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On the properties of the transition layer between the silicon substrate and the ferroelectric or high-k-dielectric insulating gap

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The dependence of the properties of buffer layers at the interfaces of silicon-ferroelectric and silicon-high-k-insulator on the material and thickness of the insulator deposited on the substrate is analyzed. Films of ferroelectric $Ba_{0.8}Sr_{0.2}TiO_3$ and high-k-insulator HfO_2 with a set of thicknesses from 20 to 150 nm and the same sizes of field contacts were deposited on the same plate of n-type silicon with natural oxide. It turned out that the capacitance values in each of the saturation regions of the high-frequency capacitance-voltage characteristics for all thicknesses of the insulating layer are close to each other. For objects with high-k-insulator, a decrease in capacitance with an increase in the thickness of the insulator was observed. The graphs of the dependences of the band bending in the semiconductor on the field voltage and the spectral density of electron traps in the buffer layers of the structures with HfO_2 on the energy in the silicon band gap are constructed. It is shown that the concentration and spectrum of electron traps at the contact of silicon with the ferroelectric are practically independent of the thickness of the insulating layer. The buffer layer at the interface of silicon with a high-k dielectric changes its properties significantly with increasing thickness of the insulator - the spectral curve of electron traps shifts deep into the band gap of the semiconductor, expands, and its minimum value decreases.

Keywords: silicon−ferroelectric/silicon−high-k-insulator interfaces, transition (buffer) layer, electron traps, high-frequency capacitance-voltage characteristics.

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1. Introduction

Ferroelectrics have been studied since the middle of the XXth century, and their electrophysical properties have already been widely used in many electronic devices [1–3]. In the nearest future electronics will handle the integral structures deposited on the silicon substrates, whose insulating layers will be made of various materials, such as high-k-dielectrics and ferroelectrics. Due to substantial mismatch between the crystalline lattices of the applied insulator and semiconductor, a so called transition (buffer) layer [2] is formed between them, which mostly consists of oxides of contacting materials. Even though usually this transition later is much thinner than the insulating gap, when the structures are recharged, it plays a significant role and prevents the development of the field effect [4–6], including opening of the channel of minority carriers. The latter is critical for the operability of certain devices, in particular, nonvolatile memory cells FeRAM, where the principle of information reading is based on measurement of this channel conductivity under the gate near the depleted surface of the semiconductor. The reason for such behavior of the buffer transition is related to high concentration of dangling bonds of silicon and metals from deposited materials therein. These dangling bonds serve as electron traps (ET), recharging of which screens the penetration of the external electric field into the substrate and provides for Fermi level pinning in silicon under high field voltages. This paper is dedicated to the analysis of buffer layer ET properties, which manifest themselves integrally in the measured high frequency capacitance-voltage characteristics (CVC) of metal−insulator−semiconductor (MIS) structures. The dependences of the transition layer properties on the silicon−insulator contact on the material and thickness of the insulator deposited on the substrate were studied.

2. Objects and methods of experimental investigations

For convenience and unambiguity of experiment results comparison, the specimens for measurements were prepared on the same silicon plate (100) KEF 4.5 with thickness of $705\,\mu$m. MIS structure were formed with insulating layers having thicknesses from 20 to 150 nm of ferroelectric composition $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) and high-k-insulator of hafnium oxide (HfO_2). Nickel electrodes with surface area of $S \cong 2.7 \cdot 10^{-4}\,cm^2$ and thickness of 100 nm were applied onto the insulator films via a shadow mask by electron-beam evaporation method. BST layers were deposited onto silicon by method of high-frequency sputtering of a polycrystalline target in the oxygen atmosphere at $600\,^{\circ}$C. For more details of the installation design and the layer deposition method see papers [7,8]. HfO_2 films were formed on silicon substrates by method of high-frequency magnetron sputtering of a ceramic target with similar composition in the mixture of argon and oxygen in the ratio of 10 : 1 at a total pressure in the chamber of 0.4 Pa. Density of gas discharge capacity was maintained at 2 W/cm^2; the deposition speed was around 200 nm/h. The details of the deposition process and description of the film morphology HfO_2 are provided in [9].

ET properties in the buffer layers were studied on the basis of the analysis of experimental CVC structures formed on the silicon substrates. Measurements of the high-frequency impedance of the objects were carried out at room temperature at the frequency of 1 MHz with the speed of $\beta = 200$ mV/s of field voltage V_g variation using precision meter LCR Agilent E4980A. The amplitude of the test signal was 25 mV. The detailed description of the experimental setup is given in paper [10].

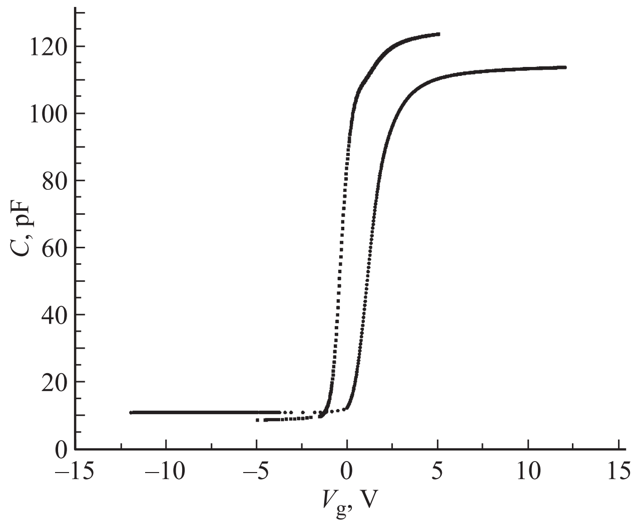

Figure 1. High-frequency capacitance-voltage characteristics of structures with $Ba_{0.8}Sr_{0.2}TiO_3$. Thicknesses of films $Ba_{0.8}Sr_{0.2}TiO_3$: 20 nm (squares), 150 nm (circles).

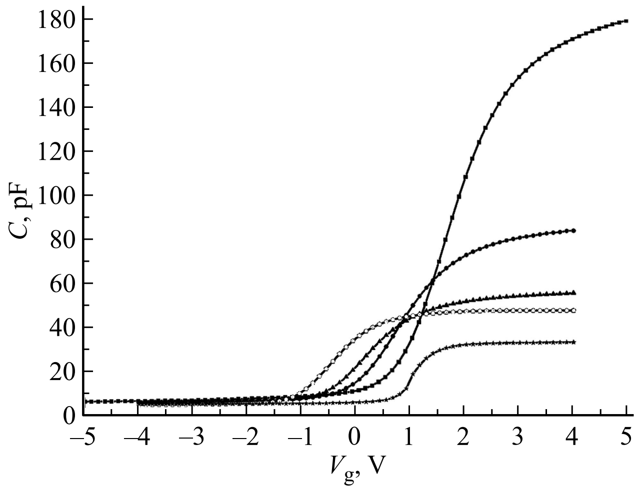

Figure 2. High-frequency capacitance-voltage characteristics of structures with HfO_2. Film thicknesses HfO_2: 20 nm (squares), 50 nm (circles), 100 nm (triangles), 120 nm (hollow pentagons), 150 nm (stars).

3. Experimental capacitance-voltage characteristics, methods of their processing and discussion of results

Curves of experimental high-frequency CVC MIS structures with insulating layers having thicknesses from 20 to 150 nm, comprising accordingly BST and HfO_2, are given in Figures 1 and 2. As shown in [4–6], the dependences $C(V_g)$, where C — measured capacity, achieving the plateau does not mean the transition to the mode of strong enrichment of the semiconductor surface in the area of maximum capacities and to the state of deep inversion of the substrate in the range of minimum capacities. In reality both capacity plateaus may be related to the Fermi level pinning in Si at the buffer layer ET, if their concentration is high, and they have U-shaped form of the spectrum. In actual practice you can decide on the ET contribution to the CVC shape of the MIS structure by the ratio of values C_{SE} and C_d with C, where C_{SE} and C_d — accordingly the capacities of the ferroelectric and high-k-insulating layers. Values C_{SE} and C_d may be determined from measurements of CVC in metal–insulator–metal structures with the same composition and thickness of insulating layers as in MIS objects. When the characteristics C_{SE}, $C_d \gg C$ are on the plateau (this is exactly the case implemented in most experiments, including in this paper, see [11,12]), then $C \cong C_s$ [4], where C_s — capacity of the charged near-surface part of the semiconductor.

Note that at the specified inequations the expression $C \cong C_s$ is true regardless of what is the phase of the insulating layer, and whether or not a unidimensional model is applicable to the description of its capacity, as it does not take into account the distribution of the domain in a ferroelectric. The physical basis for this statement is the circumstance that the Debye screening length in a semiconductor is much longer than the specific diameters of domains in a thin film of ferroelectric [13].

The value of the high-frequency capacity of the semiconductor is determined by the potential of the bend in its bands at the interface with the insulator V_s, and under the conditions of a classic Boltzman's distrubution of free electrons the following expressions are true [14]

$$C_s = C_{sfb}\frac{|1 - e^{-\nu_s}|}{\sqrt{2(\nu_s + e^{-\nu_s} - 1)}}, \quad C_{sfb} = S\sqrt{\frac{\varkappa_s q^2 N_d}{4T\pi}}. \quad (1)$$

Here $\nu_s = -\frac{qV_s}{T}$ — dimensionless bend of the bands in the semiconductor: in depletion $\nu_s > 0$, and in enrichment $\nu_s < 0$; q — elementary charge; T — absolute temperature in energy units; $\varkappa_s$ — dielectric permittivity of silicon; N_d — concentration of donor alloying in a semiconductor near the interface with the insulator. The first equation (1) is true up to the start of Si surface degeneracy, i.e. at room temperature and $N_d \approx 10^{15}\,\mathrm{cm}^{-3}$ it is knowingly met at $\nu_s > -10$. The capacity value in the state of flat bands C_{sfb} is calculated in accordance with the second equation (1) using the structure parameter values. The surface bend of the bands in the silicon substrate in the entire range of measured voltages V_g is determined from the first equation (1) and ratio $C/C_{sfb} \cong C_s/C_{sfb}$. Value $N_d \cong 8.6697 \cdot 10^{14}\,\mathrm{cm}^{-3}$ meets the rated value of substrate specific resistivity — $4.5\,\Omega \cdot \mathrm{cm}$, accordingly, at room temperature $C_{sfb} \cong 20.133585\,\mathrm{pF}$. Curves of the obtained dependences $\nu_s(V_g)$ are shown in Figure 3 and 4. They unambiguously confirm that first of all, neither the deep inversion state, nor the degeneracy of the silicon surface are achieved on all our specimens; secondly, the field voltage V_g, applied to the structures, mostly drops on the insulating layers.

The dangling bond of silicon at the interface with ferroelectric and high-k-insulator is double-charge: in electrically neutral state it may capture and release an electron. Let us introduce spectral densities of EL expressed in $\mathrm{cm}^{-2}\mathrm{eV}^{-1}$ in the buffer layer of donor $N_{sd}(E)$ (electrically neutral in the filled state, positively charged in the empty state) and acceptor $N_{sa}(E)$ (negatively charged in the filled state, electrically neutral in the empty state) types. Here E — energy of electrons in the traps counted from the bottom of the silicon conduction band deep into the band gap. Under the conditions when the difference of potentials at the boundaries of the insulating layer is nearly equal to V_g, and the change in the bend of the semiconductor bands ΔV_s in the measured range is rather high, $q\Delta V_s \gg T$, you can replace Fermi functions of energy E in the integrals for ET filling by „steps“ with the value 1, and record the approximated electrostatic equation for the contact of the insulator and the semiconductor instead of the precise one [14]

$$\frac{\varkappa_d(V_g + V_c)}{H} \approx 4\pi q \left[\int\limits_{E_F + T\nu_s}^{E_g} N_{sa}(E)dE - \int\limits_{0}^{E_F + T\nu_s} N_{sd}(E)dE \right]. \tag{2}$$

Here $\varkappa_d$ — dielectric permittivity of insulator HfO_2, V_c — contact difference of potentials between the field electrode and silicon, H — thickness of insulating gap, E_F and E_g — Fermi energy and width of silicon band gap. Dependence of the total spectral density of ET in the buffer layer $N(E) = N_{sd}(E) + N_{sa}(E)$ on energy E is expressed from the equation (2) parametrically (the parameter is voltage V_g):

$$E = E_F + T\nu_s(V_g), \quad N \approx -\frac{\varkappa_d}{4\pi q T H}\left(\frac{d\nu_s}{dV_g}\right)^{-1}, \tag{3}$$

besides, since function $\nu_s(V_g)$ drops monotonously together with voltage, then $\frac{d\nu_s}{dV_g} < 0$. In [12] for the layers formed by different methods HfO_2 the values of dielectric permittivity $\varkappa_d = 14-30$ are provided; this paper used for calculations of the spectrum $N(E)$ the number $\varkappa_d = 20$. The results for contacts with silicon of high-k-insulator of hafnium oxide are shown in Figure 5. Note that despite rather high accuracy of measurements of the values of high-frequency capacity (error in general below 1%), curves $N(E)$ in the area of energies 0.3–0.5 eV, compliant with the minimum recorded values C, demonstrates non-physical features (nonmonotonicities), related to the manifestation of noise. This is supported by applying a differentiation operation that is incorrect according to Tikhonov to the experimental data [15].

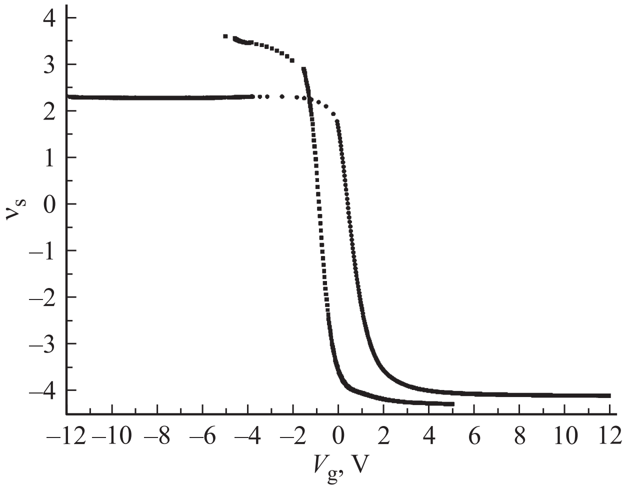

Figure 3. Dependences of band bend in silicon ν_s on field voltage V_g for structures with $Ba_{0.8}Sr_{0.2}TiO_3$. Thicknesses of films $Ba_{0.8}Sr_{0.2}TiO_3$: 20 nm (squares), 150 nm (circles).

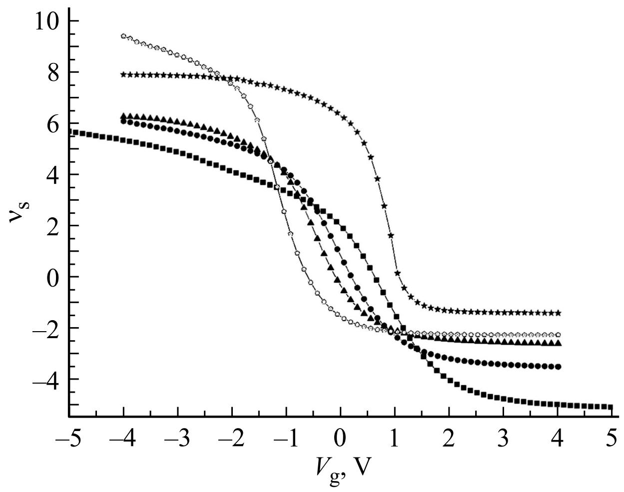

Figure 4. Dependences of band bend in silicon ν_s on field voltage V_g for structures with HfO_2. Film thicknesses HfO_2: 20 nm (squares), 50 nm (circles), 100 nm (triangles), 120 nm (hollow pentagons), 150 nm (stars).

For structures with BST there are no grounds to use a unidimensional ratio (2) to describe the contact of silicon and a ferroelectric film with spatially distributed polarization domains. In this sense directly at the interface the unidimensional bend of bands in a semiconductor (see Figure 3) determined using the experimental data must be seen as a certain average value along the contact plane. Relative to the spectral density of ET of the buffer layer between the ferroelectric and the semiconductor, you may only mention the energies in the silicon band gap, corresponding to the plateau areas at CVC, where single-domain state of the insulating layer is achieved in the high electric fields, and unidimensional representation is applicable. From the first formula (3) and data of Figure 3 it follows that for the structures with BST the steep growth $N(E)$ and Fermi level pinning related to this circumstance take place at $E = 0.16$ eV and $E = 0.34$ eV.

Let's discuss the results. Two plateaus at each CVC curve and bends of bends in silicon far from the conditions of inversion and strong enrichment of the semiconductor surface indicate high concentration and U-shaped form of ET spectrum in the buffer layers of all structures. Generally speaking, U-shaped form of the spectrum is typical for localized electron states on Si surface, function $N(E)$ in the vicinity of minimum values is achieved when the density tails are summed up from the bands of acceptor and donor type traps that are adjacent accordingly to the ceiling of the valence band and the bottom of the silicon conduction band. But concentration of dangling bonds in the metal–oxide–semiconductor structures obtained in high-temperature oxidation of Si, is at least two orders below compared to the values in the buffer layers of objects grown in the substrates with natural oxide (in curves [14] scales are $10^{10}-10^{12}$, and in Figure 5 — $10^{14}\,cm^{-2}eV^{-1}$). Besides, in our case the band of acceptor type traps is moved towards the middle of the silicon band gap, therefore at least $N(E)$ is at the distance $0.2-0.3$ eV from the bottom of the conduction band.

Differences in properties of CVC in structures with BST and HfO_2 manifest themselves: for specimens with a ferroelectric the dependence of the capacity on the insulating layer thickness is weak, and for the objects with high-k-insulator it is strong, on the contrary; compare Figures 1 and 2. These properties of the specimens with these materials result in different dependences of the ET spectrum in the buffer layer on the surface of silicon on insulator thickness. The spectrum of ETs recharged in stationary conditions near the contact with BST is concentrated in a narrow energy interval $(0.16-0.34)$ eV, and dependence $N(E)$ is hardly sensitive to the ferroelectric film thickness. The contact with HfO_2 has a longer section of energies that belong to the traps whose filling varies with voltage growth compared to a ferroelectric; as thickness of high-k-insulator increases, this area of energies moves towards the higher E and expands reaching $(0.23-0.49)$ eV; and the minimum value $N(E)$ decreases (see Figure 5). The listed facts make it possible to assume that for the structures with

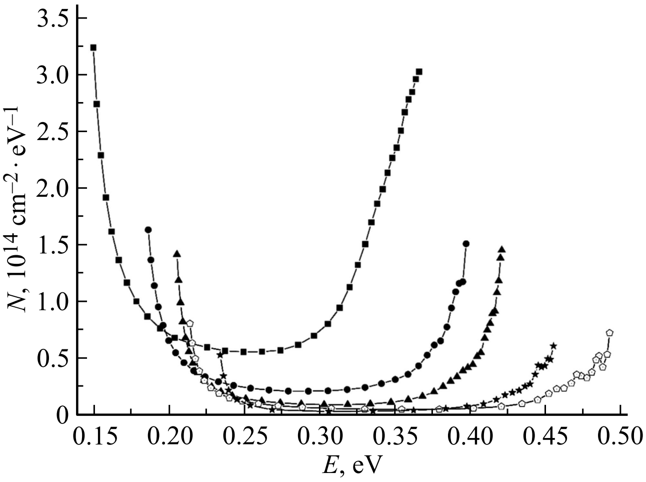

Figure 5. Spectral densities of electron traps in buffer layer between silicon and HfO_2. Film thicknesses HfO_2: 20 nm (squares), 50 nm (circles), 100 nm (triangles), 120 nm (hollow pentagons), 150 nm (stars).

the BST insulator the buffer layer traps are mostly formed by silicon dangling bonds. For the objects with hafnium oxide, apart from Si, a noticeable role in formation of traps in the transition gap is played by non-saturated bonds of partially oxidized Hf and HfO particles. As the contribution of these particles increases, the concentration of acceptor type traps in the buffer layer increases, and the maximum of their distribution by energy moves towards the ceiling of the valence band.

4. Conclusions

Let us formulate the results of the completed analysis.

1. In MIS structures with insulating layers from BST and HfO_2, grown on silicon substrates with a natural oxide, neither the state of deep inversion nor the degeneracy of the semiconductor surface are achieved.

2. Field voltage applied to MIS structures drops mostly on insulating layers.

3. Two plateaus at each CVC curve and bends of bends in silicon far from the conditions of inversion and strong enrichment of the semiconductor surface are related to Fermi level pinning on ET in buffer layers with high concentration and U-shaped form of the spectrum.

4. Concentration of dangling bonds of silicon in the metal-oxide-semiconductor structures obtained in high-temperature oxidation of Si, is at least two orders below compared to the values in the buffer layers of objects grown in the substrates with natural oxide.

5. For the MIS structures formed on the silicon plates with a natural oxide and an insulator of ferroelectric or high-k-insulator, the spectral density of ET in buffer layers is located in the middle of the band gap of the semiconductor, and its minimum is at the distance of $0.2-0.3$ eV from the bottom of the conduction band.

6. ET spectrum in buffer layers at the interface with BST is hardly sensitive to the ferroelectric film thickness. In the contact with HfO_2 as thickness of high-k-insulator increases, the spectral curve of ET moves deeper into the silicon band gap, expands, and its minimum value decreases.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K.A. Vorotilov, V.M. Mukhortov, A.S. Sigov. Integrirovannye segnetoelektricheskie ustroystva. Energoatomizdat, M. (2011). 175 s. (in Russian).
[2] J.Y. Park, K. Yang, D.H. Lee, S.H. Kim, Y. Lee, P.R.S. Reddy, J.L. Jones, M.H. Park. J. Appl. Phys. **128**, *24*, 240904 (2020).
[3] B. Wang, W. Huang, L. Chi, M. Al-Hashimi, T.J. Marks, A. Facchetti. Chem. Rev. **118**, *11*, 5690 (2018).
[4] E.I. Goldman, G.V. Chucheva, D.A. Belorusov. Ceram. Int. **47**, *15*, 21248 (2021).
[5] D.A. Belorusov, E.I. Goldman, G.V. Chucheva. Phys. Solid State **63**, *13*, 2140 (2021).
[6] E. Goldman, G. Chucheva, D. Belorusov. Ceram. Int. **50**, *6*, 9678 (2024).
[7] M.S. Ivanov, M.S. Afanas'ev. Phys. Solid State **51**, *7*, 1328 (2009).
[8] D.A. Kiselev, M.S. Afanasiev, S.A. Levashov, G.V. Chucheva. Phys. Solid State **57**, *6*, 1151 (2015).
[9] M.S. Afanasiev, D.A. Belorusov, D.A. Kiselev, V.A. Luzanov, G.V. Chucheva. Phys. Solid State **65**, *4*, 557 (2023).
[10] E.I. Gol'dman, A.G. Zhdan, G.V. Chucheva. Instrum. Experiment. Techniques **40**, *6*, 841 (1997).]
[11] E.I. Goldman, V.G. Naryshkina, G.V. Chucheva. Phys. Solid State **62**, *8*, 1380 (2020).
[12] F.M. Li, B.C. Bayer, S. Hofmann, S.P. Speakman, C. Ducati, W.I. Milne, A.J. Flewitt. Physica Status Solidi B **250**, *5*, 957 (2013).
[13] E.I. Goldman, G.V. Chucheva, M.S. Afanasiev, D.A. Kiselev. Chaos, Solitons & Fractals **141**, 110315 (2020).
[14] S.M. Sze, K. Ng Kwok. Physics of Semiconductor Devices, Willey Interscience publication, N.Y. (2007). 832 p.
[15] A.N. Tikhonov, V.Ya. Arsenin. Metody resheniya nekorrektnykh zadach. Nauka, M. (1986). 288 s. (In Russian).

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