-forming solution was applied by six spin-on deposition steps with an intermediate IR drying at 180°C (5 min) and pyrolysis of each layer at 400°C (10 min). After the last layer was formed, the films were crystallized by annealing at 600°C (15 min). The details are given in table 1. The four structures (samples Nos. 1 – 4) were formed from the solutions with fixed Pb excess $x = 0$, 5, 15, and 30 wt% in all layers. Sample No. 5 was prepared with crystallized seed PZT sublayer (2 depositions) from the solution without Pb excess, followed by the deposition of bulk film by four applications of PZT solution with a 30 wt% Pb excess and the final crystallization. The top 20-nm-thick Pt electrodes with an area of $\sim 10^{-3}$ cm$^2$ were formed by magnetron sputtering through Si shadow mask.

| Samples No. | Number of a PZT layer, Pb excess, and the corresponding annealing temperature |
|-------------|--------------------------------------------------------------------------------|
| 1           | 0%-400°C 0%-400°C/600°C                                                       |
| 2           | 5%-400°C 5%-400°C/600°C                                                       |
| 3           | 15%-400°C 15%-400°C/600°C                                                     |
| 4           | 30%-400°C 30%-400°C/600°C                                                     |
| 5           | 0%-400°C 0%-400°C/600°C 30%-400°C 30%-400°C/600°C                             |

The crystal structure was studied using a DRON-3 diffractometer ($\Theta$–$2\Theta$ mode, CuK$\alpha$ radiation). The dielectric hysteresis loops were measured by the standard Sawyer–Tower method with the sinusoidal voltage amplitude 6 V and the signal frequency 64 Hz. During the depolarization of the structure, the sinusoidal voltage amplitude was damped for 20 periods to a zero value. Then, the structure was polarized in a certain direction by applying a short (2 s) pulse $\pm 6$ V. The current-voltage curves were measured using KEITHLEY 6487 Picoameter/Voltage Source. The bias was applied as a sequence of 0.1-V steps with duration of 0.2 s, and the current was recorded at the end of a step. Since the relaxation time of the measurement circuit $\sim 10$ ms, it means that the measured signal already does not contain a current component associated with the polarization switching. The voltage was varied from zero to 3 V and then back to zero. For both bias directions, the measurements were made at various preliminary
For this purpose, the film was depolarized before each measurement and then polarized in a required direction.

### 3. Experimental results and discussion

Table 2 gives the basic information about the Pb excess content in the samples and the film texture, remanent polarization and film thickness. The latter was determined by the method of spectral ellipsometry using SE-850 ellipsometer. The X-ray diffraction patterns show the predominant Pe(111) texture along the volume diagonal and a weaker that along axes a(100) or c(001) (see figure 1 (a) curves Nos. 1,3 and No. 4, respectively). The intensity ratios of the diffraction peaks show that texture (111) in the film with crystallized sublayers is enhanced, so that direction (100) is actually suppressed (see figure 1(a) curve No. 5). Figure 1 (b) shows how strongly differ the hysteresis loops measured for the films with the fixed 0, 15, 30 wt% Pb excess across the film (Nos. 1,3,4) and with crystallized seed layer without Pb excess (No. 5).

#### Table 2. Main properties of PZT films

| Sample No. | Pb excess x, wt% | (111)/(100) | d, nm | P, µC/cm² | V, V |
|------------|----------------|-------------|-------|-----------|------|
| 1 Film x = 0 | 3.2 | 29 | 226 | P | V nonconductive |
| 2 Film x = 5 | 5 | 45 | 238 | P | V nonconductive |
| 3 Film x = 15 | 3.4 | 49 | 235 | P | V nonconductive |
| 4 Film x = 30 | 3.7 | 40 | 238 | P | V conductive |
| 5 2 crystal sublayers | 0 | 31 | 57 | P | V conductive |

A typical behavior of the transient current is shown in figure 2 (a) and (b) for samples Nos. 2 and 5, respectively. All the films demonstrate a clockwise current hysteresis with a current peak on its up-going branch and no peak on the down-going branch. At the same time, the appearance conditions of the current peaks differ fundamentally. Namely, the current in films Nos. 1-3 at both bias directions is higher than in films Nos. 4-5 in which they are opposite (figure 2 (b)). The case of Nos. 1-3 is unexpected, since the current caused by polarization switching is maximal if the bias and polarization directions are opposite to each other.
Figure 2. Current-voltage dependences of PZT films (a) No. 2 and (b) No. 5, measured at varied preliminary poling.

To study the possible grain-boundary conductivity of the films, local current distributions were measured by the c-AFM method, which provides the film surface topography and the local-current map simultaneously. All AFM measurements were made with a Ntegra Aura (NT-MDT Co.) scanning probe laboratory. The images were obtained using rigid (stiffness coefficient $k = 5 \text{ - } 20 \text{ N/m}$) conductive probes with wear-resistant diamond-coated cantilever, which retained their conductive properties even when voltages of $\pm 10 \text{ V}$ were applied. The force of the c-AFM probe interaction with the surface under study is $F \approx 500 - 1000 \text{ nN}$. The probe tip radius is $\sim 100 \text{ nm}$, and the radius of the contact area is $\sim 15 \text{ nm}$. An external bias of $\sim 8 - 10 \text{ V}$ was applied to the bottom electrode, while the top electrode was grounded. It is noteworthy that the local current distribution maps $I(x,y)$ measured by c-AFM are reproducible and independent of the type of the probe coating material.

Figure 3 shows 2D-images of (a) AFM topography and (b) local current map of film No. 1, simultaneously obtained by c-AFM. Here, the white areas of increased conductivity in figure 3 (b) are correlated with the light areas in figure 3 (a), which correspond to grain heights. Figure 3 (c) shows signal profiles of the topography $h$ and local current $I$, found from the data of (a) and (b). The minima in the topographic signal correspond to the grain boundaries. It can be seen that the current flows across the grains since the current peaks coincide with the topography hills. In addition the zero-current positions correlate with the grain boundaries, thereby indicating that the grain boundaries are nonconductive.

Figure 3. 2D images of (a) AFM topography and (b) local current map of PZT film No. 1, produced by c-AFM from $4 \times 4 \text{ µm}^2$ scanning area. The dotted line corresponds to the position of the profile. (c) Signal profiles of the topography (left scale, circles) and local current (right scale, triangles) along the profile at the length of $4 \text{ µm}$. The line for the current signals drawn as a guide to the eye.
Films Nos. 2–3 show similar topographic and local current profiles, which confirms that their grain boundaries are nonconductive, see figure 4 here and figure 5 in Ref [10].

The films Nos. 4 and 5 demonstrate the opposite behavior, when the areas of increased current are correlated with the topography of grain-boundary space, see figures 5 and 6. This indicates an increased conductivity of grain boundaries compared to the grains themselves. In PZT film with the fixed 30 wt% Pb excess, this can be caused by segregation of PbO phase at grain-boundaries during the crystalline structure formation. In PZT with crystallized seed layer without Pb excess, the grain-boundary conduction may be due to the large number of defects associated with the lead deficiency and oxygen vacancies. Figure 6 shows also that the current in PZT No. 5 flows both along the grain-boundaries and partly through the grains. However, the grain-boundary contribution to the total current is larger since the appearance conditions of the transient current peak correspond to the conductive boundaries of the grains, see figure 2 (b).

Figure 4. PZT No. 2. Signal profiles of the topography (left scale, circles) and local current (right scale, triangles). The zero signal level on the current scale does not coincide with the topography zero level. The line for the current signal is drawn as a guide to the eye.

Figure 5. PZT No. 4. Signal profiles of the topography (left scale, circles) and local current (right scale, triangles). The line for the current signal is drawn as a guide to the eye.

Figure 6. PZT No. 5. Signal profiles of the topography (left scale, circles) and local current (right scale, triangles). The line for the current signal is drawn as a guide to the eye.

Thus, the measured by c-AFM local current distributions in PZT films formed with various grain structures and different lead excess content are correlated with the polarization dependencies of the transient current and thereby confirm that the current-polarization dependence is sensitive to the conductivity of grain boundaries.
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