MULTIFUNCTIONAL MEASURING SYSTEM FOR INVESTIGATION OF FERROELECTRIC THIN FILMS

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Abstract. Developed multifunctional measuring system is useful and effective facility for investigation of physical processes in ferroelectric based structure. It makes possible to carry out measuring of basic electrophysical characteristics of ferroelectrics: studying the ferroelectric hysteresis, determining pyroelectric coefficient by static and quasy-static techniques, taking magnitude of remanent polarization, measuring dielectric constants, measuring 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,. Basing on this measuring system there were developed several methods which give an opportunity to improve the comprehension of processes in ferroelectric systems from physical point of view.

Keywords: ferroelectric films; ferroelectric hysteresis, remanent polarization; pyroelectric coefficient; pyroelectric hysteresis; 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 by earlier [2,3].

MULTIFUNCTIONAL MEASURING SYSTEM FOR FERROELECTRIC THIN FILMS

Multifunctional measuring system for ferroelectric thin films (MMSFF) under our design differs from analogous 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 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 Reference [4]). The film thickness was 0.2...0.3μm. 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. Some of them are discussed below.

MEASUREMENTS OF HYSTERESIS LOOPS AND REMANENT POLARIZATION

The determination of ferroelectric hysteresis loops themselves is easy to realize. However time we propose some original techniques.

Measurements of ferroelectric hysteresis loops by reference capacitance and reference resistors. 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.

However, the comparison of hysteresis loops, obtained by these two methods (see Figure 1) 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.

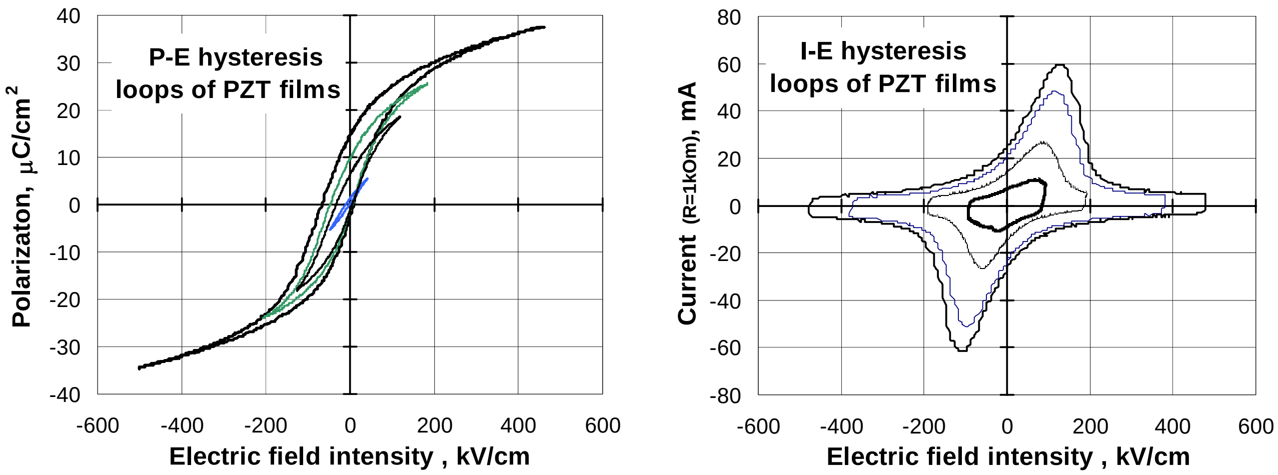


Figure 1. *Hysteresis loops: obtained by reference capacitor (the Sawyer-Tower method) and obtained by*

reference resistor method

Remanent polarization measurements. For applications it is important to know the remanent polarization P_R dependence on applied depolarizing voltage. Two methods were used for its evaluation.

Let us refer again to 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 Figure 2.

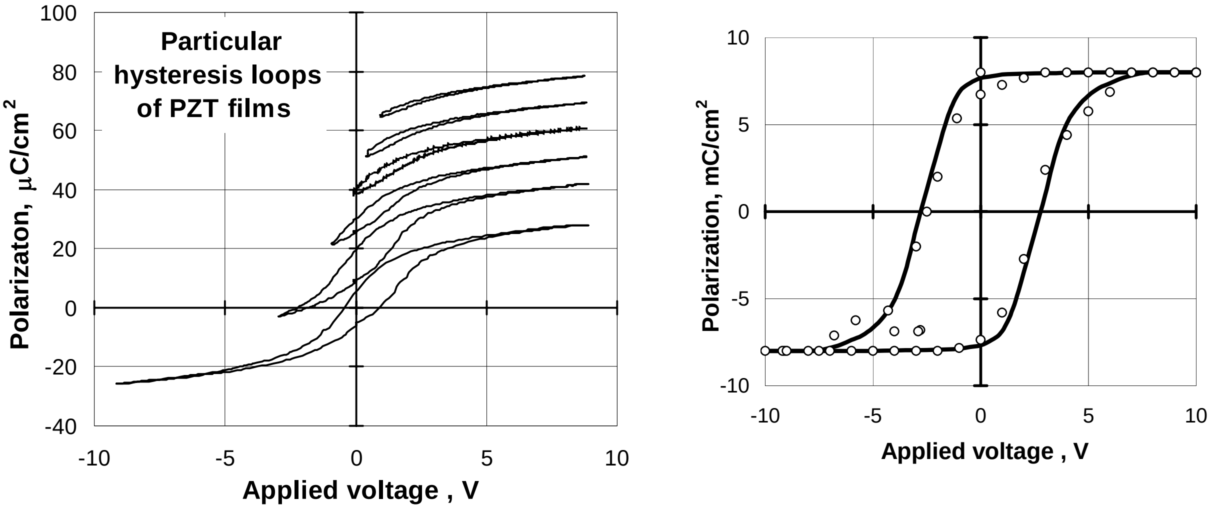


Figure 2. *Remanent polarization hysteresis obtained from measurements of nonsymmetric hysteresis loops*

On the other hand, it is more convenient for such measurements to use the pulse switching of remanent polarization [3]. 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. The remanent polarizations $-P_R$ (V) and $+P_R$ (V) vs the switching pulses amplitude thus obtained are given in Figure 3. One can see a good agreement between the data obtained by both methods.

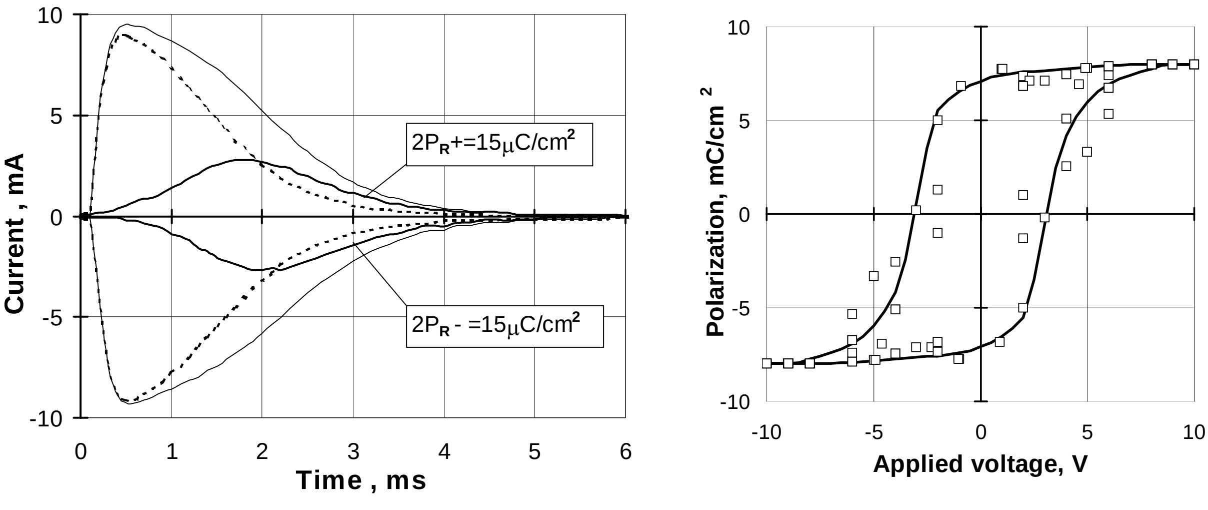


Figure 3. *Remanent polarization hysteresis obtained from loops the pulse current of polarization switching*

It should be noted that the field strength does not exceed $40 kV/cm^2$. Such a gentle repolarization can be explained by the influence of depolarizing fields inside the film and by the existence of metal-dielectric interface. One can get additional information on these interlayer effects from voltage-capacitance characteristics of such structures.

VOLTAGE-CAPACITANCE 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 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. The estimation of dielectric constant temperature coefficient gives the values of 30-40 1/K. Specific characteristics of the films under investigation are an unclosed loop after the voltage return to zero. This indicates the existence of dynamic processes in the films with relaxation times of the order of the sweep time.

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 was finished, 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 Reference [5]). 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 Reference [6]. Such a method can be useful for obtaining correct data for a theoretical analysis, and allows one to find more correctly the polarization saturation value P_S, which was in the range of 20-30 $\mu C/cm^2$ for our films.

The effect of interface layers and the process of charge transfer on the ferroelectric thin films (the thickness was 0,2…0,3μm) dielectric behavior were studied. Special 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 Reference [7]). In the case being considered is $1/C^2 \sim k(V-V_F)$, (here V_F is the voltage drop on the ferroelectric itself) and hence can by determined influence of interfacial states, and the drop of voltage in the intrinsic ferroelectric. 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 Figure 4.

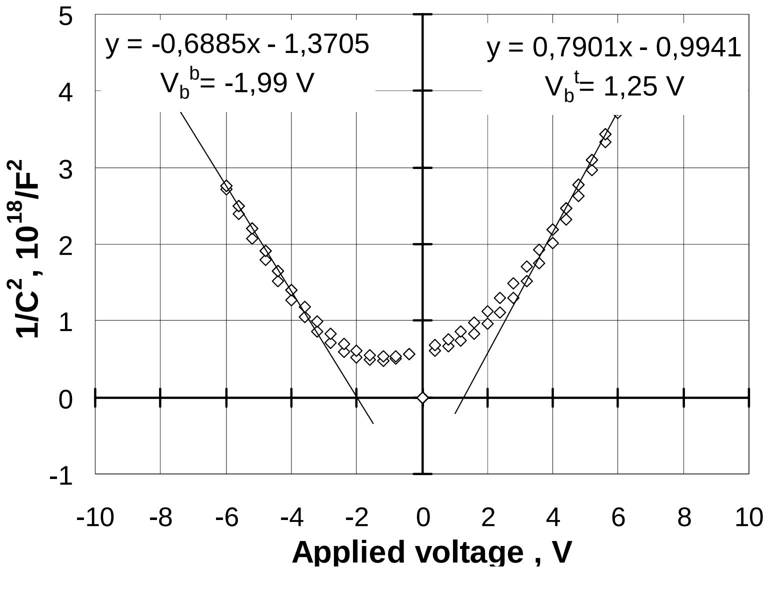


Figure 4. *C-V characteristics of Pt/BT/Pt/SiO$_2$/Si structure and plot of $(1/C)^2$ vs. V. Solid lines denote the results of linear fitting for the high field regions (magnitudes of interface states density are in region*

(0.6-2.2) 10^{-19} *1/cm*^{3}*)*

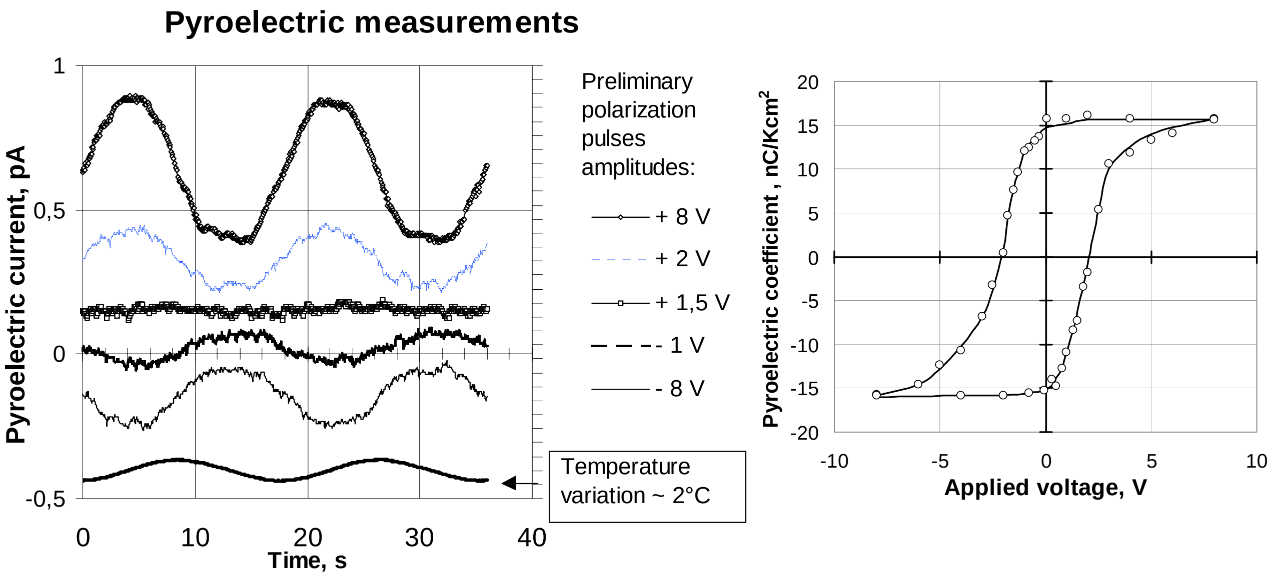
VOLTAGE-CURRENT CHARACTERISTICS

Current density for our films with the thickness about 0.2μm was 2nA/cm^2 under applied voltage of 1.0V. 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 under measuring the short circuit current just after repolarization. In this case the short circuit current decreases to the values less then 1pA within 2-3 minutes.

PYROELECTRIC MEASUREMENTS

Pyroelectric properties of the films were studied by low-frequency temperature wave method [7], when one recorded the short-circuit pyroelectric current corresponding to sine variations of the sample temperature. A specific feature of the study performed was repolarization of the sample by several predetermined voltage pulses with 10÷50μs duration.

As a result the pyroelectric coefficient was shown to depend on the preliminary sample polarization state and to vary within the limits from -20 to +20 nC/Kcm^2. Notice that the current amplitude decreases after the sign change of the pulses of altering polarization. With further increase of the switching pulses



amplitude, the phase shift between the pyroelectric current and temperature variations also changes from +90^{o} to –90^{o}(see Figure 5)

These data are generalized in order to obtain the pyroelectric hysteresis loop for the given ferroelectric sample (see Figure 5). One can clearly see the state of partial polarization. It should be mentioned that the shape of the pyroelectric coefficient loop accords well with the proper ferroelectric hysteresis loop obtained from direct measurements of remanent polarization vs applied voltage (see Figures 2,3).

Figure 5. *Pyroelectric current for different pulse amplitude during preliminary polarization and pyroelectric hysteresis loop of the 0.2μ thick PZT films. The arrows show the direction of the amplitude variation of the initial polarization pulses*

The proficiency of pyroelectric study should be particularly emphasized because it allows one not only to separate switchable and nonswitchable polarization components but to evaluate the polarization storage conditions easily and reliably. Furthermore, the determination of ohmic constituent of the pyroelectric current provides a way of examination of the free charge behavior in the films. Thus, the pyroelectric methods are an important addition to traditional methods of investigation the mechanisms for conductivity and charge mobility in the films by their voltage-capacitance and voltage-current characteristics.

This effect may lay the groundwork for integrated pyroelectric memory devices. The preliminary polarization is in fact the stored signal and its readout may be performed by ohmic or laser heating of a special-purpose metallization. It follows from simple estimations that the element of such a non-voltaic, nonvolatile memory based on the pyroelectric effect expends per cycle no more energy than 0.1nJ, so such an element might be alternative to those based on the repolarization phenomena. For multiplexing of such memory stages the CCD or MOSFET switch can be used.

One of the remarkable features of ferroelectric materials is the ability of changing their characteristic under the action of external conditions in particular being applied by electric field. We have fulfilled carefully investigations of pyroelectric coefficient dependence vs polarization conditions of thin ferroelectric films, PZT for example. These studies showed that this dependence discovers practically linear character on the other hand due to the polycrystalline structure of ferroelectric thin films "soft" polarization switch is capable in this case. Appropriate characteristics have been watched under application of a symmetric scanning voltage so as under pulses switch of polarization for various amplitudes of switching pulses.

So it was shown that analog memory could be realized in thin ferroelectric films due to their stable state remainent polarization. The two phenomenon pointed out earlier may be used in the devices performing analog multiplication of two signals, one of them is incident radiation, the other is a priori storage information in the form of specially appropriately polarized pyroelectric detector elements. This can produce sensitivity non-uniformity compensation of the UFPA elements for the purpose of the spatial noise reduction (see Reference [8]).

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.

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. 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. They may give experimental data for both theoretical studies and engineering design of various devices.

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REFERENCES

[1.] J.F. Scott, *Ferroelecrics Review*, 1, 1 (1998), pp.1-129.

[2.] P.K. Larsen, R. Cuppens, and G.A.C.M. Spierings, *Ferroelecrics,* **128**, (1992), pp.256-292.

[3.] B.M. Melnick, C.A. Paz de Aroujo, L.D. McMillan, D.A. Carver, and J.F. Scott, *Ferroelectrics*, **116**, (1991), p.73-93.

[4.] K.A. Vorotilov, M.I. Yanovskaya, L.I. Solovijewa, A.S. Valeev, V.I. Petrovsky, V.A. Vasiljev, and I.E. Obvinzeva, *Microelectronic Engineering*, **29**, (1995), pp.41-47.

[5.] V.I. Petrovsky, E.Ph. Pevtsov, A.S Sigov. *Ferroelectric thin films IV: Mat. Symp. held November 29 - December 2, 1994*, Boston. MRS, Materials Research Society, eds. by B.A.Tuttle, S.B.Desu, R.Ramesh, T.Shiosoki. Pittsburgh, Pennsylvania. **361** (1995), p.135-139.

[6.] A.S. Sigov, V.I. Petrovsky, E.Ph. Pevtsov, K.A. Vorotilov, A.S. Valeev. *Science and Technology of Electroceramic Thin Films, NATO ASI Series (E); Applied Science,* Kluwer Academic Publisher, eds. by O.Auciello and R.Waser, Dordreeht, The Netherlands, **284** (1995), pp.427-437.

[7.] B.H. Park, S.J. Hyun,T.W. Noh, and J. Lee, *Journ. of Korean Phis. Soc.*, **32**(Part IV) (1998), pp.S1405-S1409.

[8.] V.V. Chernokozin, E.Ph. Pevtsov, M.A. Pospelova, A.S. Sigov. *Ferroelectrics*, **225** (1999), pp.67 –74