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Citation: J. Appl. Phys. 107, 054103 (2010); doi: 10.1063/1.3290953
View online: http://dx.doi.org/10.1063/1.3290953
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v107/i5
Published by the American Institute of Physics.

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Effect of local surface potential distribution on its relaxation in polycrystalline ferroelectric films

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(Received 30 October 2009; accepted 12 December 2009; published online 2 March 2010)

We have studied the effect of local surface potential distribution on its relaxation in the polycrystalline ferroelectric thin films. A lower surface potential region, i.e., potential pit, is generated near a grain boundary. The deep potential pit has a faster relaxation than the area far away from the potential pit due to the acceleration of the screen charge draining near the grain boundary and the domains formed by applying higher voltage have a faster relaxation due to the larger gradient of screen charge distribution. In addition, the surface potential and its relaxation depend on the sign of applying voltage. The result shows that the surface potential distribution may influence significantly to the reliability of bit signal on the memory devices. © 2010 American Institute of Physics. [doi:10.1063/1.3290953]

I. INTRODUCTION

Ferroelectric materials have been considered for the application of memory devices due to their superior properties such as fast read/write, long retention time, and high memory density. Ferroelectric materials have spontaneous polarization, which can be reversibly switched by applying voltage, of two different polarization states and their different signs of polarization charges are used as two different bits in the memory devices. These polarization charges can be screened by internal and/or external charges. The resulted surface potential after the screening of the polarization charges can be also used as a bit signal. For as-grown ferroelectric surfaces, the surface adsorption, the intrinsic surface states, and/or the free charge in the films can screen the polarization charge. However, when the polarized domains were switched by applying voltage bias through a conductive probe, the majority of the screen charges is an injected charge which comes from the conductive probe to the film surface during applying voltage. However, there are only few works on the local charge distribution and its resultant surface potential distribution.

On the other hand, atomic force microscopy (AFM) has been widely used to observe the surface potential of ferroelectric thin films due to its high resolution and nondestructive method. Kalinin et al. reported that the screen charge behaviors of as-grown ferroelectric domains depend on the temperature in BaTiO3. They reported that the disappearance of the polarization charge affects the distribution of the screen charge. Other researchers have investigated the surface potential of the poled domains formed by the different applying voltages. As increasing the applying voltage, the initial surface potential value increases, then saturates. Also, the relaxation of the poled domains at different applying voltages has been investigated and it was found that the poled domains at higher applying voltage have a faster relaxation. On the other hand, we previously reported that the grain boundary could affect the scale of the surface potential due to the electrical properties of the grain boundary. This effect leads to generate the potential pits near the grain boundary, which has a lower surface potential distribution. This potential pit may act as a screen charge draining source. However, the role of the potential distribution on its relaxation as well as its quantitative analysis have not been sufficiently investigated. Therefore, in this study, we present the role of the local surface potential distribution on its surface potential relaxation and discuss the influence of the scale and the sign of the applying voltage on it in the polycrystalline ferroelectric thin films.

II. EXPERIMENT

The sample was a 50-nm-thick (111) preferentially oriented Pb(Zr0.25Ti0.75)O3 thin film on a Pt/Ti/SiO2/Si substrate prepared by the sol-gel method. The commercial AFM (SPA400, Seiko Inc.) was used to measure surface potential. Kelvin force microscopy (KFM) with Pt coated tip (a spring constant of 2.8 N/m and a resonant frequency of 78 kHz) was used to analyze the potential pits on the surface potential distributions of the ferroelectric domains. Initially, the domains were switched by applying voltages of −5, −7, −9, and +9 V to the bottom electrode over a scan area of 5 × 5 μm² in contact-mode AFM. Then, KFM images over a scan area of 2 × 2 μm² were acquired with an ac voltage of...
10 V at 25 kHz. Also, KFM images were acquired after 0, 25, 100, 180, and 300 min for the analysis of the surface potential relaxation.

### III. RESULTS AND DISCUSSION

Figure 1 shows the surface potential distribution and its topography of the poled domains with different applying voltages to the bottom electrode. The local surface potential distribution was observed in the poled domains. In order to analyze the local surface potential distribution, we observed the surface potential line profile extracted from the blue line of Fig. 1. It was found that the potential pit, which is the lower surface potential region, is formed near the grain boundary and each potential pit has a different depth. As we previously reported, the different depth of each potential pit is originated from the different electric properties of the grain boundaries. This difference in the electrical properties of the grain boundaries implies that the grain boundary has a deep potential pit when the grain boundary is highly conductive, whereas it has a shallow potential pit when the resistivity of the grain boundary is high. Therefore, when the potential pit is generated near the grain boundary, it presents that this pit can be a main source of the screen charge draining path. Especially, the deep potential pits can be efficiently activated as screen charge draining paths.

If the potential pits act as efficient screen charge draining paths, the relaxation time of the surface potential near the potential pits may have a faster decay than far away from the potential pits due to the acceleration of the screen charge draining. For the further investigation on the role of the surface potential distribution, i.e., potential pit, the surface potential evolution dependence on the elapsed time was observed in Fig. 2.

To analyze the surface potential relaxation behaviors near the potential pit, the elapsed time dependence on the surface potential $y$, which was obtained from Fig. 2, was fitted by an exponential function:

$$ y = y_0 + A \exp(-t/\tau), $$

where $\tau$ is the relaxation time. Then, the relaxation time was extracted from the fit by this equation. Figure 3 shows the relaxation time and the initial surface potential profiles at each position. In the poled domain produced by applying voltage of $-5$ V, there are two shallow potential pits and one deep potential pit. In this figure, the area near the potential pits has a faster relaxation time, and the deep potential pit has a faster relaxation time than two shallow potential pits. In the poled domains at applying voltages of $-7$ and $-9$ V, the same phenomena were also observed. Although some grain boundaries have very shallow potential pits or no potential pits in the initial surface potential (see red arrow of Fig. 3), the grain boundaries sometimes still act as screen charge draining paths as shown in the poled domains of $-5$ and $-7$ V. Therefore, the areas near the grain boundaries have a faster relaxation time than far away from the grain boundaries. These phenomena were also observed in the poled domains at applying voltage of $-9$ V. Eventually, the potential pit of the initial surface potential indicates that the potential pit near the grain boundary acts well as a screen charge draining source and the relaxation time depends on the depth of the potential pit.

Figure 4 shows the average surface potential, which was obtained from each entire image, as a function of the elapsed time at each applying voltage of poled domains. Although the surface potential of each applying voltage decreased as

![Figure 1](image1.png)

**FIG. 1.** (Color online) Surface potential distribution (up) and topography (bottom) of the poled domains with different applying voltages of $-5$, $-7$, and $-9$ V to the bottom electrode.

![Figure 2](image2.png)

**FIG. 2.** (Color online) Surface potential profile, which was obtained from the blue line of Fig. 1, as a function of the elapsed time at each applying voltage.
the elapsed time passed in the figure, the downward polarization formed by applying voltage maintained its polarization state during the whole measuring time (not shown here). Thus, the surface potential relaxation was not affected by polarization reversal.

The initial surface potential of the poled domain at applying voltage of $-5 \, \text{V}$ has a smallest value, and the initial surface potential of $-7 \, \text{V}$ increases as increasing applying voltage from $-5$ to $-7 \, \text{V}$. However, the initial surface potential does not increase any more and slightly decreases at the applying voltage of $-9 \, \text{V}$. In the previous works, it was reported the surface potential value increases, then saturates as increasing the applying voltage because of the Coulombic repulsion between screen charges.12–14 Whereas, in this study, the surface potential decreases at the applying voltage of $-9 \, \text{V}$. During the domain switching process of $-9 \, \text{V}$, a larger amount of screen charges compared to the applying voltages of $-5$ and $-7 \, \text{V}$ were injected to the film surfaces.6 A large amount of screen charges also might increase the Coulombic repulsion between screen charges and this increased repulsion leads to accelerate the screen charge draining during or just after domain switching process because the Coulombic repulsion is one of sources to migrate charges.12–14 Due to the screen charge draining near the grain boundaries, the large gradient of screen charge distribution was generated. This gradient on the amount of screen charges leads to accelerate the lateral diffusion of screen charges and it may lead to accelerate faster draining of the screen charges via grain boundaries.

This phenomenon can be explained by schematic diagram of Fig. 5. At the applying voltage of $-5 \, \text{V}$ [Fig. 5(a)], the small amount of screen charges with small deviation exists on the film surfaces and screen charges near grain boundaries are smaller than the far away from the grain boundaries due to screen charge draining phenomenon via grain boundaries. When the applying voltage increases up to $-7 \, \text{V}$ as presented in Fig. 5(b), the overall amount of screen charges increases and the screen charge distribution has larger gradient compared to the applying voltage of $-5 \, \text{V}$. However, when the applying voltage increases up to $-9 \, \text{V}$, the large amount of screen charges was already drained via grain boundaries during or just after domain switching process. Due to large amount of screen charge injection and draining, the screen charge distribution has large gradient as presented in Fig. 5(c). As a result, the average surface potential values at applying voltages of $-5$ and $-9 \, \text{V}$ are similar, whereas, the gradient of screen charge distribution is very different on each applying voltage. Although the surface potential values are similar at both applying voltages, the large gradient at applying voltage of $-9 \, \text{V}$ may lead to accelerate the screen charge transfer on ferroelectric surfaces because screen charges migrate due to Ohm’s law or the diffusion process,12–14 and it also may lead to accelerate the screen charge draining via grain boundaries.

This phenomenon was also found at the surface potential distribution of Fig. 1. In the poled domains at applying voltage of $-5 \, \text{V}$, there are only several potential pits and the size of potential pits is also small. However, in the poled domains

$$\text{FIG. } 3.$$ (Color online) Relaxation time ($\tau$) and initial surface potential profiles at each applying voltage. The relaxation time was obtained from the fits at the each position of Fig. 2 by Eq. (1). The initial surface potential profile was obtained from Fig. 2.

$$\text{FIG. } 4.$$ (Color online) Average surface potential, which was obtained from Fig. 1, as a function of the elapsed time at each applying voltage. The solid line was obtained from the fits by Eq. (1).

$$\text{FIG. } 5.$$ (Color online) Schematic diagram of screen charge distribution at applying voltages of (a) $-5$, (b) $-7$, and (c) $-9 \, \text{V}$ to bottom electrode. Each segment presents grain and boundaries between segments presents grain boundaries.
at applying voltages of $-7$ and $-9$ V, the number of potential pits much more increases and the area of potential pits is also larger. The obtained results show the large gradient on screen charge distributions at the applying voltages of $-7$ and $-9$ V. This surface potential distribution can be confirmed by surface potential roughness. Each surface potential roughness of the poled domain at applying voltages of $-5$, $-7$, and $-9$ V is $164.2$, $246.3$, and $253.2$ mV. The poled domains at higher applying voltage have a larger surface potential roughness, which presents that there is a large gradient of screen charge distribution. It was already shown in the direct observations on the potential profile of Fig. 2.

The trends can be also observed in the relaxation of the average surface potential. The relaxation time of each poled domain at applying voltage of $-5$, $-7$, and $-9$ V is $104.7$, $84.9$, and 83.7 min. As increasing the applying voltage, the relaxation time becomes faster. Although the initial potential values of $-5$ and $-9$ V are similar, the relaxation time of $-9$ V is much faster due to the large gradient of screen charge distribution. Interestingly, the difference on the relaxation time of $-7$ and $-9$ V is not so large. In addition to the gradient of screen charge distribution, the amount of screen charges can affect the relaxation of screen charges. Thus, although there is difference on the initial surface potential values of $-7$ and $-9$ V the resultant relaxation time of both cases can have similar value due to the competition of these two factors on the relaxation behaviors. The results indicate that the number of the injected screen charges during domain switching process may affect the relaxation time because the amounts and gradient of screen charges lead to migration of screen charges by Coulombic repulsion, Ohm’s law, or the diffusion process. Although the surface potential of the poled domains experiences fast relaxation for several hours, the domains maintained their polarization state, and the ferroelectric surfaces still have overscreen state.

In Fig. 6, it was also found that the surface potential distribution depends on the sign of the applying voltage. As shown in Fig. 6, the initial absolute surface potential value of $-9$ V is much larger than that of $+9$ V and is about three times of it. This small absolute value at the applying voltage of $+9$ V leads to small variation near the grain boundaries (not shown here), therefore, the surface potential roughness of $+9$ V (82.3 mV) is much smaller than that of $-9$ V (253.2 mV). In addition, the relaxation time of the poled domains at applying voltages of $-9$ and $+9$ V are 83.7 and 17.6 min, which shows that the poled domains at applying voltage of $+9$ V have much faster relaxation time. On the other hand, the surface potential value already saturates at around 1 h, and the small portion of the surface potential was only changed at the applying voltage of $+9$ V.

This asymmetry of the surface potential behaviors induced from the amount of screen charges may be originated from (1) different electron/hole generation rate, (2) the presence of the internal built-in electric field near the ferroelectric/electrode interface, (3) different screen charge of as-deposited state, or (4) different amounts of trap sites. When the electron/hole generation rate is different, the amount of the screen charges depends on the sign of applying voltages. During applying a negative (positive) voltage through the conductive probe, electrons (holes) can be injected onto the film surfaces. It can be excluded because the threshold voltage of electron injection is smaller than that of hole injection, therefore, the amount of electrons should be larger than that of holes. (2) When there is an internal build-in electric field ($E_i$) near the ferroelectric/electrode interface, this field does not depend on the external applying voltage ($E_{ext}$) and always aligns in one direction. Therefore, it generates self-polarized region near the ferroelectric/electrode interface as shown in Fig. 7. If this self-polarized region aligns as downward polarizations and the negative voltage is applied to the bottom electrode, the internal field of this self-polarized region can enhance the total electric field and, eventually, the different total electric field along the thickness direction can lead to different amount of screen charges. The resultant screen charge distribution can be presented as shown in Fig. 7. Due to the presence of the internal built-in electric field, the number of screen charges with applying voltage of $-9$ V can be much larger and these screen charges can be detected as surface potential. (3) The screen charge of the as-deposited state also affects the number of the resultant screen charges. The as-deposited state of the present ferroelectric thin films has positive surface potential, which can imply that the positive charges originally remain on the ferroelectric surfaces. In this situation, the negative applying voltage may lead to increase positive charges compared to the positive applying voltage on the ferroelectric surfaces. (4) The number of trap sites depends on the hole and electron. The obtained surface potential can be sometimes decided by a limited number of
trap sites. These three reasons among four possible reasons may be responsible for the asymmetry of the surface potential behaviors and the smaller amounts of screen charges at applying positive voltage.

IV. SUMMARY

We have studied the effect of the local surface potential distribution on its relaxation in the polycrystalline ferroelectric thin films. The potential pit with lower surface potential distribution is generated near the grain boundary and the deep potential pit has a faster relaxation than far away from the potential pit due to the acceleration of the screen charge draining near the grain boundary. For the higher applying voltage, there is larger number of potential pits and it has a faster relaxation due to the larger gradient of the screen charge distribution. In addition, the sign of applying voltage affects the surface potential value and its relaxation behaviors. The result shows the local potential pit near the grain boundary may influence significantly to the reliability of the surface potential distribution and this indicates that it can affect the reliability of the device performance in the memory devices.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Seung-Hyun Kim from Inostek Inc. for preparing the ferroelectric thin films. This work was supported by the Samsung Electronics and the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government (MEST) (Grant No. 2009-0052806). The submitted manuscript has been in part created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. DOE Office of Science Laboratory, is operated under Contract No. DE-AC02-06CH11357.