Polarization switching and dielectric properties of ferroelectric thin films

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Abstract: We designed multifunctional measuring system for ferroelectric thin films which differs from analogous ones by open architecture. Special model taking into account interface layers close to metal electrodes has been suggested. These procedures have been used for investigation of ferroelectric structures based on $Pt/PbZr_{0.52}Ti_{0.48}O_3/Pt/Ti/SiO_2/Si$ (PZT). Appreciable asymmetric capacitance-voltage curves and hysteresis loops behavior has been obtained for some specimens. These results provide an explanation for the models, which describes the Pt/PZT/Pt structure as a series circuit of three depletion layer capacitors. To explain the electrical asymmetries, we assumed that they came from the interfacial state difference between the top Pt/PZT and the bottom PZT/Pt. Following this method for the high field voltage, we could obtain values of associated parameters, such as the depletion layer capacitance, bulk permittivity, and space-charge density. This work was supported by RFBR (N 01-02-16607, N 02-02-06353), DERF (N 03 03 062), and by NFO (N 16-04-1999).

Keywords: ferroelectric films; ferroelectric hysteresis; polarization; dielectric properties; capacitance-voltage characteristics.

INTRODUCTION

Integration of active dielectric materials in microelectronics was very intensive last decade. It gave rise to a new generation of microelectronic devices, such as uncooled pyroelectric arrays, microelectromechanical systems, non-volatile random access memory, microwave integrated circuits [1]. Our research group applied first attempts in this field in the early nineties, beginning from the works dealt with the technology of ferroelectric thin films integrated with silicon CMOS structures. Consequently, the importance of the investigation of the electrophysical properties of ferroelectrics is beyond question. However, fewer works were devoted to the problems of measuring equipment design and the measuring experimental techniques for ferroelectric films. This paper presents some our developments in this area which were carried out during last decade. Our main concern in the present work was to develop and improve the basic ideas of the combined approach to some electric measurements of ferroelectric films proposed earlier [2].

MULTIFUNCTIONAL MEASURING SYSTEM FOR FERROELECTRIC THIN FILMS

Multifunctional measuring system for ferroelectric thin films (MMSFF) under our design differs from analogous ones by open architecture. This opens a possibility for the explorers of easy and low cost changing its configuration. MMSFF is quite adopted with hardware and software of the leading company in the field of measuring technique and systems of data acquisition. The base configuration of MMSFF allows one to make measurements in temperature range from 10 to 200°C (±1°C). Normalized metrological characteristics are provided by the usage of standard measuring tools (LRC-meter, electrometer, temperature control units) connected with PC by means of General Purpose Interface Bus. MMSFF also contains board of extension ISA or PCI bus including ADC with buffer intrinsic memory of 50 ns minimum time conversion and DAC.

MMSFF admits:

- Studying the ferroelectric hysteresis by means of reconstruction loop taking into account the differential capacity of "empty" capacitor (applied voltage varies from -200 to +200 V, scanning frequency is 0,01...10 kHz, reference capacity is 10...100 nF, error of the polarization value is no more than 10%).

- Determining pyroelectric coefficient by static and quasy-static techniques (period of low-frequency temperature wave is varied from 0,1 to 50 s, the limitation of current sensitivity is 10^{-14}A, error of the method is no more than 20%).

- Taking magnitude of remanent polarization using two couples of switching current pulses (switching voltage range is from -15 to +15 V, rise time of pulses is no more than 0,1 s, maximum frequency is 500 kHz, error of the measurement is no more than 10%).

- Measuring dielectric characteristics of the films with the use of programmable voltage sweep (range of the applied voltage is up to 200 V, test signal frequency and amplitude is in the range 0,1...1000 kHz and 0,05...1 V, error of the measurement is no more than 0,1%).

- Measuring the specimen electrical conductance in the same range of voltage sweep (current sensitivity is 10^{-14} A, error of the measurement is no more than 20%).

MMSFF was mainly used for testing the ferroelectric films, which were designed for applications in memory devices and IR-sensors. The examined specimens were $Pt/PbZr_{0.52}Ti_{0.48}O_3/Pt/Ti/SiO_2/Si$ (PZT) multilayer structures on silicon substrates with SiO_2 interlayers fabricated by the sol-gel technology from colloidal solutions produced by the electrochemical synthesis in methylcellosolve (see Ref. [3]). The film thickness was 0.2...0.3 μm. The lead content of the source solutions was optimized as regards to the best parameters of the ferroelectric hysteresis loop, breakdown voltage, and dielectric losses. From the same standpoint, the optimum regimes of heat treatment were chosen as well. Using this equipment original measurement procedure of the ferroelectric structures behavior have been designed and approved.

MEASUREMENTS OF HYSTERESIS LOOPS AND REMANENT POLARIZATION

The simplest method of ferroelectric film properties investigation is the well known Sawyer-Tower procedure. It is important in this case to eliminate the shunt influence of measuring amplifier, i.e. to use circuits with very high input impedance. This is especially important for the case of low frequency (less than 100 Hz). As an alternative it is possible to propose the measurement of the current in reference resistance with subsequent integration (see Fig.1)

However, the comparison of hysteresis loops, obtained by these two methods reveals some differences. That is connected evidently with an existence of intrinsic leakage in the film at the measurement frequency. Really, the expression for the current value I at a series resistor can be given as: $I=[C+V(dC/dV)]dV/dt+VG$, where C and G are correspondingly the non-linear sample capacitance and conductivity, V is the applied voltage. Under the integration, the linear part of conductivity can be taken into account on the base of closed charge loop consideration, the influence of higher-order terms leads to the hysteresis loop expansion. Such an estimation of the linear part yields about 1.5 mS.

For applications it is important to know the remanent polarization dependence on applied depolarizing voltage. Two methods were used for its evaluation. In the first method we used the nonsymmetric hysteresis loops. If the voltage scanning (from $-V_{max}$ to $+V_{max}$) is symmetric, the sample is fully repolarized and the cross points of the loop with the ordinate axis determines $+P_R$ and $-P_R$ values. For the asymmetric scanning, only partial repolarization takes place: from $+P_R$ to $-P_R(V)$ value or from $-P_R$ to $+P_R(V)$, where $-V_{max} < V < V_{max}$. The results of correspondent measurements are displayed in Fig.2.

In the second method the pulse switching of remanent polarization was used. It is more convenient for such measurements to use the pulse switching of remanent polarization. In this case a couple of pulses is applied to the sample with determined state of polarization, the first one polarizes it in the opposite direction and charges a ferroelectric capacitor, and the second one only charges the capacitor. The switching charge magnitude is determined as an integral of the appropriate current pulses difference. One can see a good agreement between the data obtained by both methods.

CAPACITANCE-VOLTAGE CHARACTERISTICS

As the hysteresis loops represent integrally the result of external electric field action, they also must contain the information on capacitance-voltage characteristics for the differential capacitance. The shape of C-V characteristics of PZT films for 1 V/s linear sweep voltage only slightly depends on test signal frequency in the range of 0.1-1000 kHz. To establish the connection between hysteresis loop and C-V characteristics we used the Sawyer-Tower method, applying to the sample the sweep voltage nonsymmetric with respect to zero. The differential capacitance value was determined according to the slope of the loop part, when the polarization pulse switching came to an end, i.e. at the beginning of the sweep voltage reverse. The values of differential capacitance for positive and negative nonsymmetric loops calculated by this method show the good correlation with the results of direct measurements by LRC-meter (see Fig.3).

The C-V characteristics displayed in Fig.3 are typical for PZT films on silicon substrate. Decreasing of permittivity by several tens percents in view of frequency increasing from 0.1 kHz to 1 MHz is typical for such specimens. From subsequent experiments we concluded that such a behavior of C-V can be ascribed to existence of the interface states in intermediate layers of the ferroelectric structure. The permittivity increase with increasing temperature for these specimens in the range from 30 to 200°C has analogous explanation. The estimation of dielectric constant temperature coefficient gives the values of 30…40 1/K. By fitting the C-V data vs temperature and frequency dispersions with a model capacitance of this structure the space-charge density and mobility were estimated. According to our evaluations this mobility is negligible (less than $1 \cdot 10^{-3}$ $m^2/V \cdot s$). It also can be explained by the influence of intermediate layers dielectric properties with high density of surface states.

Voltage-current characteristics in our analysis confirm these results. Under 1.0V applied voltage the current density for the films with the thickness about 0.2 μm was 2 nA/cm^2. But it increases by several powers of 10 under applied voltage of few volts. And one can see current relaxation to a constant value with the time constant of few minutes. The same situation takes place when measuring the short circuit current just after repolarization. In this case the short circuit current decreases to the values less then 1 pA within a few minutes.

An interesting specific feature of C-V characteristics for specimens with ferroelectric films deposed on a superconductor have been observed as distinct from PZT based structures. The results for $PbZr_{0,52}Ti_{0,49}O_3/Y_1Ba2Cu_3O_{7-x}$ (PT/YBCO) heterostructures are displayed in the Fig.4. These structures have been grown on $LaAlO_3$ substrates using a Nd:YAG pulsed deposition system (A.M. Grishin et al. [5], Royal Institute of Technology, S-100 44, Stockholm, Sweden). We observed specific abnormal monotony on sweep forward motion in C-V curves (undershoots of permittivity). As for pure ferroelectrics without superconductors such an effect doesn't appear at all, the influence of polarisation switching processes upon dielectric properties of high-temperature superconductors occurs. An observable effect of permittivity undershoots may be used for development of electronic devices with non-linear dependence of capacitance vs applied voltage (variconds and varicaps, for example).

A good agreement of these data stimulated attempts of making the hysteresis loop reconstruction, excluding the component caused by a nonlinearity of the dielectric constant. For this purpose we subtracted the curve of the direct voltage-capacitance characteristic measurement from the result of differentiation of the initial hysteresis loop, and reconstructed the hysteresis loop again by the integration. The results obtained are discussed in detail in Ref. [6].

The effects of interface layers and of the process of charge transfer on the ferroelectric thin films dielectric behavior were studied. A specific model taking into account interface layers close to metal electrodes has been suggested. These procedures have been used for investigation PZT structures. Appreciable asymmetric capacitance-voltage curves and hysteresis loops behavior have been obtained for some specimens. These results provide an explanation for the model which describes the Pt/PZT/Pt structure as a series circuit of three depletion layer capacitors, according to Schottky diode model (see Ref. [7]). In the case being considered, $1/C^2 \sim k(V-V_F)$ (here V_F is the voltage drop on the ferroelectric itself), and hence the influence of interfacial states, and the voltage drop in the intrinsic ferroelectric can be determined. To explain the electrical asymmetries, we assumed that they came from the interfacial state difference between the top Pt/PZT and the bottom PZT/Pt. Following this method for the high field voltage, we could obtain values of associated parameters, such as the depletion layer capacitance, bulk permittivity, and interface states and space-charge density. An example of this technique is shown in Fig.5.

Using these principles allows one to fabrication optimise technological methods for preparation of structures based on ferroelectric films important for practical applications.

CONCLUSIONS

Developed multifunctional measuring system is useful and effective facility for investigation of physical processes in ferroelectric based structures. It makes possible to carry out determination of basic electrophysical characteristics of ferroelectrics: studying the ferroelectric hysteresis, determining pyroelectric coefficient by static and quasy-static techniques, taking magnitude of remanent polarization, measurements of dielectric characteristics, measurements of the specimen electrical conductance. The measuring system has open architecture and it is easy to readjust it to solve specific problems including applications, for example, optimization of technological processes of ferroelectric films fabrication for memory devices or uncooled focal plane arrays. Combined studies of C-V characteristics, polarization saturation, remanent polarization, and pyroelectric coefficient show that developed and improved methods complete each other and have a good correlation. Basing on this measuring system there were developed several methods which give the opportunity to improve the comprehension of the processes in ferroelectric systems from physical point of view. They may give experimental data for both theoretical studies and engineering design of various devices.

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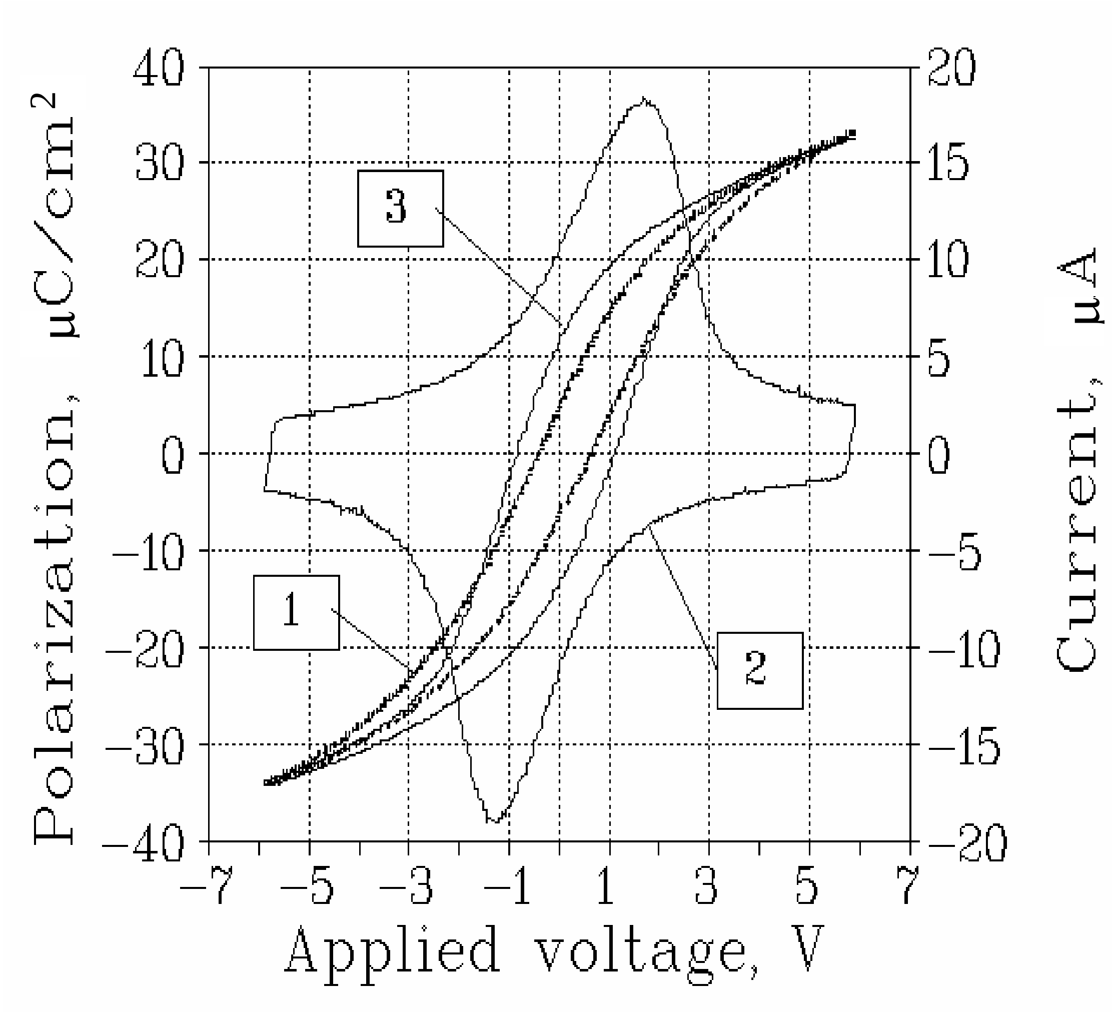

Figure 1. Ferroelectric hysteresis loops of PZT films: obtained by reference capacitance (curves 1), measured by reference resistors and the result of its integration (curves 2 and 3 correspondingly).

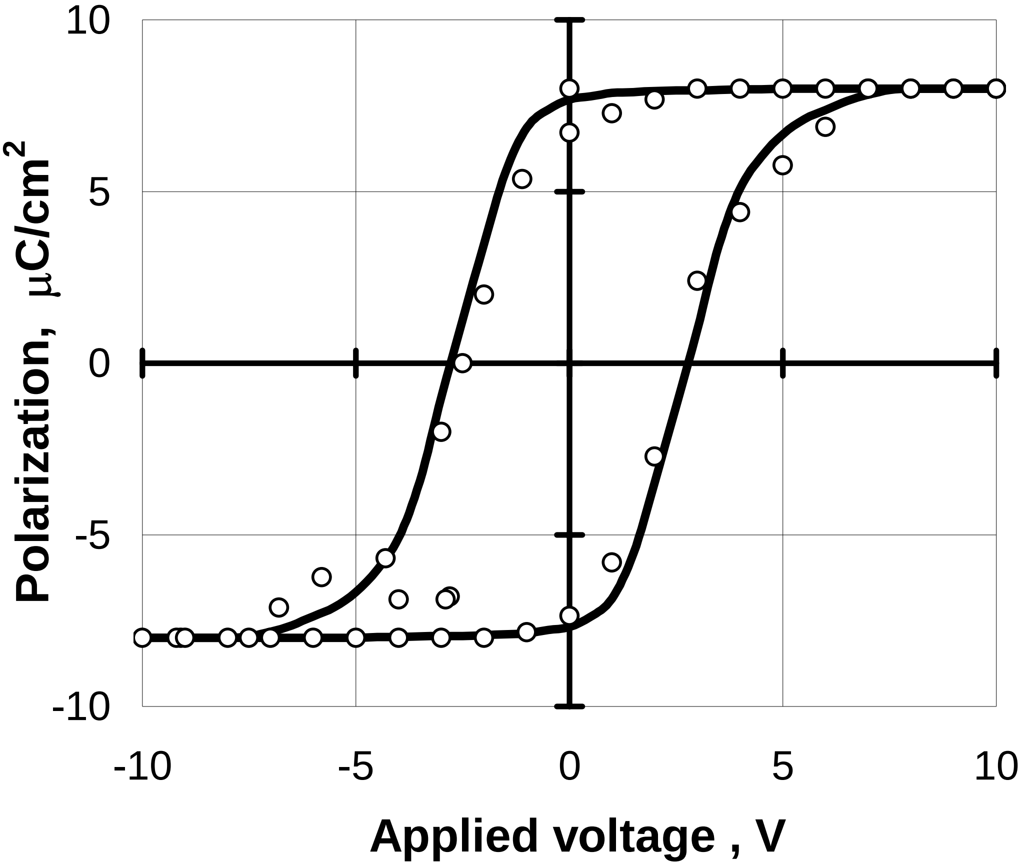

Figure 2. Remanent polarization hysteresis obtained from measurements of nonsymmetric hysteresis loops

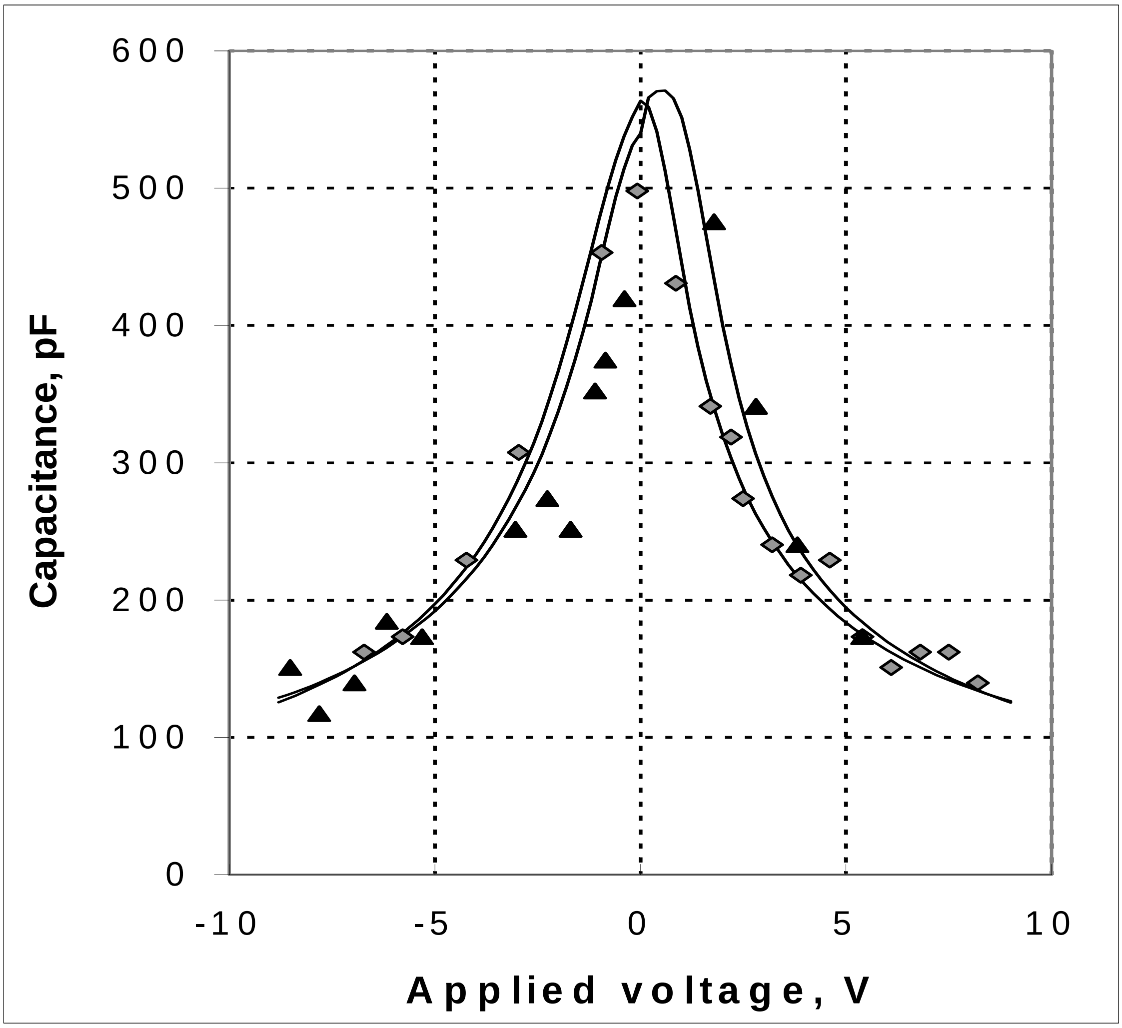

Figure 3. C-V characteristics of PZT structure: results of direct measurements and calculated curves based on the derivatives of nonsymmetric hysteresis loops.

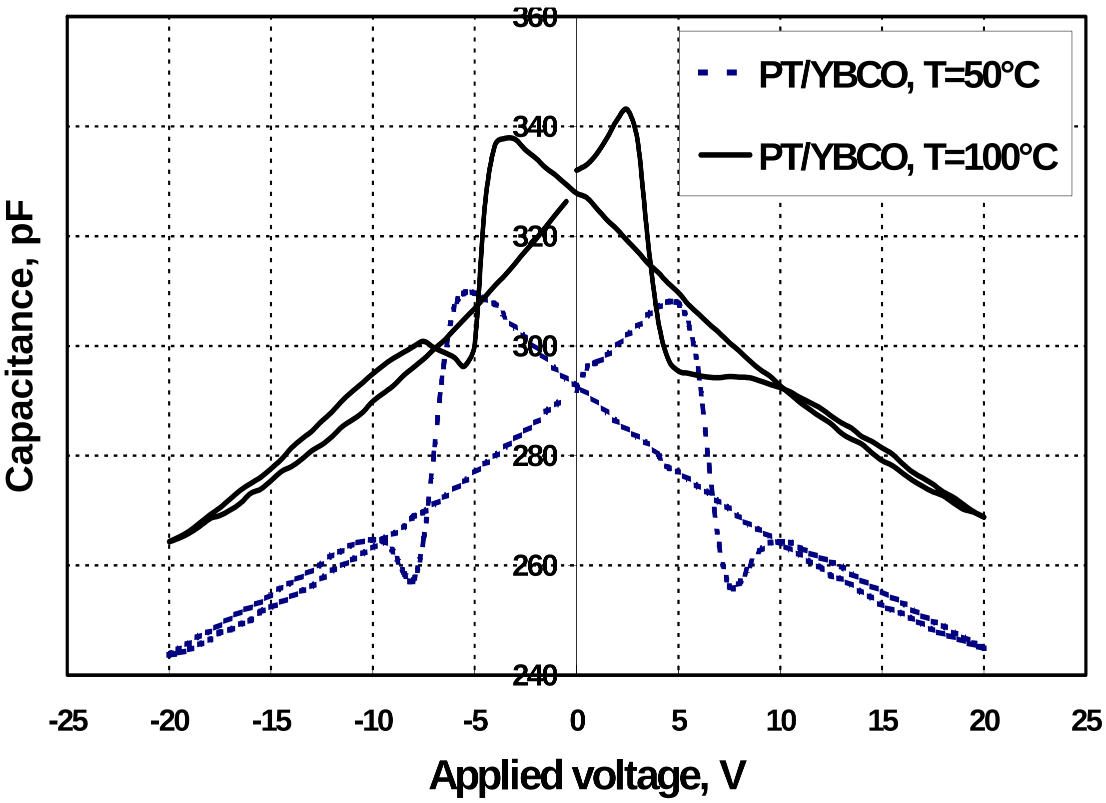

Figure 4. Capacitance-voltage characteristics of the PT/YBCO structure.

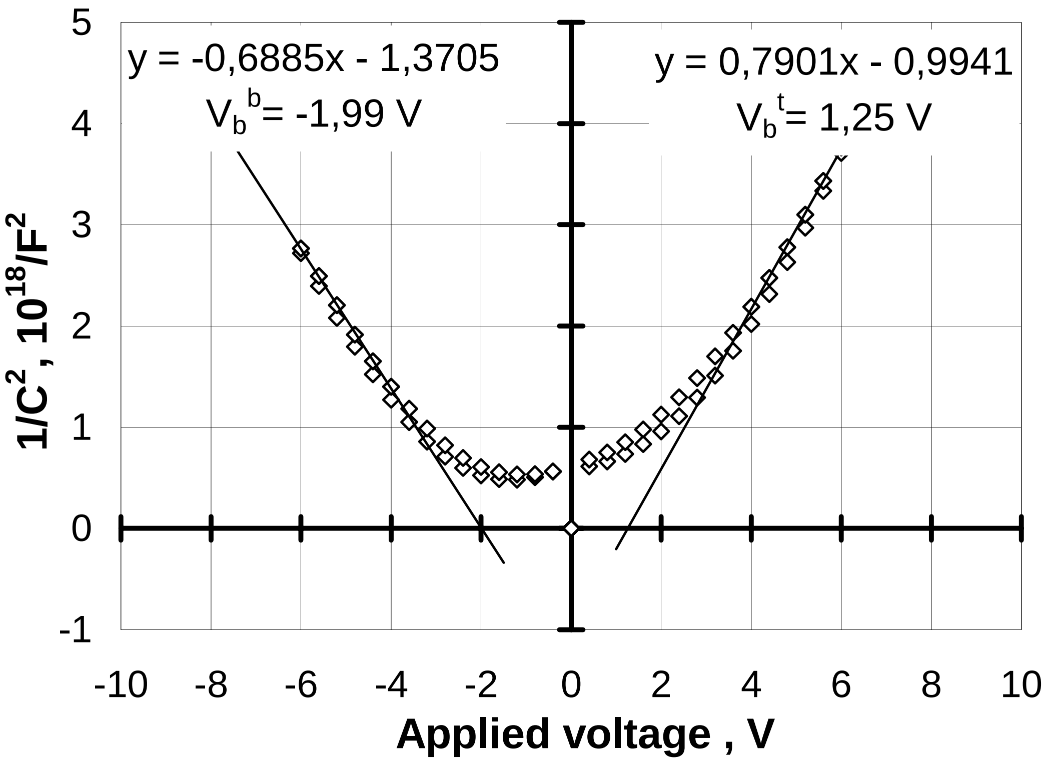

Figure 5. The Schottky diode model in the PZT structure. Thin lines denote the results of linear fitting for high field regions (magnitudes of interface states density are in region 0.6...2.2 10^{19} 1/cm^3).