ISSN 1063-7850, Technical Physics Letters, 2018, Vol. 44, No. 12, pp. 1188–1191. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © Yu.Yu. Illarionov, A.G. Banshchikov, N.S. Sokolov, S. Wachter, M.I. Vexler, 2018, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2018, Vol. 44, No. 24, pp. 150–157.

Nonmonotonic Change in the Tunnel Conductivity of an MIS Structure with a Two-Layer Insulator with an Increase in Its Thickness (by the Example of the Metal/SiO_2/CaF_2/Si System)

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Received September 24, 2018

Abstract—The effect of increasing the tunnel current in a metal–calcium fluoride–silicon structure with addition of a silicon dioxide layer between fluoride and metal (which seems paradoxical at first glance) has been considered. This effect of nonmonotonic change in the tunnel conductivity with an increase in the insulator thickness may occur at a relatively high bias at the structure and is related to the tunnel-barrier deformation, at which electrons are tunneling through its part formed by the oxide. At low biases, the occurrence/thickening of an additional layer leads to a natural decrease in the current. Similar behavior is possible in principle for some other combinations of materials.

DOI: 10.1134/S1063785018120441

Metal–insulator–semiconductor (MIS) structures, in which the insulator film consists of two tunnel-transparent layers or can be considered such [1], are used in various modern microelectronic devices. Combinations of materials can be different (e.g., the high-k insulator over the thin SiO_2 film or vice versa). Structures of this type also include systems with nonideal metal adhesion (vacuum bridge is formed) and MIS systems with a dielectric film subjected to postprocessing. For example, this dielectric film can be composed of a calcium fluoride (CaF_2) layer with a subsequent deposition of a SiO_2 layer (additional oxidation) in order to overgrow the defects.

One might expect that the presence of an additional layer will always reduce the through current (because of the tunnel-barrier thickening) and, accordingly, increase the tunnel resistance of the structure at any voltage.

However, it is shown in this study that the situation may be more complicated, and the tunnel conductivity of a two-layer insulator may be higher. The case in point is conventional tunneling (without resonance phenomena), which is simulated within the simple Wentzel–Kramers–Brillouin approximation. The model can be experimentally confirmed using the aforementioned system with the SiO_2 layer deposited on fluoride at the voltage polarity corresponding to electron injection from metal (positive voltage at Si). (The practical interest in CaF_2 is due to the prospects of its application in three-dimensional architecture devices: a close matching of the CaF_2 and silicon lattice constants allows one to grow layers of one material on the other [2].)

The energy-band diagram of the metal–double insulator (SiO_2/CaF_2)–silicon structure is shown in Fig. 1a. It was easily calculated based on our conventional models [3]. The barrier heights were as follows: $\chi_m = 3.17$ eV, $\chi_i = 2.38$ eV, and $\xi = 0.77$ eV.

With the band bending in the semiconductor disregarded (Figs. 1b–1e), the applied bias voltage V is divided between the insulator layers, which provides the validity of the proportion $F_i/F_{ox} = \varepsilon_{ox}/\varepsilon_i$ for the fields in fluoride (F_i) and oxide (F_{ox}) layers. We assume provisionally that the oxide permittivity ε_{ox} is much smaller than the fluoride permittivity ε_i (i.e., $\varepsilon_i \gg \varepsilon_{ox}$); actually, $\varepsilon_i > \varepsilon_{ox}$ for the fluoride–dioxide system but with no margin: the values are 8.43 and 3.9, respectively. We discuss the character of possible changes in the current at a fixed thickness of the main insulator d_i and oxide thickness d_{ox} increasing from zero.

In the absence of oxide, the voltage drops at the main insulator (Fig. 1b); however, when SiO_2 is added, the voltage entirely drops at this layer due to the ratio between ε_i and ε_{ox} (Fig. 1c). Figures 1d and 1e show the energy band diagrams of these systems at close-to-

zero V, when the bands are barely bent. In this case (Fig. 1d, 1e), it is obvious that the presence of oxide will make the tunnel barrier less transparent and decrease the current created by electrons with energies near the metal Fermi level E_{Fm}. However, in the case of a two-layer insulator, an increase in V (Figs. 1b, 1c) may cause a situation in which almost solely the oxide layer is involved in the through tunneling (Fig. 1c). In this case, the current may increase, especially if the carrier effective mass in SiO_2 is smaller than that in the main insulator.

Let us now consider the real metal/SiO_2/CaF_2/Si(111) structure with specific parameters. We assume that fluoride thickness d_i is 1.5 nm (this value corresponds to about five monolayers) and consider the behavior of electron current j_e at a positive bias at the substrate for several oxide thicknesses d_{ox}. Current j_e is calculated from the simple formula

$$j_e = 4\pi q m_0 (kt)^2 h^{-3} T_e(E_{Fm}), \quad (1)$$

where $T_e = T_{ox}T_i$ is the probability of tunneling through the two-layer barrier (T_{ox} and T_i are the probabilities of tunneling through the oxide and fluoride layers, respectively) and kt is the thermal energy. It was verified that a more accurate calculation with the integration over energies [3] barely makes any changes, but relies on very cumbersome formulas.

The calculation of probabilities T_{ox} and T_i from the Wentzel–Kramers–Brillouin formula

$$T_{ox} = \exp\left[-\frac{4\sqrt{2m_{ox}}}{3\hbar q F_{ox}}(\tilde{\chi}_{mox}^{3/2} - (\tilde{\chi}_{mox} - qF_{ox}d_{ox})^{3/2})\right], \quad (2a)$$

$$T_i = \exp\left[-\frac{4\sqrt{2m_i}}{3\hbar q F_i}((\tilde{\chi}_{mi} - qF_{ox}d_{ox} - \xi)^{3/2} - (\tilde{\chi}_{mi} - qF_{ox}d_{ox} - \xi - qF_i d_i)^{3/2})\right] \quad (2b)$$

takes into account the conservation of the transverse electron wave vector at the CaF_2/Si interface with a large magnitude (at the Si(111) orientation). For this purpose, we proposed [4] an approximated formula, which specifies the effective barrier enhancement depending on the difference between the electron energy and the bottom of the silicon conduction band E_{c0} (the larger the difference is, the weaker this effect): $\Delta E = \Delta E_0 \exp[-(E_{Fm} - E_{c0})/E_s]$, where $\Delta E_0 = 2.44$ eV and $E_s = 1.0$ eV. In the formulas for T_{ox} and T_i, this increase is taken into account by replacing the potential-barrier height χ_m with

$$\tilde{\chi}_{mox|i} = \chi_m + m_0 m_{ox|i}^{-1}\Delta E, \quad (3)$$

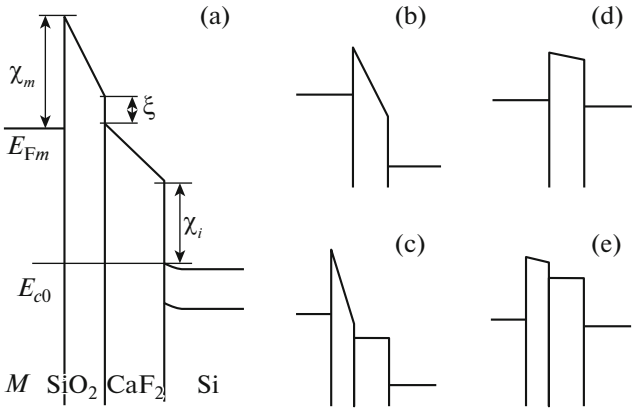

Fig. 1. (a) Fragment of the energy band diagram of the MIS structure with two-layer SiO_2/CaF_2 insulator and (b–e) deformation schemes of one- and two-layer tunnel barriers for the case of significantly different permittivities.

where subscripts ox and i refer to oxide and fluoride, respectively. The effective electron masses are $0.42m_0$ for SiO_2 and $1.0m_0$ for CaF_2.

Figure 2 shows the calculated dependences of current j_e on the substrate bias. Strictly speaking, the argument along the abscissa axis is the sum of the total bias at the insulators U and flat-band voltage V_{FB}. However, in many cases (always for p-Si and at a sufficiently high doping level and/or strong thermal generation in silicon for n-Si), the band bending in Si is small, and one can approximately assume that the substrate bias V is plotted on the axis. In addition, the calculation made it possible to check that the hole tunnel current j_h (Si–metal valence band) in this system is much smaller than j_e; therefore, the curves in Fig. 2 can be considered as the expected current-voltage characteristics for the corresponding structures.

It can be seen that, at voltages of up to about 3 V, the occurrence and thickening of the oxide layer lead (according to the theory) to a decrease in the current density. However, afterward, the appearance of a segment of rapid current growth is predicted for the SiO_2/CaF_2 system (at certain oxide thicknesses, this growth can be larger than that in the metal/CaF_2/Si system). This behavior is consistent with simple considerations based on the data in Fig. 1: the finiteness of the $\varepsilon_{ox}/\varepsilon_i$ ratio does not result in any serious modifications. It was revealed that the conservation of the transverse wave vector (which is important in the range of small V values, where, assuming that $\Delta E = 0$, the calculated currents would have increased by several orders of magnitude) is also insignificant for the effect under consideration because the injection at $V \sim$ 3 V occurs much above the band edge. In the limit of very large oxide thicknesses, the currents naturally decrease at all voltages.

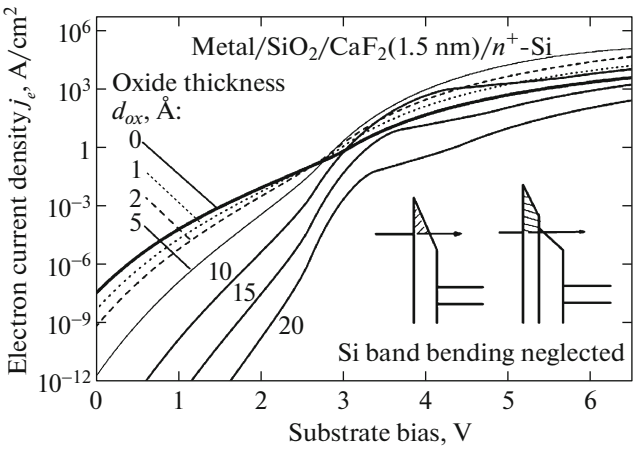

Fig. 2. Calculated dependences of the electron-injection current in the MIS structure with one dielectric (calcium fluoride) layer and an additional oxide layer. The band bending in silicon is neglected.

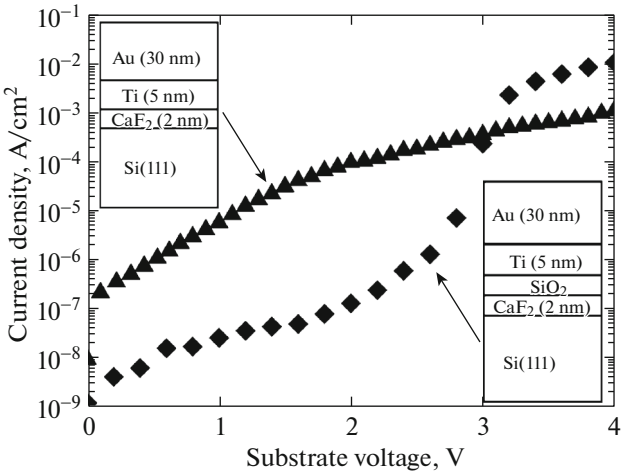

Fig. 3. Measured current–voltage characteristics of the MIS structures with fluoride and an additional oxide layer. At small V values, the addition of oxide reduces the current, whereas at high voltages the effect is inverse.

It is of interest that the described specific features can be experimentally observed. We grew CaF_2 layers with a thicknesses of six monolayers on n-Si(111) by molecular-beam epitaxy with subsequent annealing. An important technological feature was the low growth temperature (250°C), which minimized the number of defects (pinholes). An additional silicon dioxide layer with a thickness of several nanometers was deposited on some samples over the fluoride layer. The SiO_2 layer and metal contacts (work function ~4.2 eV) were deposited by ion sputtering.

The static characteristics of these structures were recorded using a standard probe installation. The specific features of the current-voltage characteristic are more important than the current values.

In this study, it would be more convenient to use p-Si-based structures (which are in the accumulation mode with knowingly small band bending in silicon at the given polarity); however, we chose n-Si because n substrates are generally more important for potential applications of the CaF_2/Si systems in devices. In this case, the application of a positive potential to the substrate (depletion/inversion mode) may result in the lack of minority carriers, which leads to significant band bending in Si and a current plateau in the current–voltage curve [5]; this would hinder the interpretation of the results. We observed this behavior previously for some Au/CaF_2/n-Si diodes with an extremely thin fluoride layer and weak thermal generation in the silicon bulk [6]. External illumination made it possible to increase the injection of minority carriers and current at the plateau. However, in this case, it was verified that their photosensitivity was almost absent, which is indicative of small band bending (there is hardly any possibility for reducing this bending).

Figure 3 shows typical measured characteristics. The nominal fluoride thickness was 2 nm; however, its effective value was smaller (about 1.5–1.7 nm) due to the presence of inhomogeneities. It is noteworthy that the curve shapes for the structures with CaF_2 and SiO_2/CaF_2 are different: the sample with a double layer exhibits a sharp increase in the current in some relatively narrow voltage range, which can be misinterpreted as a manifestation of damage (however, it was established that the characteristic is stable and repeated at rerecording). In complete agreement with the theoretical prediction, a significant (by several orders of magnitude in comparison with values for the structure without oxide) falloff of the current is observed at low voltages, and the effect becomes inverse at voltages of 3–4 V. The current at $V \sim 3.5$ V in the double-layer case may be higher by a factor of 5–10. A qualitatively similar behavior was detected for all structures under investigation.

The obtained result may be important in two aspects. Concerning tunnel MIS structures, this is a new behavioral feature, which can be implemented for different combinations of materials. As applied to the technology of fluoride films, the found increase in the current with addition of oxide indicates that one can reduce leakages by such thickening only in some voltage range. Note that previously some researchers [7] recommended additional oxidation of samples for overgrowing pinhole defects in thin CaF_2 films. As follows from our data, at small SiO_2 thicknesses, this action is fruitful only in some limited (although sufficient for practical purposes) range.

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Translated by A. Sin'kov