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

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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(Zr₁₋ₓ,Tiₓ)O₃ (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 PbZr₀.₅₄Ti₀.₄₆O₃ + 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 mm² were deposited on the free film surface by sputtering. Thus, the Pt/PZT/Pt/TiO₂/SiO₂/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-
Figure 1. SEM image of a cross section (a) and X-ray diffraction pattern (b) of the PZT film ($T_{\text{ann}} = 565 ^\circ \text{C}$)

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

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

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 ($U_{\text{rev}}$) 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:

$$\varphi_b = V_b + \xi + \frac{kT}{q},$$  \hspace{1cm} (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.
For calculating the value of $\varphi_b$, we may only take into account the cut-off value of $V_b$, because $\xi = k \cdot T / q < 0.1 \, \text{V}$. The similar calculation was carried out for PZT films with different annealing temperatures. Figure 4 shows the values of $\varphi_b$ 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:

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

where $A^*$ is Richardson’s constant, $\Phi_B^0$ the potential barrier height at zero applied field, $E_m$ the electric field strength, $\varepsilon_0$ the vacuum permittivity and $\varepsilon_{op}$ the high frequency (optical) dielectric constant. Equation 2 may be presented as:

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

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 $\Phi_B^0$ from the slope, and the Richardson constant from the cut-off along the ordinate axis.

For the films with $T_{\text{ann}} = 545–570^\circ\text{C}$, 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]:

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

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

$$J \approx \exp \left\{ -\frac{q}{kT} \left( \Phi_B^0 - \frac{qP}{4\pi\varepsilon_0\varepsilon_{op}\varepsilon_{st}} + \frac{2qN_{\text{eff}}V}{8\pi\varepsilon_0\varepsilon_{op}\varepsilon_{st}} \right) \right\} \tag{6}$$

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

$$J \approx \exp \left\{ -\frac{q}{kT} \left( \Phi_B^0 - \frac{qP}{4\pi\varepsilon_0\varepsilon_{op}\varepsilon_{st}} \right) \right\} \tag{7}$$

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

$$\Phi_{B,\text{app}}^0 = \Phi_B^0 - \sqrt{\frac{qP}{4\pi\varepsilon_0\varepsilon_{op}\varepsilon_{st}}} \tag{8}$$
Thus, the $\Phi_0$ values determined on the basis of the equations 2 and 3 are in fact the $\Phi_{app}$ value presented in equation 8. On the basis of the experimental data, the value of the polarization term of $(qP/4\pi\varepsilon_0^2\varepsilon_{app}\varepsilon_{st})^{1/2}$ in equation 8 was estimated. We took a spontaneous polarization equal to $100\mu\text{C/cm}^2$ as the polarization value $P$ in this expression. The $\varepsilon_{app}$ value determined from the $I$-$V$ curves at various temperatures was about 6 [14]. The $\varepsilon_{st}$ 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 $\varphi_b$ value obtained from the $C$-$V$ curves takes into account the contribution of spontaneous polarization, but $\varphi_b$ 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