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PHYSICS OF SEMICONDUCTOR DEVICES

Features of Carrier Tunneling between the Silicon Valence Band and Metal in Devices Based on the Al/High-*K* Oxide/SiO_2/Si Structure

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Abstract—The features of electron tunneling from or into the silicon valence band in a metal–insulator–semiconductor system with the $HfO_2(ZrO_2)/SiO_2$ double-layer insulator are theoretically analyzed for different modes. It is demonstrated that the valence-band current plays a less important role in structures with $HfO_2(ZrO_2)/SiO_2$ than in structures containing only silicon dioxide. In the case of a very wide-gap high-*K* oxide ZrO_2, nonmonotonic behavior related to tunneling through the upper barrier is predicted for the valence-band–metal current component. The use of an insulator stack can offer certain advantages for some devices, including diodes, bipolar tunnel-emitter transistors, and resonant-tunneling diodes, along with the traditional use of high-*K* insulators in a field-effect transistor.

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1. INTRODUCTION

Over the last decade, oxide materials with a high permittivity ε_H, which are called high-*K* oxides, have been intensively studied due to the miniaturization of field-effect transistors [1, 2]. Films of these materials, including HfO_2, Ta_2O_5, and ZrO_2 ($\varepsilon_H \sim 25$) are often formed on an ultrathin silicon-dioxide (SiO_2) sublayer ($\varepsilon_I = 3.9$) on Si [1] to improve the quality of the interface.

In studying the current in metal–insulator–semiconductor (MIS) systems, including those with a multilayer insulator, researchers (see, for example, [3]) often limit consideration to the analysis of electron leakage from the *n*-channel induced at the SiO_2/Si interface (current j_{cm}). Much less attention is paid to the charge transport (j_{vm}) between the valence (v) band of silicon and the metal. However, we should specify that many years ago, when the question about the application of tunnel-thin oxides in field-effect transistors had not arisen yet, currents j_{cm} and j_{vm} were studied together in the context of the amplification properties of a MIS structure: the degree of asymmetry j_{cm}/j_{vm} roughly determined the gain. Devices based on these properties were called bipolar transistors with a MIS emitter [4] and fabricated with a single-layer SiO_2 barrier. Studying the component j_{vm} is of fundamental importance not only for fabrication of the above-mentioned devices, but also for the use of a MIS structure as an injector of hot electrons into silicon [5] (in this case, it is desirable to minimize this component) or as a resonant-tunneling diode (RTD) [6]. In MIS-RTDs, the current j_{vm} involves the resonant and excess parts; the latter should be reduced.

In a brief report [7], the potential advantages of the application of a double-layer insulator over SiO_2 in tunnel injectors are discussed. In this study, we describe in more detail the model of tunneling between the silicon v-band and metal in Al/high-*K* oxide/SiO_2/Si structures. In Section 2, we recall the main idea. Then, in Section 3, we present the mathematical aspects of the model. Section 4 is devoted to the results of calculation and Section 5 presents the experimental facts of the suppression of low-energy electron transport in the case of a double-layer insulator.

2. ON Si v-BAND–METAL TUNNELING THROUGH THE HIGH-*K*/SiO_2 COMPOSITE BARRIER

Each high-*K* material has a unique set of parameters. However, the common feature is that the middle of the valence band in many of these materials in the flat-band mode $V = V_{FB}$ of the MIS structure lies lower in energy than the middle of the silicon band (Fig. 1). Thus, we can expect that a reduction in the tunneling probability upon the addition of a high-*K* layer to the SiO_2 layer will concern mainly the component j_{vm}.

The band gap E_{gH} of high-*K* oxides is rather wide. Therefore, carrier tunneling, including that from and

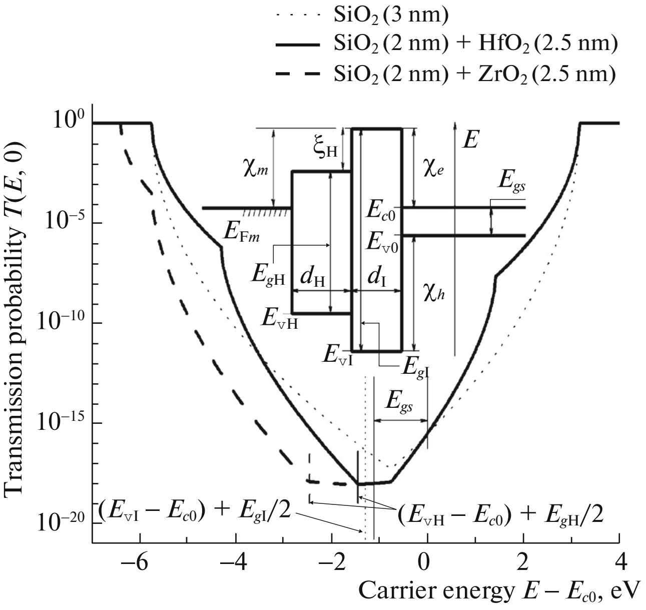

Fig. 1. Tunneling probability in the structure with high-K/SiO$_2$ at $V = V_{FB}$ (see diagram in the inset); $\chi_m = 3.17$ eV. Thicknesses d_I and d_H were selected to ensure approximately equal T values at $E - E_{c0} \sim 0$.

into the Si v-band, can occur through both the lower and upper barriers. This detail is reflected in the expression of the component of a particle wave vector in the z tunneling direction

$$k_z^2 = \max\left[\frac{2m_{cz}(E - E_C)}{\hbar^2}, \frac{2m_{vz}(E_C - E_g - E)}{\hbar^2}\right] - \frac{2m_{h\perp}E_\perp}{\hbar^2}, \tag{1}$$

where $E_c = E_c(z)$ is the coordinate-dependent energy of the edge of the conduction band; E_g, m_c, and m_v are the piecewise constant (e.g., $E_g = E_{gH}$, E_{gI}, or E_{gs}, the latter being for Si) band gaps and electron/hole masses in the barrier; E is the total carrier energy, and $E_\perp$ (in Si) is the transverse carrier energy. At the tunneling distance, k_z^2 is negative. In HfO$_2$, $E_{gH} = 5.7$ and in ZrO$_2$, $E_{gH} = 7.8$ eV; the c-band discontinuity ξ_H to SiO$_2$ is 1.75 eV in both cases; the effective carrier masses in the investigated materials were assumed to be $m_{cH} = m_{vH} = 0.15m_0$, according to the data reported in [1, 8–10]. The parameters of SiO$_2$ are well-known: $E_{gI} = 8.9$ eV, $m_{cI} = 0.42m_0$, $m_{vI} = 0.33m_0$, and the c-band discontinuity at the interface with Si is $\chi_e = 3.15$ eV. The masses in the insulators are isotropic; the masses in Si are denoted by e and h instead of c and v: for example, $m_{v\perp[\mathrm{Si}]} = m_{h\perp}$. The sometimes made assumption about the participation of only the hole barrier in the transport from the valence band is eliminated.

The above note concerning suppression of the v-band current in the presence of an additional high-K oxide layer suggests that the structure operates at low voltages close to $V = V_{FB}$. Figure 1 shows the example of predominate reduction of the tunneling probability T at energies a bit lower than the Si v-band edge, i.e., at $E - E_{c0} \leqslant -E_{gs}$, at $V = V_{FB}$. We can expect that with a sharp increase in the negative voltage on the metal ($V < 0$) the relative role of the current j_{vm} will increase: the diagram changes its shape and particles will be transferred in the allowed valence band of the high-K material. The effect of the high-K layer on the currents j_{cm} and j_{vm} in specific devices is discussed in Section 4.

3. APPROACH TO SIMULATING THE VALENCE-BAND CURRENT

In our discussion below, we assume the potential distribution (band profile) in the investigated MIS structure to be precalculated. The calculation technique was generalized in [11] for all modes.

We present expressions for the current between the silicon valence band and the metal. The energies E_{c0} (E_{v0}) and $E_{c\infty}$ ($E_{v\infty}$) used below correspond to the edge of the Si $c(v)$-band at the interface with SiO$_2$ and in the bulk and $q\varphi_s$ is the band bending in silicon. If the bands in Si are bent downward ($E_{v0} < E_{v\infty}$), then

$$j_{vm} = j_{vm}^{\text{cont}} = \frac{4\pi q}{h^3}\sum_{a,b} m_\perp^{ab} \int\limits_{-\infty}^{E_{v\infty}} \Delta f_{vm}(E) \int\limits_{0}^{E_{v\infty}-E} \Theta^{ab}(E, E_\perp) dE_\perp dE, \tag{2}$$

where $m_\perp^{ab} = \gamma_{h\perp,a}m_{h\perp,a}\gamma_{e\perp,b}m_{e\perp,b}(\Sigma\gamma_{e\perp,b}m_{e\perp,b})^{-1}$ and if they are bent upward, the contribution of the hole well is added:

$$j_{vm} = \frac{q}{\pi\hbar^2}\sum_{a,i}\frac{\gamma_{h\perp,a}m_{h\perp,a}}{\tau_{\mathrm{AR}}(E_{a,i})} \times \int\limits_{E_{v0}-q\varphi_s}^{E_{v0}-E_{a,i}} \Delta f_{vm}(E) T^a(E, E_{v0} - E - E_{a,i}) dE + j_{vm}^{\text{cont}}, \tag{3}$$

where Δf_{vm} is the difference between the Fermi functions of the Si v-band and Al, and τ_{AR} is the period of hole motion in the surface well. The general form of the formulas is well-known from available publications, similarly to the conduction-band current. However, we should explain some details that are of fundamental importance for our study and not always considered in the theory.

(i) The total energy limit in (2) is not E_{v0}, but $E_{v\infty}$; at $E_{v0} < E_{v\infty}$, this allows us to take into account the transport in Si, including the through transport, at large band bending. In the latter case, we assume the start–finish points of tunneling to be the v-band of the quasi-neutral bulk of silicon and the metal (and vice versa), but not the well, which is formed in this mode in the c-band of silicon and breaks the tunneling distance.

(ii) The tunneling probability Θ should be calculated using the transfer matrix technique. In the general case, the transfer distance can involve parts of the band gap of silicon, SiO_2, and the high-K material. When the Wentzel–Kramers–Brillouin (WKB) formula $T = \exp(-2\int|\min(0, k_z^2)|^{1/2}dz)$ is valid, Θ is replaced with T.

(iii) When finding Θ by any technique, the coordinate dependences $k_z(z)$ of the particle wave vector are used: the upper and lower barriers are taken into account at each point; the particle “chooses” the weaker barrier in accordance with (1).

(iv) Summation over (a) hole and (b) electron types is introduced. Indices a and b “run through/over” the variants of heavy/light holes ($a = hh$, lh) and heavy/light electrons ($b = he$, le); $\gamma_\perp$ denotes the degeneracy. This can be important when taking into account tunneling in Si, which is most probable with the combination of the smallest masses $m_{hz,\,a}$ and $m_{ez,\,b}$. The values for Si(100) are $m_{z,\,he} = 0.916m_0$, $m_{\perp,\,he} = 0.190m_0$, $\gamma_{\perp,\,he} = 2$, $m_{z,\,le} = 0.190m_0$, $m_{\perp,\,le} = 0.417m_0$, $\gamma_{\perp,\,le} = 4$, $m_{z,\,hh} = 0.291m_0$, $m_{\perp,\,hh} = 0.433m_0$, $\gamma_{\perp,\,hh} = 1$, $m_{z,\,lh} = 0.245m_0$, $m_{\perp,\,lh} = 0.230m_0$, and $\gamma_{\perp,\,hh} = 2$.

The current j_{cm} between the metal and silicon c-band is written similarly. It is clear that a formula like (3) for it will be especially valid at $E_{c0} < E_{c\infty}$. The authors of the most recent publications focus their attention on this current when studying electron leakage from the n-channel of a field-effect transistor.

4. RESULTS OF CALCULATION OF THE VALENCE-BAND CURRENT

We first consider the case of the injection of electrons into silicon (Subsection 4.1) and then, into the metal (4.2). The first case is valid for a transistor with a tunnel emitter on n-type Si (the topology of this device [4] is similar to the p-channel field-effect transistor where the connected source and drain serve as a base terminal and the substrate serves as a collector) and a luminescent MIS diode [5] on p-type Si. The case of electron injection from silicon is, first of all, the well-known situation of leakage in an n-channel field-effect transistor; in addition, upon positive bias voltage applied to the metal, a MIS diode on p^+-Si is of interest, where resonant tunneling (RT) can occur upon nonequilibrium depletion [6].

4.1. Injection of Electrons into Si (Bipolar Transistor with a MIS Emitter and MIS Diode)

In the mode under investigation, the contribution of j_{vm}^{cont} to the current j_{vm} is small, summation over b in (2) is excluded, and summation over a allows the simplification $j_{vm}^{\text{cont}} = 4\pi q h^{-3}\gamma_{h\perp}m_{h\perp}\int\ldots(\gamma_{h\perp} = \sum\gamma_{h\perp,a}$ and $m_{h\perp} = \gamma_{h\perp}^{-1}\sum\gamma_{h\perp,a}m_{h\perp,a})$. T can be undoubtedly used instead of Θ. For the problems solved in this study, the description of current from the well of the v-band can also be simplified by replacing the ladder of levels $E_{a,\,i}$ with the effective level E_0 determined upon finding the voltage distribution in the MIS structure [11]. Then,

$$j_{vm} \approx \frac{q}{\tau_{\text{AR}}(E_0)}\left[\frac{\gamma_{h\perp}m_{h\perp}}{\pi\hbar^2}\right.$$
$$\left.\times\int\limits_{E_{v0}-q\varphi_s}^{E_{v0}-E_0}\Delta f_{vm}(E)T(E, E_{v0}-E-E_0)dE\right] + j_{vm}^{\text{cont}}. \tag{4}$$

Our calculation was performed using this formula, although the expression in brackets is sometimes changed for the product $N_sT(E_{v0} - E_0, 0)$, where N_s is the two-dimensional hole density and the term j_{vm}^{cont} is disregarded. Moreover, using the rough approximation of a triangular well [12] to determine E_0 and τ_{AR}, we can obtain

$$j_{vm} \approx \frac{q^{2/3}\varepsilon_0\varepsilon_{\text{I}}^{5/3}F_{\text{I}}^{5/3}}{2^{4/3}m_{hz}^{1/3}\hbar^{1/3}\lambda_0^{1/2}\varepsilon_s^{2/3}}$$
$$\times T\left[E_{v0} - \lambda_0\left(\frac{q\hbar\varepsilon_{\text{I}}F_{\text{I}}}{\varepsilon_s\sqrt{2m_{hz}}}\right)^{2/3}, 0\right], \tag{5}$$

where $\lambda_0 = 2.34$ is the first zero of the Airy function. Formula (5) can be used for qualitative interpretation. In (5), F_{I} is the field in SiO_2 related to N_s as $N_s = \varepsilon_0\varepsilon_{\text{I}}F_{\text{I}}/q$.

Figure 2a shows the dependences of the v-band current on field F_{I} in the SiO_2 layer; the second layer was zirconium and hafnium oxides. In addition, we performed calculation for the Al/vacuum/Si system (here, $F_{\text{I}} = F_{\text{vac}}/3.9$). In the MIS structure containing only SiO_2 or HfO_2/SiO_2, the function $j_{vm}(F_{\text{I}})$ is monotonous and holes tunnel through the lower barrier. However, in the case of ZrO_2/SiO_2, there is a region where the current j_{vm} decreases with increasing field F_{I}. In this region and to the left of it, transport occurs through the upper barrier, which lowers the probability of transmission. This is first recompensated by an increase in the first term in (5), but then j_{vm} decreases. After that, tunneling is replicated at the lower barrier and growth is observed again. In the artificial case of the “vacuum layer” instead of insulators, the current does not increase at high fields. We repeat that F_{I} is the field in SiO_2; in $HfO_2(ZrO_2)$, it amounts to $F_{\text{H}} = F_{\text{I}}\varepsilon_{\text{I}}\varepsilon_{\text{H}}^{-1}$.

Figure 2b shows the dependences of the currents in the v- and c-bands on the difference between the

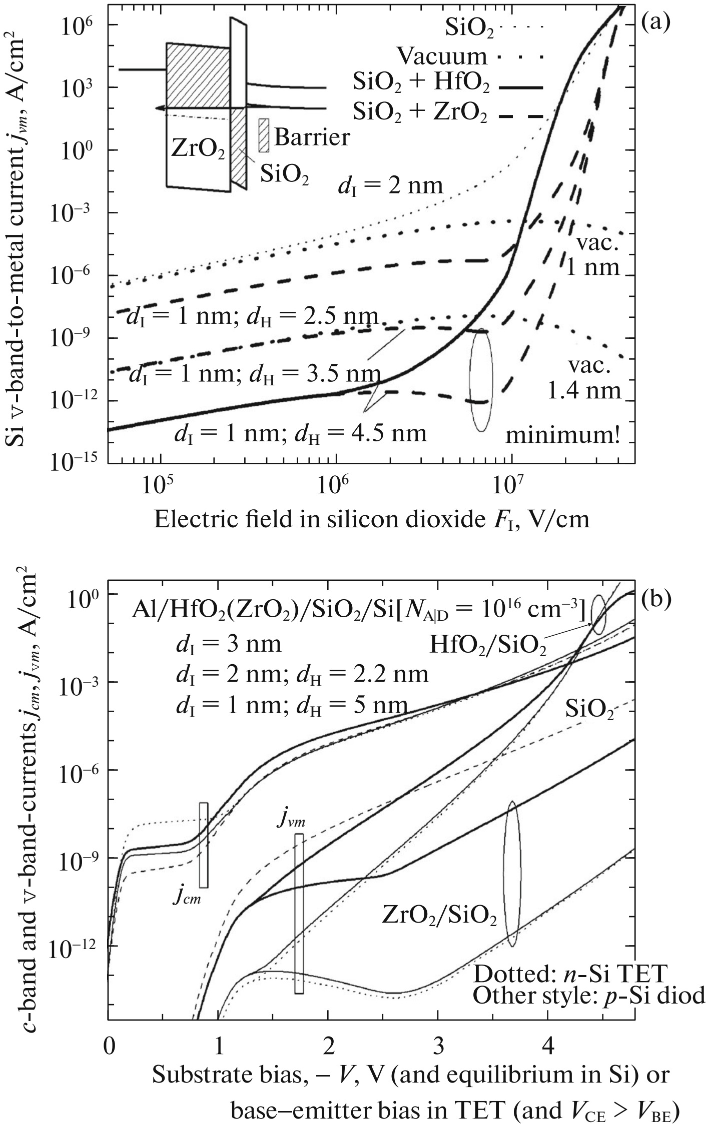

Fig. 2. Calculated v-band–metal tunneling current j_{vm} in the mode $V < 0$ vs. (a) field in SiO_2 and (b) voltage between the metal and induced hole layer (the figure is supplemented with curves j_{cm}). In the wide-gap high-K material (ZrO_2), the current j_{vm} can behave nonmonotonically. Figure 2b illustrates the suppression of j_{vm} at low voltages as due to the bilayer insulator.

Fermi level in the metal and quasi-Fermi level in the silicon v-band E_{FV}. If the structure is formed on p-Si, such a mode corresponds to accumulation and the above-mentioned difference is equal to the applied bias accurate to the sign ($-V$). As applied to the structure on n-type Si, the same polarity corresponds to depletion-inversion and the axis argument in Fig. 2b in terms of a bipolar transistor is the base-emitter voltage V_{BE} (the inversion layer serves as a base). In these coordinates, the role of doping is almost insignificant. In addition, here the layer thicknesses are chosen to ensure approximately equal currents j_{cm} in all cases. (We note that at a work function of the metal larger than that of Al, j_{cm} near 0 can become lower than j_{vm}, instead of stabilization). It can be seen that in the case of a bilayer insulator, the current j_{vm} at moderate $|V|$ values is smaller than in the case of SiO_2, so the ratio $j_{cm} : j_{vm}$ is increased. For an injection diode on p-type Si, this implies minimization of the nonproductive component and for a transistor, amplification is enhanced. At very high voltages, the current j_{vm}, as expected, increases. The intermediate drop of j_{vm} for ZrO_2/SiO_2 is similar to that shown in Fig. 2a; it can lead to multistability of the structure on n-Si. In this structure, a balance between the supply and escape of minority charge carriers $j_B \approx j_{vm}$ is established, where j_B is the base current; i.e., at specified V_{CE} and j_B for the case of the nonmonotonic behavior of j_{vm}, several

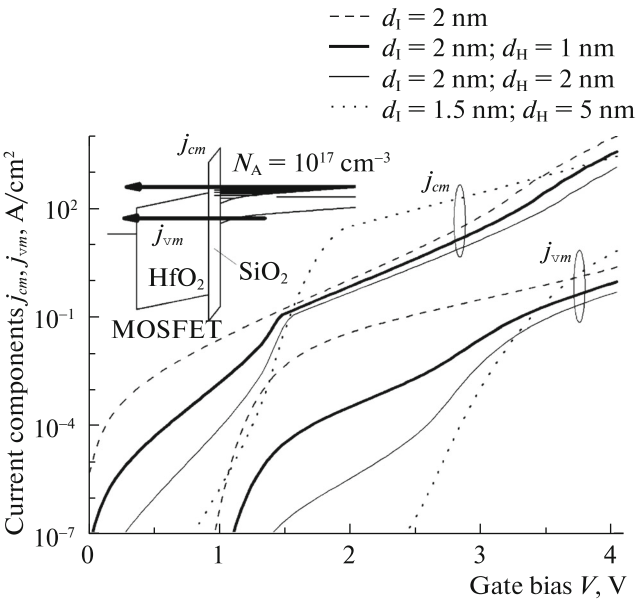

Fig. 3. Calculated electron and hole tunneling currents in the standard mode of testing an n-channel field-effect transistor. The component ratio j_{cm}/j_{vm} increases for a high-K/SiO$_2$ system.

(three) states with different $qV_{BE} (= E_{Fm} - E_{Fv})$ and j_{cm} can be implemented. The limit $j_B = 0$ corresponds to the diode in the case of depletion.

4.2. Injection of Electrons into the Metal (Field-Effect MIS Transistor and MIS Diode)

In the standard mode of testing an n-channel field-effect transistor on p-type Si or a diode on n-type Si at $V > 0$, the equilibrium conditions in Si are satisfied; $q\varphi_s$ is undoubtedly smaller than $E_{gs} + E_{he,1}$ ($E_{he,1}$ is the lower electron level in the well of the c-band) and often even $q\varphi_s < E_{gs}$. RT transport is excluded and the calculation can certainly be performed using the WKB technique:

$$j_{vm} = \frac{4\pi q}{\hbar^3}\sum_{a,b} m_\perp^{ab} \int_{-\infty}^{E_{v\infty}} \Delta f_{vm}(E) \times \int_{0}^{E_{v\infty}-E} T^{a,b}(E, E_\perp) dE_\perp dE. \tag{6}$$

This mode was considered in detail in available publications, but attention was focused only on the current j_{cm}, since it decreases due to the high-K insulator. It is quite obvious that in this situation we have $j_{vm} \ll j_{cm}$ and, in the case of a bilayer insulator, the difference between components further increases (see the example in Fig. 3).

The effect of suppression of the component j_{vm} is noticeable in the range $V \sim 2$ V and weakens with increasing V, since electrons from even the Si v-band will be transferred over the edge of the HfO$_2$ conduction band. Certainly, damping of the tunneling transport with low energies in the presence of an additional high-K layer may affect not only j_{vm} but also j_{cm}. The current of the c band in the investigated mode consists mainly of currents from levels similar to the first term in (3). As was shown in [13] and confirmed by our calculations, in the MIS structure with SiO$_2$ the current j_{cm} is determined by leakage from the first level, while in the case of a HfO$_2$/SiO$_2$ double-layer insulator the current from the second and third levels can prevail. This is the case of a thin SiO$_2$ layer and low V values ($V <$ 1–1.5 V at the chosen parameters of the MIS structures); for higher V, electrons start passing through the high-K layer over the barrier (at $\varepsilon_H = \infty$, all curves $j_{cm}(V)$ for $d_I = 2$ nm would merge on the right).

In contrast to the above-considered n-channel transistor and diode on n-type Si, the MIS diode on the p-type Si substrate at $V > 0$ operates under conditions of nonequilibrium depletion, when the band bending $q\varphi_s$ can be significantly larger than E_{gs}. Upon heavy doping N_A, in this case the resonant-tunneling transport of carriers [6] can occur between the Si v-band and metal through the levels of the c-band $E_{b,i}$. Formula (2) can be used for calculating j_{vm} without transformation to formula (6) and the probability Θ will acquire large values at combinations of E and $E_\perp \sim E_\perp^* = m_{e,b\perp} m_{h,a\perp}^{-1} (E - E_{c0} - E_{b,i})$ corresponding to RT transmission (there is no need to purposefully find the levels).

In the described situation, the current j_{cm} is determined by thermal generation in the bulk of Si, has a small value, and does not pose a problem. However, the excess current, which is included in the current j_{vm} and is owing to the nonresonant transport of electrons with energies below the levels $E_{b,i}$, often becomes quite noticeable. To suppress it, the use of high-K/SiO$_2$ double-layer insulators may not be a bad solution. The probability of tunneling will be somewhat lower due to the presence of an additional layer at all energies, but the main reduction will occur for low-energy electrons ($E < E_{c0}$). This situation was discussed in detail in [6], where it was shown that the RT features in the MIS-RTD with a composite insulator should be more pronounced than in the case of SiO$_2$.

5. EXPERIMENTAL EVIDENCE

The energy redistribution of tunneling in the case of a double-layer insulator was not purposefully investigated in the experiments. However, there have been many publications devoted to field-effect transistors with HfO$_2$/SiO$_2$, where we can find the measurement

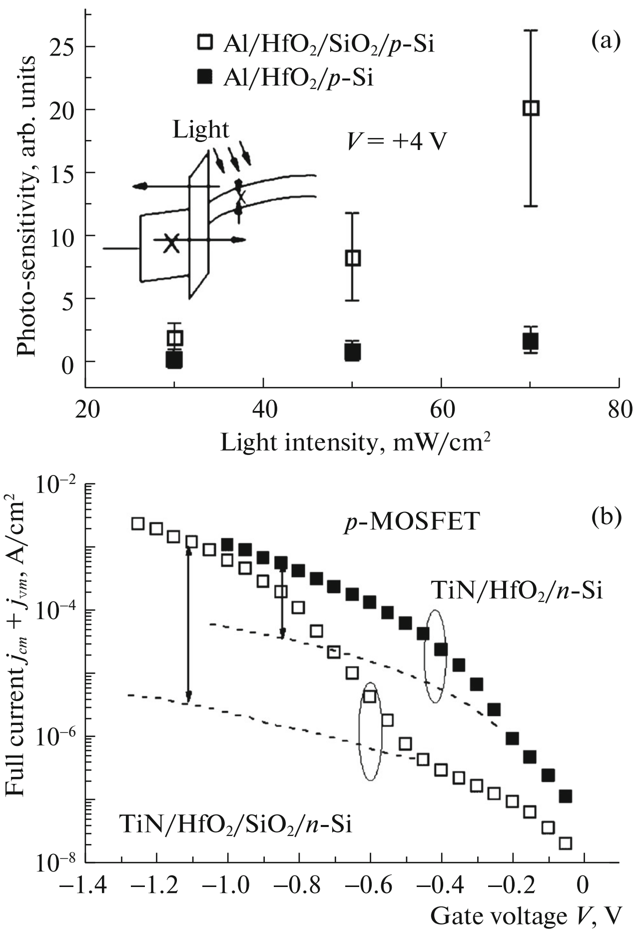

Fig. 4. Experimental evidence in favor of (a) suppression of the valence-band current in the case of a bilayer insulator in the mode $V > 0$ and (b) appearance of the current j_{cm} against the background of j_{vm} at low voltages and an increase in j_{cm}/j_{vm} in HfO_2/SiO_2. The data were taken from [17, 18] and replotted for the sake of convenience.

data that concern the subject of this study, although the studies cited below had different goals.

First of all, the presence of a considerable hole current in the structures with HfO_2/SiO_2 was demonstrated [14, 15]. This is important, since it could happen that the surface states at the high-K oxide boundaries have an excessively high density, which masks any effects. Some results prove the increasing role of j_{vm} at high negative biases V, which is consistent with our expectations. In particular, Rothschild et al. [14] mentioned the feature of the logarithmic derivative $d(\ln j)/dV$ upon transformation of the HfO_2 hole barrier from trapezoidal to triangular. In [15], Lu et al. noted the contribution of j_{vm} to the charge transport and generation of defects at $V \sim -4$ V. In [16], the change of the dominant component from j_{cm} to j_{vm} at certain thicknesses of the SiO_2 sublayer was discussed.

In experimental study [17], Pang et al. proved the suppression of the v-band current in a double-layer system, which weakens the undesirable recombination and thus enhances the efficiency of the MIS photodetector on p-Si under conditions of $V > 0$ (Fig. 4a). In [18], Southwick et al. studied the currents in $TiN/HfO_2/SiO_2/Si$ and $TiN/SiO_2/Si$ structures at different temperatures; the curves for the structure based on n-type Si at 300 K ($V < 0$) from [18] are presented in Fig. 4b. Taking into account the chosen metal (TiN instead of Al), near zero the current j_{vm} prevails; then, as $|V|$ is increased, the current j_{cm} comes into play (for more details, refer to [18]). Extrapolating the hole current to the left (dashed line), one can take the ratio of the currents marked with the arrow as amplification; in the double layer, as was predicted by us, this ratio is obviously larger.

Meanwhile, generally speaking, theoretical considerations about suppression of the low-energy part of the tunneling current seem clear and hardly need to be proved. The degree of validity of the conclusions is completely determined by the reliability of information on the high-K barrier, i.e., the effective masses and band discontinuities at the heterointerfaces. To date, here the essential convergence of the data, if not their complete certainty, has been attained [1, 2, 8–10].

6. CONCLUSIONS

We theoretically demonstrated that the use of a high-K/SiO_2 double-layer insulator (e.g., HfO_2/SiO_2) instead of a single layer of SiO_2 should lead to considerable suppression of the current between the metal and silicon v-band, especially the low-energy part of this current. This can be useful for transistors with a tunneling MIS emitter and tunneling MIS injectors in general. However, at high negative voltages applied to the metal, the current j_{vm} in the high-K/SiO_2 system can prevail. In the model, we considered tunneling through both the upper and lower barriers formed by the oxide band gaps; due to the effect of the upper barrier, the valence-band current as a function of voltage can behave nonmonotonically in the ZrO_2/SiO_2 system. We discussed the experimental evidence in favor of the idea of using high-K/SiO_2 structures in injection MIS devices. As applied to such structures, this can be a new field of their application, along with the traditional use of high-K materials as a gate insulator in field-effect transistors.

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