Moscow University Physics Bulletin
Vol. 51, No. 3, pp. 42–47, 1996

Vestnik Moskovskogo Universiteta. Fizika
UDC 615.315.592

INFLUENCE OF POLARIZATION STATE OF FERROELECTRIC FILMS ON ELECTROPHYSICAL PROPERTIES OF SILICON–FERROELECTRIC STRUCTURES

N. L. Levshin, A. N. Nevzorov, and A. G. Petrukhin

The influence of the polarization state of a ferroelectric on the voltage–capacitance and voltage–current characteristics of metal–ferroelectric film–silicon structures has been studied. The thermofield processing has been demonstrated to cause not only the repolarization of the ferroelectric but also the recharging of electron traps. The mass spectroscopy method was used to record the desorption of various atoms and molecules from the surface of the structure on heating above the phase transition temperature.

1. INTRODUCTION

The semiconductor–ferroelectric film structures are fairly promising materials for storage cells. In recent years, the properties of these structures have been extensively studied (see, e.g., [1, 2]). At the same time, certain questions concerning the influence of polarization of ferroelectric films on capacitance and current characteristics are still unclear. In this work, we studied silicon with a deposited ferroelectric film as a model system.

2. MEASUREMENT PROCEDURE

The residual polarization of ferroelectrics was varied by means of thermofield processing (TP): the samples were heated to a temperature T_n and then cooled in a constant electric field $E \cong 3 \times 10^5$ V·m^{-1}. The processing was assigned the sign + or − (TP$^+$ or TP$^-$) depending on the potential of the gate electrode. To elucidate the influence of substrates on the polarization of ferroelectric films, measurements were performed for films deposited on silicon with n-type and p-type conduction.

High-frequency voltage–capacitance characteristics were taken at sweep voltages of ±10 V. The gate voltage varied linearly at a rate of 0.25 V·s^{-1}. The test signal frequency was 300 kHz. The voltage–capacitance and voltage-current characteristics were measured in the air. We have shown earlier that measurements of voltage–capacitance characteristics of similar structures in vacuum and in the air give identical results [3]. The characteristics of the Si–ferroelectric–metal structures studied in this work and the processing temperatures T_n are given in Table 1. Ferroelectric films of thickness d were deposited on silicon substrates by high-frequency reactive sputtering [4]. Aluminum electrodes were applied to samples *1* and *2* and SnO_2 electrodes to samples *3* and *4*; electrode area was about 1 mm^2. The thermal desorption spectra of some samples were studied in a linear heating mode (heating rate of 1 K/s) to obtain additional data on the adsorption properties of the outer surfaces of structures. The gas phase was analyzed with the help of an MX-7301 monopole mass spectrometer. The mass spectral measurements were made in oilless vacuum of about 5×10^{-6} Pa.

Table 1

Sample No.	Type of Si substrate	Ferroelectric film	T_c, K	T_n, K	d, μm	Q_d, el.ch.·cm^{-2}	ΔU, V	$\Delta U(\mathrm{TP}^+)$, V	$\Delta U(\mathrm{TP}^-)$, V
1	n	$Ba_{0.9}Sr_{0.1}TiO_3$	375	390	0.8	2×10^{12}	1.4	1.9	0.6
2	p	$Pb_{0.95}Sr_{0.05}(Zn_{0.53}Ti_{0.47})O_3$ $+Nb_2O_5$ (1%)	575	490	0.5	3.8×10^{12}	3.1	1.9	4.3
3	p	$PbTiO_3$:La	650	490	1.22	1.3×10^{12}	2.6	2.4	4.0
4	n	$PbTiO_3$:La	650	490	1.65	1.8×10^{12}	3.0	6.5	3.7

3. VOLTAGE–CAPACITANCE CHARACTERISTICS OF STRUCTURES AT VARIOUS STATES OF FERROELECTRIC POLARIZATION

The voltage–capacitance characteristics of structures shown in Fig. 1 exhibit hysteresis prior to and after the thermofield processing. Various authors who studied voltage–capacitance characteristics of metal–ferroelectric–semiconductor structures observed hysteresis related to repolarization of ferroelectrics (clockwise direction for p-type and anticlockwise for n-type semiconductor substrates) [3, 5], "trap" ("injection") hysteresis related to charge transfer from a semiconductor to ferroelectric traps [6, 7], or the absence of hysteresis [3, 6]. With no hysteresis, evidently, the contributions of polarization and trap hystereses, which have different signs, compensated each other. Figure 1 shows that when the type of conduction of the semiconductor substrate changes, the direction of voltage–capacitance curve changes too.

In studies of voltage–capacitance characteristics a slowly varying sweep voltage and a high-frequency test signal voltage are applied to a sample. The traps situated at the ferroelectric–semiconductor interface and capable of recharging under the action of a high-frequency voltage will be called "fast" surface states. The traps that are recharged under the action of sweep voltage will be called "slow" states. The repolarization of a ferroelectric and the recharging of slow states affect the field within the ferroelectric, and this is the reason why voltage–capacitance curves exhibit hysteresis. Depending on the relative contributions of the competing mechanisms, polarization- or trap-type hysteresis is observed. The width of the hysteresis loop is determined by the same factors. The presence of hysteresis of one or another sign is related to the procedure used for manufacturing ferroelectric–semiconductor structures (specifically, the preparation procedure determines the concentration of traps), to the conditions of measurements (applied voltage [6]), and the method of thermofield processing [3]. All four structures studied in this work exhibited polarization-type hysteresis at room temperature. The voltage–capacitance hysteresis loop will be analyzed in terms of the following parameters: (a) shift along the voltage axis (from $V = 0$), ΔV; (b) width ΔU measured at the capacitance of plane zones; and (c) maximum slope.

In the structures based on n-type substrates in the initial state, the voltage–capacitance hysteresis loop is shifted to negative voltage values. The structures based on p-type substrates showed shifts to positive voltages. The embedded charge Q_d values estimated from the shifts of the middle points of the hysteresis loop at the capacitance of plane zones are given in Table 1. The embedded charge value depends, evidently, on the nature of the ferroelectric and the technique of sample preparation, while its sign is determined by the type of the substrate conduction. The latter conclusion conforms with the results obtained in [6].

It was found in [8] that the initial ferroelectric polarization is determined by the type of the substrate conduction. Later, this conclusion was independently substantiated by measurements of Stark shifts of the fluorescence maximum of a dye deposited on a ferroelectric–semiconductor structure [9]. The assumed polarization state is shown in insets in Fig. 1.

With p-type substrates, the hysteresis loop shifted towards positive voltages after TP^- and towards negative ones after TP^+. Such shifts of voltage–capacitance curves after thermofield processing can be caused by ferroelectric repolarization. In structures with n-type Si, TP^- and TP^+ shifted the curve to the negative

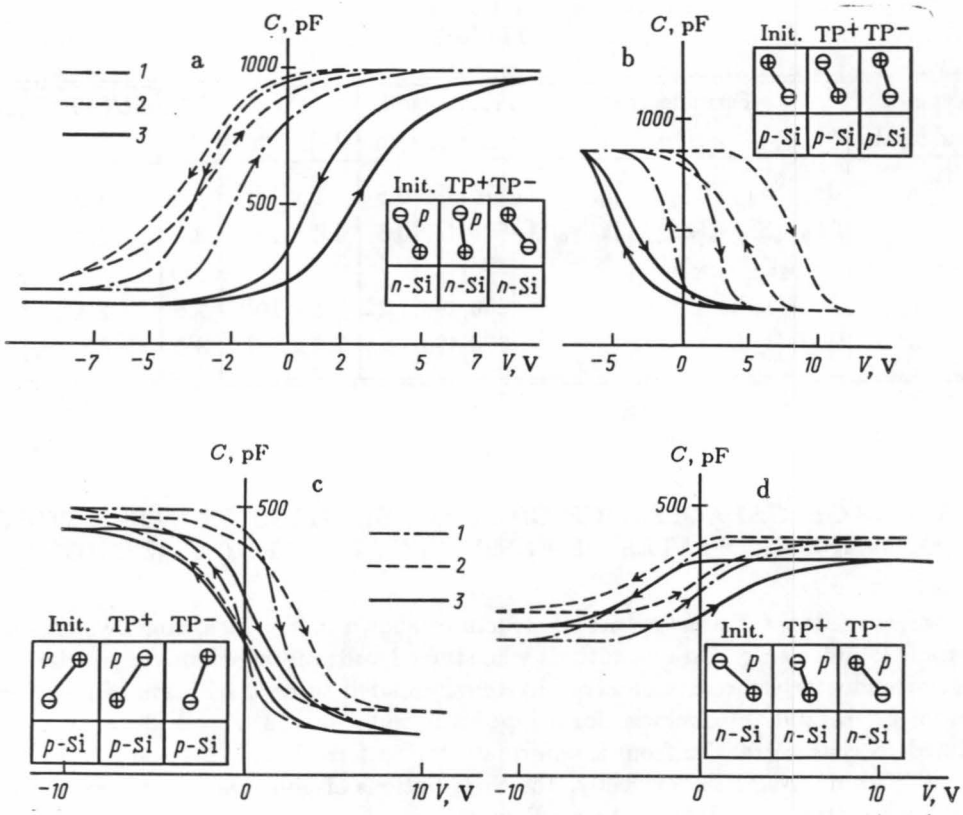

Fig. 1

Voltage–capacitance characteristics of sample *1* (*a*), *2* (*b*), *3* (*c*), and *4* (*d*) prior to (1) and after TP^- (2) and TP^+ (3).

and positive voltage values, respectively, which can be explained by the change of the imbedded charge and by the recharge of slow states during thermofield processing.

Consider the second parameter of the voltage–capacitance hysteresis loop, width ΔU, in more detail. Hysteresis of voltage–capacitance curves of ferroelectric–semiconductor structures can be related to repolarization of the ferroelectric, recharging of slow states, and also to migration of ions due to slowly varying voltage. It was shown in [9] that the drift of ions in such structures is insignificant. The ΔU values (Fig. 1) are listed in Table 1. The following trends can be noticed. For *n*-type substrates, TP^+ broadens the loops whereas TP^- narrows them. Conversely, for *p*-type substrates, TP^+ has a narrowing and TP^- a broadening effect. TP^+ of samples with *n*-type substrates and TP^- of samples with *p*-type silicon should decrease the deviation of the polarization vector from the normal to the film surface. As a result, the repolarization of the ferroelectric and, therefore, the hysteresis loop width cannot increase, which is at variance with the data given in Table 1. We may speculate that the observed loop width variations are related to the thermofield processing-induced reversal of the sign of slow states localized at the ferroelectric–semiconductor interface and in the bulk of the ferroelectric. An exception is sample 4, for which thermofield processing of both signs increases the ΔU value. It appears that for this sample, the major part is played by the repolarization during processing.

Additional information on the contribution of recharging of traps during thermofield processing is given by the data on optical charging of these traps caused by photoinjection of charge carriers from Si into a ferroelectric [9]. Thus, TP^- of a sample with an *n*-type substrate resulted in a great positive charging by light quanta whose energy exceeded the forbidden gap width of the ferroelectric. Light absorption by the ferroelectric itself can then be accompanied by the photodomain effect [10]. Under optical charging, the charges captured by the ferroelectric slow states can change the local fields in the ferroelectric and thus affect the domain structure. In other words, the polarization and trap contributions to hysteresis are interrelated.

Thermofield processing of either sign decreases the slopes of voltage–capacitance curves, which is evidenced by the increase in the concentration of fast states and by the rise of the fluctuations of surface potential. The mechanisms of the effect of fluctuation fields in a dielectric on the spectrum of fast states is a debated topic. The field and the strain-relay race mechanisms are discussed [11]. In the structures studied, the second mechanism appears to be fairly probable. Correctly calculating the density of fast states in them is, however, impossible because of the hysteresis of voltage–capacitance characteristics.

4. VOLTAGE–CURRENT CHARACTERISTICS OF STRUCTURES FOR VARIOUS STATES OF FERROELECTRIC POLARIZATION

In order to obtain additional information, we studied voltage–current characteristics of the structures prior to and after the thermofield processing (Fig. 2). The initial characteristic (curve *1*) is shifted along the voltage axis, which, according to [2], is caused by polarization of the ferroelectric and by the formation of an additional potential barrier at the ferroelectric–silicon substrate interface, which is responsible for the existence of some threshold voltage for current rise. This observation agrees with contact potential difference measurements [9]. TP^- caused the film depolarization and threshold voltage disappearance. TP^+ performed immediately after TP^- did not restore the threshold voltage completely and changed the slope of the curve. It follows that the thermofield processing not only causes repolarization of the ferroelectric but also brings about certain irreversible changes in the film.

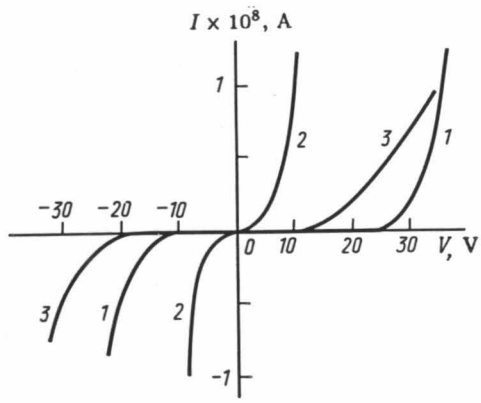

Fig. 2

Voltage-current characteristic of sample *1* prior to (1) and after TP^- (2) and TP^+ (3).

5. TEMPERATURE DEPENDENCE OF VOLTAGE–CAPACITANCE CHARACTERISTICS

Irreversible changes in a ferroelectric film during thermofield processing should affect the voltage–capacitance characteristics. We, therefore, studied the influence of heating above the critical point on voltage–capacitance curves. Heating sample 1 from 295 to 375 K gradually shifted its voltage–capacitance characteristic to negative voltage values without noticeable changes in the shape of the curve (Fig. 3). The hysteresis loop width increased somewhat. Starting from 375 K (phase transition point, T_c), the loop was deformed and eventually, at the highest temperature of 385 K which corresponded to the paraphase state of the film, degenerated to curve *3* in Fig. 3. The shape of curve *3* plots a double hysteresis loop of the dependence of polarization on the electric field strength observed in the paraphase state of $BaTiO_3$ at a temperature close to the critical point [12]. The opposite transformations were observed when the sample was cooled. The process was not completely reversible, for the final voltage–capacitance characteristic was shifted to the negative voltage values.

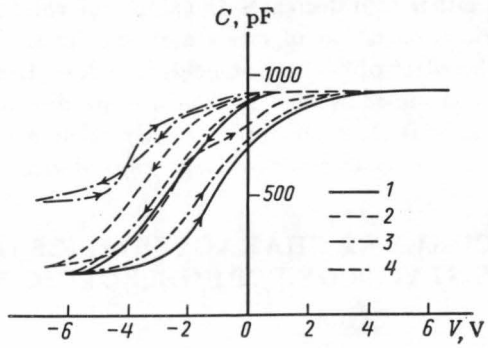

Fig. 3

Voltage–capacitance characteristics of sample *1* at various heating temperatures: T = 295 K (1), 355 K (*2*), and 385 K (*3*) and voltage–capacitance characteristic after cooling the structure to T = 295 K (*4*).

The distortions of voltage–capacitance characteristics show the destruction of the domain structure of the film undergoing the ferroelectric–paraelectric phase transition. A wide temperature range (about 20 K) within which these changes take place makes it possible to classify this transformation as "smeared" phase transitions. A comparatively low value of $\varepsilon \sim 80$ is characteristic of smeared phase transitions in ferroelectric films.

6. INFLUENCE OF FERROELECTRIC PHASE TRANSITION ON THERMAL DESORPTION SPECTRA

One of the reasons for irreversibility of changes in voltage–capacitance characteristics can be a change in the composition of the adsorption phase on the structure outer surface when the sample is heated above the critical temperature. We, therefore, studied the thermal desorption spectra of samples *1* and *2*.

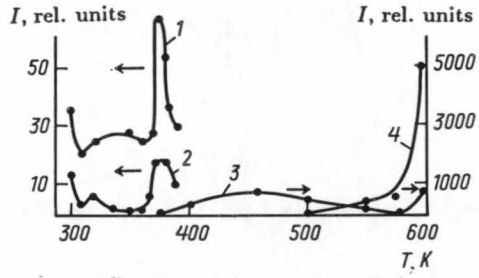

Fig. 4

Temperature dependences of thermal desorption yield of H_2O (*1* and *3*) and O_2 (*2* and *4*) for samples *1* (*1* and *2*) and *2* (*3* and *4*).

Figure 4 shows that at a ferroelectric phase transition temperature peaks corresponding to H_2O and O_2 thermal desorption were observed for sample *1*. The phase transition in sample *2* was accompanied by the evolution of H_2O, O_2, CO, CO_2, O, and other atoms and molecules or their fragments. The reference spectra (those of thermal desorption from silicon substrates) had no distinctive features at temperatures corresponding to phase transitions in ferroelectric films. We did not study thermal desorption for sample *2* at temperatures above 600 K because of the low thermal stability of the structure. The low-temperature ($\sim$ 470 K) peak of thermal desorption of H_2O is, evidently, related to desorption of coordination-bonded H_2O molecules. A similar peak was observed for TiO_2 at a similar temperature ($\sim$ 400 K), and it was shown by the IR and NMR techniques [13] that this peak corresponded to desorption of coordination-bonded water molecules. At a higher (phase transition) temperature, we observed the growth of thermal desorption of

residual water, which was retained in a small amount, from the surface of the structure. The activation of thermal desorption at the phase transition temperature (T_c) is related to crystal lattice restructuring, when the amplitudes of lattice vibrations increase drastically. This is accompanied by a sharp increase in the anharmonicity of vibrations of adsorption complexes, and an excessive vibrational energy facilitating the desorption and dissociation processes is accumulated in the surface phase [11]. We observed a similar effect for the semiconductor–metal phase transition in vanadium dioxide films [14]. The atoms and molecules undergoing desorption can be the components of adsorption complexes on the surface, regular lattice atoms, or film impurities.

7. CONCLUSIONS

To summarize, the following conclusions can be drawn from the data obtained.

1. The initial polarization state of a ferroelectric-semiconductor structure is determined by the type of substrate conduction.

2. The effective means of ferroelectric repolarization is the thermofield processing which changes the voltage–capacitance and voltage–current characteristics of the sample substantially.

3. The changes in these characteristics are caused not only by the ferroelectric repolarization but also by the recharging of electron traps.

4. Heating above the ferroelectric phase transition temperature is accompanied by the desorption of various atoms and molecules, which causes changes in the concentration and charge of the traps.

The authors are thankful to V. F. Kiselev and S. N. Kozlov for valuable comments and to A. V. Zoteev for providing the facilities for measurements of thermal desorption spectra.

REFERENCES

1. S. V. Tolstousov, V. M. Mukhortov, E. N. Myasnikov, and V. P. Dudkevich, *Zh. Tekh. Fiz.*, vol. 55, no. 1, p. 127, 1985.
2. Y. Xu, C. J. Chen, R. Xu, and J. D. Mackenzie, *J. Appl. Phys.*, vol. 67, no. 6, p. 2985, 1990.
3. L. B. Gorodnik, N. L. Levshin, and A. N. Nevzorov, *Vestn. Mosk. Univ. Fiz. Astron.*, no. 3, p. 84, 1986.
4. J. K. G. Panitz and Hu. Cheng-Cheng, *Ferroelectrics*, vol. 27, no. 1–4, p. 161, 1980.
5. D. N. Sandzhiev, N. A. Kosonogov, E. A. Savchenko, *et al.*, *Zh. Tekh. Fiz.*, vol. 60, no. 1, p. 196, 1990.
6. K. V. Belenov, E. A. Goloborod'ko, O. E. Zavadovskii, *et al.*, *Zh. Tekh. Fiz.*, vol. 54, no. 9, p. 1782, 1984.
7. I. L. Baginskii and E. G. Kostsov, *Avtometriya*, no. 4, p. 88, 1988.
8. V. M. Mukhortov, S. V. Tolstousov, S. V. Biryukov, *et al.*, *Zh. Tekh. Fiz.*, vol. 51, no. 7, p. 1524, 1981.
9. V. B. Zaitsev, V. F. Kiselev, A. G. Petrukhin, *et al.*, *Poverkhnost': Fiz. Khim. Mekh.*, no. 10, p. 71, 1995.
10. V. M. Fridkin, *Ferroelectrics–Semiconductors* (in Russian), Moscow, 1976.
11. V. F. Kiselev, *Kinet. Katal.*, vol. 35, no. 5, p. 714, 1994.
12. A. S. Sonin and B. A. Strukov, *Introduction to Ferroelectricity* (in Russian), Moscow, 1970.
13. V. F. Kiselev and O. V. Krylov, *Adsorption Processes on the Surfaces of Semiconductors and Dielectrics* (in Russian), Moscow, 1978.
14. V. F. Kiselev, N. L. Levshin, and S. Yu. Poroikov, *Dokl. Akad. Nauk SSSR*, vol. 317, no. 6, p. 1408, 1991.

7 July 1995 Department of General Physics and Molecular Electronics