Processing and Application of Ceramics 13 [3] (2019) 277–280
https://doi.org/10.2298/PAC1903277K

The influence of polarization on properties of the potential barrier at metal-ferroelectric interface

Mikhail V. Kamenshchikov[1], Alexander V. Solnyshkin[1,*], Igor P. Pronin[2], Alexey N. Belov[3]

[1] *Tver State University, Tver, Russia*
[2] *Ioffe Institute, St. Petersburg, Russia*
[3] *National University of Electronic Technology, Zelenograd, Moscow, Russia*

Received 6 November 2018; Received in revised form 25 May 2019; Accepted 6 August 2019

Abstract

The barrier properties of a capacitor heterostructure based on a ferroelectric lead zirconate-titanate were investigated by using the methods of current-voltage and voltage-capacitance characteristics. The variable values of the potential barrier on the PZT-Pt interface were determined by the C-V method (from 0.5 to 1.6 eV) and the I-V method (from 0.5 to 0.7 eV). The spontaneous polarization influence on the potential barrier at the PZT-Pt interface was estimated.

Keywords: *films, lead zirconate titanates, ferroelectric properties, interfaces, potential barrier*

I. Introduction

Ferroelectric films are already used widely in modern microelectronics. Lead zirconate titanate $Pb(Zr_{1-x},Ti_x)O_3$ (PZT) films are one of the most perspective ferroelectric materials for applications in microelectromechanical systems (MEMS), pyroelectric and piezoelectric sensor devices, field-effect transistors, ferroelectric memory devices (FeRAM), etc. [1,2]. The properties of PZT films are not well understood yet, in contrast to the bulk ceramic materials, particularly when it comes to the subject of interface effects in heterostructures. The properties of the entire heterostructure can be often determined by the characteristics of a single heterojunction. If spontaneous polarization is taken in account, modelling and analysis of the physical processes at the ferroelectric-metal (or semiconductor) interfaces in the heterostructures become more complicated [3,4].

In this work, barrier effects due to the presence of a ferroelectric-metal interface (PZT-Pt) are investigated and the spontaneous polarization contribution to the potential barrier at the PZT-Pt interface is estimated. The potential barrier values at the PZT-Pt interface are determined by various methods taking into account the spontaneous polarization of the ferroelectric layer. Thus, the analysis of capacitance-voltage (C-V) characteristics and current-voltage (I-V) characteristics obtained experimentally in a wide temperature range was carried out.

II. Materials and methods

PZT-based film capacitor structures were the objects of studies in this paper. The films have n-type conductivity due to the oxygen vacancies [5]. The ferroelectric capacitors were deposited on the single crystal silicon wafers. A silicon oxide insulating layer, titanium oxide adhesive layer and bottom platinum electrode were previously formed on the silicon wafers. Deposition of the PZT layer was performed by two-step *ex-situ* method using radio-frequency magnetron sputtering from the ceramic target of $PbZr_{0.54}Ti_{0.46}O_3$ + 10 mol% PbO at the temperature of 150 °C. The single target was preliminary prepared on the base of PZT powder with PbO excess. After the PZT layer deposition, the structures without top electrodes were annealed at temperatures 540–570 °C (T_{ann}) for 1 h. It was necessary to create a perovskite structure having ferroelectric properties. Finally, top platinum electrodes with area from 0.01 to 0.1 mm^2 were deposited on the free film surface by sputtering. Thus, the $Pt/PZT/Pt/TiO_2/SiO_2/Si$ heterostructures with various annealing temperatures were prepared [6].

The thickness was estimated by scanning electron microscopy (SEM) on a JEOL JSM-35CF. The thick-

---

[*] Corresponding author: tel: +7 4822 581493,
e-mail: *a.solnyshkin@mail.ru*

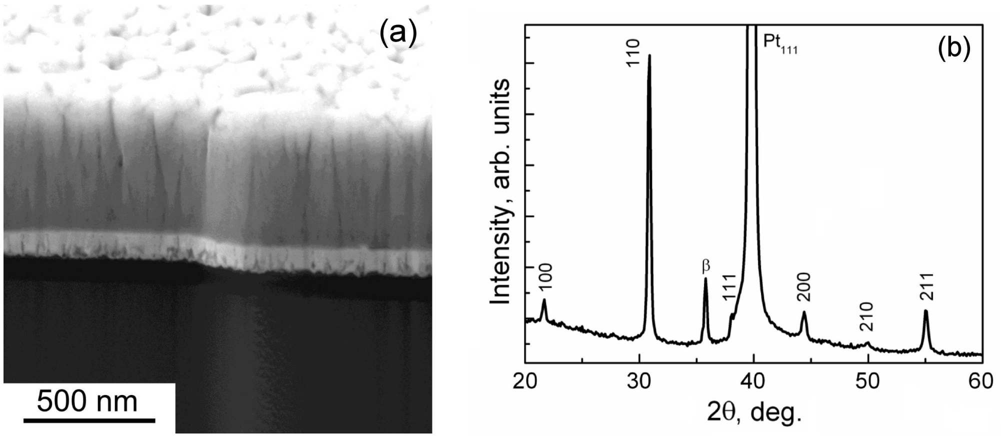

Figure 1. SEM image of a cross section (a) and X-ray diffraction pattern (b) of the PZT film (T_{ann} = 565 °C)

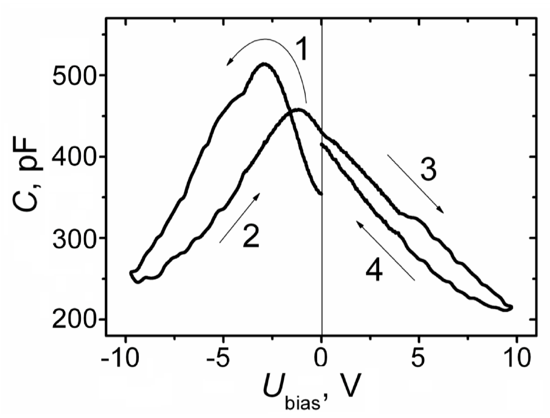

Figure 2. Dependence of capacitance versus the bias voltage for the Pt/PZT/Pt structure with T_{ann} = 565 °C (measurement conditions are $U_\sim$ = 0.1 V, f = 1 kHz)

ness of the PZT layer is equal to 500 nm (Fig. 1a). The X-ray diffraction analyses of the heterostructure were made with a DRON 3 diffractometer using CuK$_\alpha$ radiation (Fig. 1b). Thus, the PZT layers were polycrystalline films. These films had a self-polarization, thus it was not necessary to polarize them before the experiments.

C-V characteristics were measured by immittance meter E7-20. This device allowed applying the bias to the samples from −40 to 40 V in steps of 0.02 V in the range of −4 to 4 V and 0.2 V at higher voltages. The frequency of the test signal (f) may be changed from 25 Hz to 1 MHz, and its amplitude ($U_\sim$) may be varied from 40 mV to 1 V. *I-V* characteristics were obtained by applying the DC voltage to the samples using the power supply comprising of the battery of electrochemical cells and the voltage divider. The current through the sample was registered by the weak current meter U5-11. The detailed description of the experimental set-up is presented in previous paper [7]. The bias applied to the film had been assumed positive if a positive potential was applied to the top electrode, or vice versa.

III. Results and discussion

The analysis of the capacitance-voltage dependencies experimentally obtained at room temperature was performed. A typical *C-V* characteristics for thin-film capacitors based on PZT are shown in Fig. 2. It was already shown [8] that the shape of *C-V* characteristics depends on the annealing temperature. Also, it was found that the *C-V* characteristics obtained in repeated measurement cycles are different from the first one [9]. In this study, the results of the primary cycle of the *C-V* characteristics measurements were used.

The value of the potential barrier at the PZT-Pt interface was determined on the basis of *C-V* characteristics according to the model proposed by Rhoderick [10]. This model was applied to ferroelectrics [11,12]. For the estimation of potential barrier, the dependence of $1/C^2$ on the bias (U_{rev}) for reverse paths (curves 2 and 4 in Fig. 2) was plotted (Fig. 3). Extrapolation to the voltage-axis of the linear section of this dependence gives the value of V_b which is included in the potential barrier:

$$\varphi_b = V_b + \xi + \frac{kT}{q} \tag{1}$$

where $\xi = \frac{kT}{q} \cdot \ln \frac{N_c}{N_d}$ and V_b is the voltage cut-off, k the Boltzmann constant, T the temperature, N_c the effective density of states and N_d the donor concentration.

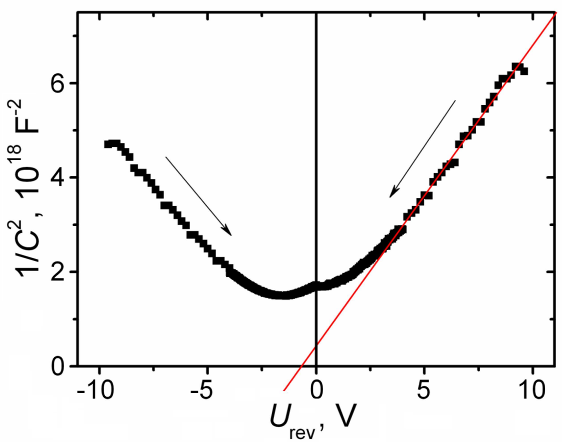

Figure 3. $1/C^2$ vs U_{rev} for the Pt/PZT/Pt film with T_{ann} = 545 °C (measurement was carried out at $U_\sim$ = 0.1 V, f = 1 kHz)

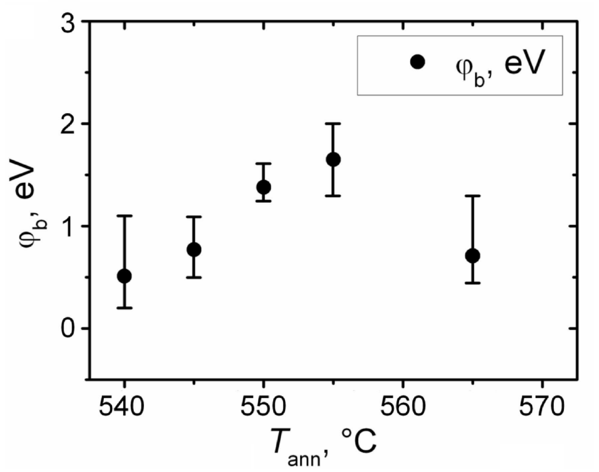

Figure 4. Dependence of φ_b obtained from *C-V* characteristics on the annealing temperature

For calculating the value of φ_b, we may only take into account the cut-off value of V_b, because $\xi = k \cdot T/q <$ 0.1 V. The similar calculation was carried out for PZT films with different annealing temperatures. Figure 4 shows the values of φ_b calculated by equation 1 for the PZT film structures with various annealing temperatures.

The value of the potential barrier at the Pt-PZT interface was also determined on the basis of *I-V* characteristics, which is described in detail by Pintilie *et al.* [13]. In this case, the current density is:

$$J = A^* T^2 \exp\left(-\frac{q}{kT}\left(\Phi_B^0 - \sqrt{\frac{qE_m}{4\pi\varepsilon_0\varepsilon_{op}}}\right)\right) \tag{2}$$

where A^* is Richardson's constant, Φ_B^0 the potential barrier height at zero applied field, E_m the electric field strength, ε_0 the vacuum permittivity and ε_{op} the high frequency (optical) dielectric constant. Equation 2 may be presented as:

$$\ln\frac{J}{T^2} \approx \ln A^* - \frac{q\Phi_B^0}{kT} - f(V^{1/2}) \tag{3}$$

or

$$F(T) \approx \ln A^* - \frac{q\Phi_B^0}{kT} \tag{4}$$

The dependence of $\ln(J/T^2)$ on $V^{1/2}$ (Fig. 5a) at a constant temperature should be straight, and its cut-off on the y-axis gives the value of $F(T)$. From the graph $F(T)$ versus $1/T$ (Fig. 5b) it is possible to extract the value of the potential barrier of Φ_B^0 from the slope, and the Richardson constant from the cut-off along the ordinate axis.

For the films with T_{ann} =545–570 °C, the value of the potential barrier at the Pt-PZT interface calculated from the *I-V* curves varies from 0.1 to 0.3 eV without any specified tendency related to the annealing temperature.

As it can be seen from equation 2, the key value in the exponent is the electric field strength of E_m, which, in the case of ferroelectrics, depends on the polarization P [13]:

$$E_m = \sqrt{\frac{2qN_{eff}V}{\varepsilon_0\varepsilon_{op}}} + \frac{P}{\varepsilon_0\varepsilon_{st}} \tag{5}$$

where ε_{st} is the static dielectric constant. Then equation 2 takes the form:

$$J \approx \exp\left(-\frac{q}{kT}\left(\Phi_B^0 - \sqrt{\frac{q}{4\pi\varepsilon_0\varepsilon_{op}}\left(\frac{P}{\varepsilon_0\varepsilon_{st}} + \sqrt{\frac{2qN_{eff}V}{\varepsilon_0\varepsilon_{st}}}\right)}\right)\right) \tag{6}$$

If $\sqrt{\frac{2qN_{eff}V}{\varepsilon_0\varepsilon_{st}}} \ll \frac{P}{\varepsilon_0\varepsilon_{st}}$, the conduction current is:

$$J \approx \exp\left(-\frac{q}{kT}\left(\Phi_B^0 - \sqrt{\frac{qP}{4\pi\varepsilon_0^2\varepsilon_{op}\varepsilon_{st}}} - \sqrt{\frac{q^2N_{eff}V}{8\pi\varepsilon_0\varepsilon_{op}P}}\right)\right) \tag{7}$$

Polarization-dependent and voltage-independent terms can be considered as values defining the "apparent" potential barrier:

$$\Phi_{B,app}^0 = \Phi_B^0 - \sqrt{\frac{qP}{4\pi\varepsilon_0^2\varepsilon_{op}\varepsilon_{st}}} \tag{8}$$

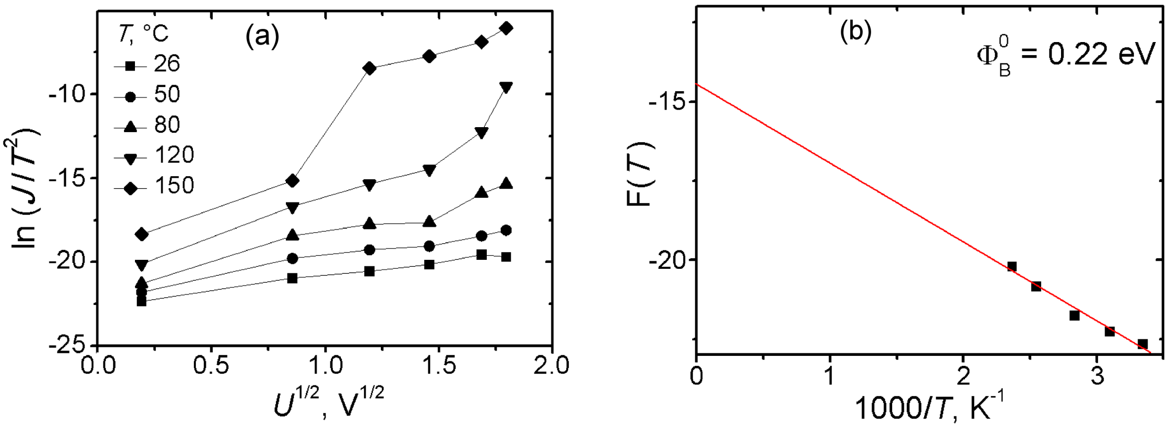

Figure 5. Plots of ln (J/T^2) vs $V^{1/2}$ (a) and *F(T)* vs *1/T* (b) for determining the value of potential barrier based on the *C-V* characteristics for the PZT film with T_{ann} = 540 °C

Thus, the Φ_B^0 values determined on the basis of the equations 2 and 3 are in fact the $\Phi_{B,app}^0$ value presented in equation 8. On the base of the experimental data, the value of the polarization term of $(qP/4\pi\varepsilon_0^2\varepsilon_{op}\varepsilon_{st})^{1/2}$ in equation 8 was estimated. We took a spontaneous polarization equal to 100 μC/cm^2 as the polarization value P in this expression 8. The ε_{op} value determined from the *I-V* curves at various temperatures was about 6 [14]. The ε_{st} value was assumed equal to 200 that was the average value of the dielectric constant at a test signal frequency of 1 MHz and its value of 40 mV and under high bias field of 200 kV/cm. Such conditions were chosen to reduce the contribution of the domain wall oscillation to the dielectric response [9]. Thus, the polarization term contribution to the potential barrier value was approximately estimated as 0.4 eV. Apparently, this accounts for the difference in the potential barrier values calculated for the PZT-Pt interfaces on the basis of *I-V* and *C-V* characteristics. Thus, the calculation of the φ_b value obtained from the *C-V* curves takes into account the contribution of spontaneous polarization, but φ_b determined from the *I-V* curves does not include it.

IV. Conclusions

In this paper, the estimations of potential barrier near the Pt-PZT interface in the Pt/PZT/Pt/TiO$_2$/SiO$_2$/Si heterostructure were carried out. The potential barrier value at the PZT-Pt interface was determined on the basis of the *I-V* and *C-V* curves measured experimentally. Calculations performed using the *C-V* and *I-V* characteristics yield from 0.5 to 1.6 eV and from 0.5 to 0.7 eV, respectively. The contribution of the spontaneous polarization of the ferroelectric layer to the potential barrier at the PZT-Pt interface is numerically determined to be equal to 0.4 eV.

Acknowledgement: This work was supported by the Russian Science Foundation (Grant N 15-19-00138).

References

1. J.F. Scott, “Applications of modern ferroelectrics”, *Science*, **315** [5814] (2007) 954–959.
2. L.W. Martin, A.M. Rappe, “Thin-film ferroelectric materials and their applications”, *Nat. Rev. Mater.*, **2** (2016) 16087.
3. M. Dawber, J.F. Scott, “Calculation of Schottky barrier height of platinum/lead zirconate titanate interface”, *Integ. Ferroelectrics*, **38** [1-4] (2001) 161–169.
4. L. Pintilie, M. Alexe, “Metal-ferroelectric-metal heterostructures with Schottky contacts. I. Influence of the ferroelectric properties”, *J. Appl. Phys.*, **98** [12] (2005) 124103.
5. I.P. Pronin, E.Y. Kaptelov, E.A. Tarakanov, L.M. Sorokin, V.P. Afanasjev, A.V. Pankrashkin, “Self-polarization and migratory polarization in thin-film ferroelectric capacitor”, *Integ. Ferroelectrics*, **49** [1] (2002) 285–294.
6. I.P. Pronin, E.Y. Kaptelov, S.V. Senkevich, V.A. Klimov, N.V. Zaitseva, T.A. Shaplygina, V.P. Pronin, S.A. Kukushkin, “Crystallization of thin polycryctalline PZT films on Si/SiO$_2$/Pt substrates”, *Phys. Solid State*, **52** [1] (2010) 132–136.
7. A.V. Solnyshkin, A.S. Troshkin, A.A. Bogomolov, I.P. Raevski, D.N. Sandjiev, V.Yu. Shonov, “Current-voltage characteristics and photostimulated conductivity in ferroelectric heterogeneous structure Al/Sn$_2$P$_2$S$_6$/Al”, *Integ. Ferroelectrics*, **106** (2009), 61–69.
8. M.V. Kamenshchikov, A.V. Solnyshkin, I.P. Pronin, “Peculiarities of C-V characteristics of PZT films depending on annealing temperature”, *Ferroelectrics*, **508** [1] (2017) 108–114.
9. M.V. Kamenshchikov, A.V. Solnyshkin, I.P. Pronin, “Dielectric response of capacitor structures based on PZT annealed at different temperatures”, *Phys. Lett. A*, **380** [47] (2016) 4003–4007.
10. E.H. Rhoderick, *Metal-Semiconductor Contacts*, Clarendon Press, Oxford, 1978.
11. B.H. Park, S.J. Hyun, C.R. Moon, B.-D. Choe, J. Lee, C.Y. Kim, W. Jo, T.W. Noh, “Imprint failures and asymmetric electrical properties induced by thermal processes in epitaxial Bi$_4$Ti$_3$O$_{12}$ thin films”, *J. Appl. Phys.*, **84** [8] (1998) 4428–4435.
12. M. Maleto, E. Pevtsov, A. Sigov, A. Svotina, “Polarization switching and dielectric properties of PZT structures”, *Integ. Ferroelectrics*, **43** [1] (2002) 65–70.
13. L. Pintilie, I. Vrejoiu, D. Hesse, G. LeRhun, M. Alexe, “Ferroelectric polarization-leakage current relation in high quality epitaxial Pb(Zr,Ti)O$_3$ films”, *Phys. Rev. B*, **75** (2007) 104103.
14. M.V. Kamenshchikov, A.V. Solnyshkin, A.A. Bogomolov, I.P. Pronin, “Conductivity and current-voltage characteristics of PZT thin-film heterostructures”, *Phys. Solid State*, **53** [10] (2011) 2080–2084.