Transient carrier transport and rearrangement of space charge layers under the bias applied to ferroelectric M/PZT/M structures

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Abstract. A drift-diffusion model of unsteady carrier transport in M/PZT/M structure is proposed to account for the formation of the current peak in the current–voltage curves, which is not caused by the domain switching and observed only when the bias and polarization directions coincide. In the model, electrons generated by oxygen vacancies are trapped by titanium deep centers at room temperature and can move by hopping between titanium atoms in the electric field. The polarization is constant across the film thickness while it is zero within defective layers near the contacts. It is shown that a pronounced current peak is formed when an accumulated space-charge layer appears near one of the contacts under the action of the polarization and this effect is purely unstationary.

1. Introduction

Lead zirconate titanate Pb(Zr,Ti)O$_3$ (PZT) is one of the most widespread and promising materials for integrated ferroelectric devices, including nonvolatile ferroelectric random access memory, field-effect transistors, microelectromechanical systems, pyroelectric sensors, transducers [1-3]. This is due to the comparatively low crystallization temperature, strong spontaneous polarization and large piezoelectric coefficients. The basic element of all these devices is the ferroelectric capacitor M/PZT/M, while the most important factor that controls the device performance is the leakage current. The main attention in the leakage study has been paid to the identification of mechanisms responsible for the current flowing across PZT capacitors [4-9]. The current measured in PZT films usually contains a strong relaxation component that lasts up to tens of seconds. This means that current-voltage characteristics, which are commonly measured by applying voltage steps with a duration shorter than 1-2 s, turn out to be "transient" in the sense that the relationship between the current and voltage at each point depends on the earlier measured points of the current-voltage curves. Whereas the expressions for the emission current are used, derived by considering the steady carrier transport in the space charge layer [10].

To analyze leakage currents in ferroelectric capacitors in our previous paper [11], an approach has been proposed which is generally accepted in semiconductors but has never been used for this purpose in ferroelectrics, namely, a consideration of carrier transport in the diffusion-drift approximation. The corresponding model of unsteady carrier transport in the M/PZT/M structure has been used to account for the formation of the current peak in the current–voltage curves, which is not caused by the domain switching and observed in epitaxial [12] or some polycrystalline PZT films [13] only when the bias and polarization directions coincide. Using the numerical simulation, the pronounced current peak is shown to appear when (a) an accumulated space-charge layer arise near one of the contacts under the action of...
polarization and (b) this contact is cathode, which is only possible when the polarization and bias directions coincide. However to simplify the task in the simulation [11], we neglected the asymmetry of the current-voltage curves and hysteresis loops. We considered that the top and bottom electrodes of the M/PZT/M structure have similar properties, therefore we limited to considering only positive bias. In this paper, we do numerical simulation of transient current in PZT films taking into account the difference in the Schottky barrier height of the top and bottom electrodes and its different reduction in the electric field as well as the different width of the top and bottom defective layers. In addition, special attention is paid to the emergence conditions of the current peaks on the current-voltage characteristics.

2. The polarization dependence of the transient current

Figure 1 shows the current–voltage characteristics measured in epitaxial 210-nm-thick Pb(Zr$_{0.48}$Ti$_{0.52}$)$_3$O$_3$ film at varied preliminary polarization, the details are given in [11-12]. To erase the prehistory before the measurement, the film was depolarized by applying a sinusoidal voltage with amplitude decaying from 10 V to zero, shown in figure 2. The domain switching current flowing in the Sawyer-Tower circuit during the first hysteresis loop is presented in figure 3 as a function of time.

![Figure 1](image1.png)

**Figure 1.** Current–voltage characteristics of PZT film, measured at positive (curve 1) and negative (curve 2) preliminary polarization.

![Figure 2](image2.png)

**Figure 2.** Family of depolarizing hysteresis loops measured for 20 periods of sinusoidal voltage at a frequency of 64 Hz.

![Figure 3](image3.png)

**Figure 3.** The domain switching currents flowing in the Sawyer-Tower circuit during the first hysteresis loop versus time.

After the depolarization, the film was polarized in positive (negative) direction by applying a short pulse of +10V (-10 V), and acquired the $+P_R$ ($-P_R$) remanent polarization after switching off the voltage. Then the bias was applied to the film by sequence of steps of 0.1 V in amplitude with 0.2 s duration, the voltage amplitude varied from 0 to 5 V and then back to 0. The current was recorded at the end of the step, which is 100 times longer than the domain switching time, ~2 ms, see figure 3. This means that the
measured current does not contain contribution from the domain switching current, since the latter has already passed through the measurement circuit. Figure 1 shows that for the both bias directions the peaks of transient current arise only in case the directions of the bias and polarization coincide, which differs principally from the domain switching current.

Similar current peaks, or plateau and dip have been observed in the current-voltage curves [7-9], which were interpreted by authors as a negative differential resistance and were explained by double injection of carriers into PZT film and trap filling process [7-8] or polarization recovery current [9].

3. The description of the model

A detailed description of the model is given in [11]. Here are only the basic equations and assumptions. It is assumed that the PZT film has electronic conductivity. Following [14-15], we believe that electrons originated due to oxygen vacancies are trapped by Ti$^{3+}$ deep centers. The energy of the vacancies is 0.2-0.5 eV [16] and the energy of Ti$^{3+}$ center $E_{T_1}$ is 1 eV relative to the conduction band bottom [14]. It can be shown that at room temperature all electrons are captured by Ti$^{3+}$ levels, there are practically no electrons in the conduction band, and all vacancies are positively charged. Near the contact, Ti$^{3+}$ levels either lose electrons, which gives rise to an uncompensated positive charge of vacancies, or capture electrons that gives rise to an uncompensated negative charge of electrons. As a result, a bend of the Ti$^{3+}$ level appears. It is assumed that electrons move under the action of the electric field via hopping between Ti$^{3+}$ centers. The electron transport is considered in the diffusion-drift approximation with an effective mobility $\mu$ considered to be constant while the vacancies are considered to be immobile. The polarization is assumed to be constant outside the thin defective layers near the contacts where it is equal to be zero. In this case, the polarization manifests itself only through the polarization charge at the interface between the defective layers and the ferroelectric layer, and it is not included in the equations themselves which have the usual form

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial x}\left(\mu \left( n \frac{\partial \phi}{\partial x} - \frac{kT\partial n}{q \partial x}\right)\right), \quad \epsilon_0\epsilon_d f \frac{\partial^2 \phi}{\partial x^2} = -q(N_{S_{vac}} - n),$$

$$\epsilon_0\epsilon_d E^- = \epsilon_0\epsilon_f E^+ + P \quad \text{at} \quad x = h_{D1},$$

$$\epsilon_0\epsilon_f E^- + P = \epsilon_0\epsilon_d E^+ \quad \text{at} \quad x = L - h_{D1} - h_{D2}. \quad (3)$$

Here $n$ is the electron density, $\mu$ is the electron mobility, $\phi$ is potential, $\epsilon_0$ is the permittivity of free space, $\epsilon_d$ and $\epsilon_f$ are the dielectric constants of the defective layer and ferroelectric, respectively, $N_{S_{vac}}$ is the total number of oxygen vacancies, $E$ is the electric field, $P$ is the polarization, $L$, $h_{D1}$ and $h_{D2}$ are the thicknesses of the film and defective layers, while the superscripts "-","+" indicate the values of the electric field to the left and right from the boundary. The OX axis is directed from the left to the right (from the bottom contact to the top one).

The following boundary conditions were imposed at the contacts:

$$J_n = V_R(n_{e1} - n), \quad \phi = -\phi_{BT1,1} + \Delta \phi_1 + V \quad \text{at} \quad x = 0,$$

$$J_n = -V_R(n_{e2} - n), \quad \phi = -\phi_{BT2,2} + \Delta \phi_2 \quad \text{at} \quad x = L,$$

$$n_{e1,2} = N_{T_1}^S \exp\left(-\frac{q}{kT}(\phi_{BT1k} - \Delta \phi_k)\right), \quad \Delta \phi_{1,2} = \left(\frac{qE_{1,2}}{A\pi\sigma_\phi}\right)^{1/2},$$

where $J_n$ is the electron flux density, $V_R$ is the effective recombination rate, $V$ is the external bias, $n_{e1,2}$ is the equilibrium electron concentration at the contact (at the point of the maximum barrier height), $\phi_{BT1,2}$ are the barriers for the electrons captured by Ti$^{3+}$ levels, $\Delta \phi_{1,2}$ are the barrier depression, $N_{T_1}^S$
is the total number of titanium atoms per unit volume, and $\varepsilon_s$ is the dielectric constant, intermediate between the static and high-frequency values.

Analytical dependence of the polarization on the applied bias has been presented in the form

$$P = P_0 + P_S \tanh \left( \frac{V + V_C}{2\delta} \right),$$

(6)

where the constant $P_0$ was introduced to account for the difference in the coercive strength and remanent polarization at positive and negative bias, seen in figure 2, $P_S$ is the saturated polarization. This expression approximates the experimental hysteresis loop rather well if we put $P_0 = 10 \mu C/cm^2$, $P_S = 83 \mu C/cm^2$, $V_C = 3.15 V$ and $2\delta = 2.814 V$, assuming that the dielectric constant is equal to $\varepsilon_f = 160$.

4. Calculation results and conclusions

The calculations were performed for a film thickness of 210 nm, similar to that used in the experiment described in section 2. The numerical simulation carried out in [11] for the symmetric structure allowed us to obtain the following estimates of the main parameters:

$$\mu = 4 \cdot 10^{-11} cm^2/V s, N_{vac}^2 = 2 \cdot 10^{19} cm^{-3}, \phi_{RTI,1,2} = 0.7 V, \varepsilon_{d,f} = 160, \varepsilon_s = 10, h_{D,1,2} = 1 nm.$$

(7)

In the present calculations, we started from these values, adjusting them to ensure better agreement of the theory with the experiment.

Figure 4 shows the steady-state distributions of electrons over the film thickness obtained by numerical simulation of equations (1) - (6) at zero bias for several values of $P_S$ in the symmetric structure. It can be seen that the polarization causes asymmetry of the space charge layers. At the positive polarization, the left layer thickness increases while the thickness of the right one decreases and, starting with a certain value of $P_S$, the right layer of the space charge, which was originally depleted, becomes accumulated.

The current-voltage curves calculated for the same structure at the positive bias are shown for different $P_S$ values in figures 5 and 6 for positively and negatively pre-polarized film, respectively. Similar results are obtained for the negative bias. The current-voltage characteristics were calculated by the same procedure as that used for their measurement. The external bias was applied to a pre-polarized film in steps of the same height $\Delta V = 0.1 V$ and duration $\Delta T = 0.2 s$ within the range from 0 to 5 V, and the calculated current at the end of a step was recorded as the value corresponding to the applied bias. The stationary solutions served as the initial state of the film as discussed above. It is seen that, firstly, the current peaks do occur only when the signs of the polarization and applied bias coincide. Second, with increasing polarization, the peak shifts towards higher bias. Finally, thirdly, distinct current peaks occur only when an accumulated layer of space charge is formed near one of the contacts with a sufficiently large excess of the electron density over the vacancy concentration. In other cases, the current-voltage curves have only a weakly expressed maximum. This difference in the current-voltage characteristics can be easily understood from the analysis of figure 4.

For example, consider the case of positive polarization. If the bias is positive, the electrons will move from right to left. Therefore, as the applied voltage increases from 0 to ~2.9 V, the thickness of the left depleted layer rapidly decreases due to the electrons arriving from the accumulated layer, while the right layer still remains accumulated. This leads to a decrease in the film resistance, with the current growing superlinearly as a result. At the same time, the electron density in the accumulated layer falls with increasing voltage and at $V > 2.9 V$, the accumulated layer becomes depleted. Beginning at this instant of time, the film resistance starts to grow again because the thickness of the right-hand depleted layer increases and this layer begins to take on an increasing part of the external bias. As a result, the electric field within the film begins to decrease and, consequently, so does the electric current. On the other hand, in the negatively polarized film an accumulated layer appears at the left contact and a depleted one at the right contact. With increasing applied bias, the depleted layer thickness begins to grow, which leads to an increase in the film resistance in the whole range of bias variation from 0 to 5 V. As a result, the current variations turn out to be substantially smaller than that for the positive polarization.
Figure 4. The distributions of the electron density across the film thickness calculated at $V = 0$ for the polarization $P_0 = 0$ and $P_S$, $\mu\text{C/cm}^2$: 1 – 0; 2 – 33; 3 – 53; 4 – 73; 5 – 93.

Figure 5. The current-voltage curves calculated for positively poled film and the polarization $P_0 = 0$ and $P_S$, $\mu\text{C/cm}^2$: 1 – 53; 2 – 63; 3 – 73; 4 – 83; 5 – 93.

Figure 6. The current-voltage curves calculated for negatively poled film, the polarization $P_0 = 0$ and $P_S$, $\mu\text{C/cm}^2$: 1 – 53; 2 – 63; 3 – 73; 4 – 83; 5 – 93.

The results presented above concerned a symmetric structure for which $J$-$V$ curves are also symmetric. However, both the $J$-$V$ curves in figure 1 and hysteresis loop in figure 2 are asymmetric. An attempt to adjust the calculated $J$-$V$ curves to the experimental one in the whole range of positive and negative bias using a set of parameter values (7) was unsuccessful. Therefore, a numerical simulation was performed in which the parameters characterizing the properties of the right and left contacts varied independently. Nevertheless, we could not achieve a rather good agreement of the calculation results with the experiment for negative bias. One of the calculation options is shown in figure 7. It is seen that the calculated peak is wider and shifted to the center by 0.6 V. This can be explained by a lower value of the remanent polarization, and, consequently, a lower electron density in the accumulated layer. Attempts to adjust the both peaks led to the fact that the calculated peak for the positive bias shifted to the right and grew strongly in magnitude. It is possible that this discrepancy is due to the adopted polarization model which assumes that polarization inside the film is constant and does not depend on the local value of electric field.

It should also be noted that the appearance of the current peaks is a purely unsteady effect. It can be shown that the conduction currents inside the film near the contacts are not equal to each other, and their difference determines the rate of accumulation of a positive space charge in the film during the current measurement.
Figure 7. Current-voltage characteristics measured in the epitaxial PZT film at positive (curve 1, squares) and negative (curve 2, triangles) preliminary polarizations and calculated for the case of coincidence of the bias and polarization directions (solid line). In the simulation, $\phi_{BT1} = 0.65 \text{ V}$, $\phi_{BT2} = 0.7 \text{ V}$, $h_{D,1} = 1.2 \text{ nm}$, $h_{D,2} = 1 \text{ nm}$, the other parameters were similar for both barriers.

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