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The band-gap width of the nanometer-thick silicon dioxide

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The band gap dependence on thickness d_S of ultrathin silicon dioxide films has been studied using the Projection Augmented Wave method within the Density Functional Theory. It is shown that the value of E_{gS} for ultrathin silicon dioxide films is less than its values for bulk crystals and increases with increasing thickness. For this, parameters of the band structure of the silicon dioxide tetragonal modification (stishovite) were calculated for the film thicknesses ranging from the thinnest-oxide thickness of 0.3 nm to 3.68 nm. It was found that the condition for minimizing leakage currents requires additional analysis since it is not satisfied for all thicknesses of oxide dielectrics.

Keywords: band gap, electronic structure, silicon dioxide, high-K dielectrics, ultrathin films.

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The most promising electronic devices made from silicon are field-effect transistors [1–4]. A serious parasitic effect in such transistors is tunneling current between the channel and gate, which causes charge leakage. In [3] it is shown that leakage currents sometimes amount up to 1 A at the voltage of 1 V. To suppress parasitic currents, authors of [5,6] proposed to form between the substrate and high-dielectric-permittivity oxide (the so-called high-K dielectric which may be one of the transition-metal oxides: HfO_2, ZrO_2, etc.) an ultrathin SiO_2 layer which would not only serve as a part of the sub-barrier layer but also prevent leakage currents. As the results of [6,7] show, minimization of leakage currents implies fulfillment of inequality $\xi > E_{gS} - E_{gE} - \xi$ ($\xi > 0$), where E_{gS} and E_{gH} are the band-gap widths of SiO_2 and high-K dielectric, respectively, while ξ represents the conduction band discontinuity at the HfO_2/SiO_2 interface.

In view of the fact that the silicon dioxide band structure depends, among other things, on the SiO_2 thickness [8], in this work the dependence of the silicon dioxide band-gap width E_{gS} on its film thickness d_S was considered; in addition, analysis of conditions for minimizing leakage currents was performed based on numerical calculations of the electronic structure of ultrathin SiO_2 films.

When silicon dioxide is used jointly with a high-K dielectric, the potential barrier of the tunneling contact under consideration consists of two thin layers (as shown in Fig. 1 as per [5]): a film of silicon dioxide and a film of high-K dielectric; each of them has its own thickness and band-gap width (d_S and E_{gS} for silicon dioxide, d_H and E_{gH} for the high-K dielectric), E_{Fm} represents the metallic electrode Fermi level, E_C and E_V are the silicon band gap boundaries. In this case, silicon dioxide thickness d_S reaches ultralow values. Due to great interest shown by researchers in such tunneling systems, the band structure parameters of SiO_2, HfO_2, ZrO_2 and other high-K dielectrics are at present well-studied both theoretically and experimentally [1–4]. It has been established that E_{gS} (the SiO_2 band-gap width) is 9.0 eV with the admissible shift of the conduction band bottom $\Delta_{gS} = \pm 3.2$ eV [3], which exceeds the bandgap widths of HfO_2 and ZrO_2 each having E_{gH} of 5.8 eV with the admissible band shifts of 1.4 and 1.5 eV, respectively. Authors of most studies associate shift Δ_{gS} with peculiar spatial features of different SiO_2 crystal lattice types, namely, with the existence of different modifications of the silicon dioxide unit cells: tetragonal, trigonal, hexagonal, cubic, etc. [9,10]. However, modeling of even an ultrathin dielectric SiO_2 layer is typically performed by researchers based on calculations of E_{gS} and other band-structure parameters obtained for bulk crystals without accounting

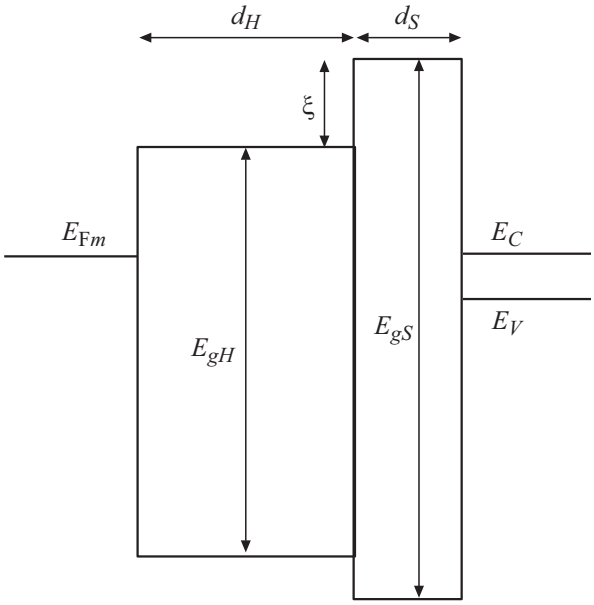

Figure 1. Energy band diagram of a double-layer tunneling barrier.

for their dependence on the film thickness. Therefore, let us calculate the band-structure parameters for different thicknesses (from 0.3 to 3.68 nm) of the films of silicon dioxide in the stishovite modification.

The calculations will be performed in the framework of the Density Functional Theory by the Projection Augmented Wave method (PAW) [11] using program code VASP (Vienna *ab initio* simulation package). For the exchange-correlation potential, use the Generalized Gradient Approximation (GGA) in the form proposed in [12]. As pseudopotentials, standard pseudopotentials VASP are taken. In calculation, the partition number in integrating over the irreducible part of the Brillouin zone was chosen equal to 22. Self-consistent calculations provided optimized positions of all atoms and total energy of the system; then the compound band structure, density of electronic states, etc., were calculated. During optimization, there was imposed a requirement that the forces acting upon the atoms be lower than 1 eV/nm. The obtained results will be refined by additional calculations using Green functions (GW) [13].

Fig. 2 presents the E_{gS} dependence on d_S for the modification with the tetragonal lattice cell (stishovite) having a closer packing than other modifications due to that in this case there are six instead of four oxygen atoms per silicon atom.

Analysis of the presented calculations showed that the band-gap width for ultrathin films with thickness d_S of 0.3 to 0.8 nm increases from 4.95 to 5.71 eV which is beyond the limits of admissible shift Δ_{gS} and is significantly lower than E_{gS} of bulk SiO_2 crystals. The E_{gS} value increases with increasing thickness from 5.71 eV and reaches 8.05 eV at $d_S = 3.68$ nm tending to the band-gap width of the stishovite bulk crystal which amounts to 8.11 eV.

Now, calculate band-gap width E_{gH}. As the high-K dielectric, consider hafnium oxide in the bulk-crystal approximation. The calculation results are shown in Fig. 3. According to them, E_{gH} for the monoclinic modification of the crystal is 5.79 eV. Comparing E_{gS} values for different

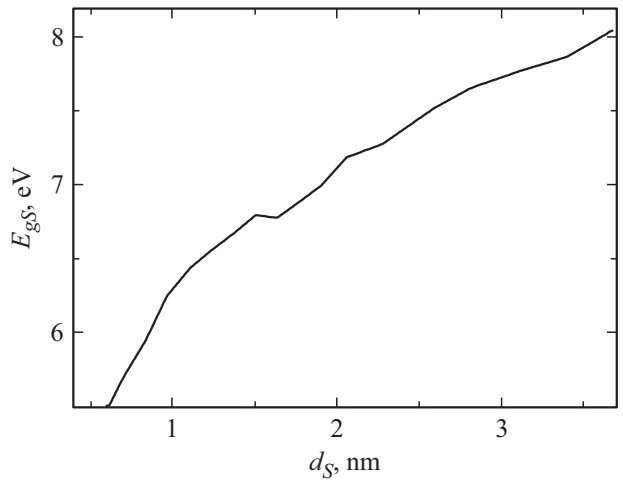

Figure 2. Band-gap width versus film thickness for SiO_2 with the tetragonal cell (stishovite).

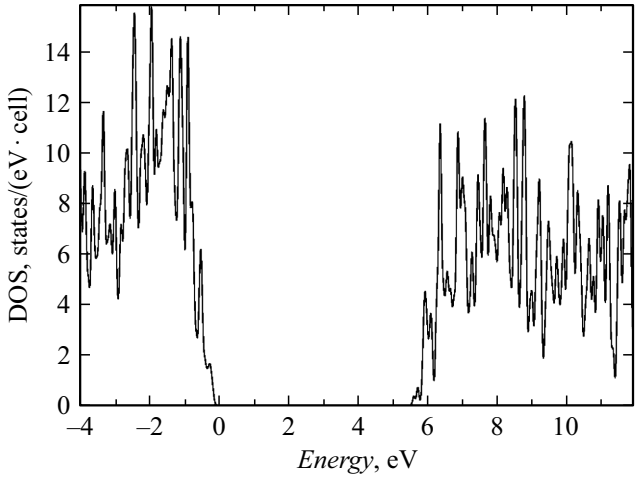

Figure 3. Density of electronic states (DOS) of the bulk HfO_2 crystal.

Calculations of silicon dioxide E_{gS} at different d_S

d_S, nm	E_{gS}, eV	d_S, nm	E_{gS}, eV
0.3	4.95	1.79	6.9
0.57	5.4	1.91	7.0
0.71	5.71	2.06	7.19
0.84	5.95	2.28	7.28
0.97	6.25	2.59	7.52
1.11	6.44	2.82	7.66
1.24	6.56	3.13	7.78
1.37	6.67	3.4	7.87
1.51	6.8	3.68	8.05
1.64	6.78		

thicknesses of SiO_2 and E_{gH} for bulk HfO_2, we can see that the above-mentioned condition for leakage minimization can be satisfied for films of silicon dioxide in the stishovite modification below 0.8 nm in thickness. Indeed, as the Table shows, difference $\Delta\varphi = E_{gS} - 5.79$ eV that is negative for SiO_2 films below 0.8 nm thick becomes positive at $d_S = 0.84$ nm and then increases with increasing d_S and almost reaches bulk-crystal $\Delta\varphi$ values at $d_S = 3.68$ nm.

Most likely, in the case of ultralow thicknesses this minimization condition becomes totally irrelevant and needs revision. Thus, in view of a considerable decrease in band-gap width E_{gS} with decreasing d_S, the use of ultralow films of oxide dielectrics needs correction of some approaches to studying properties of nanomaterial-containing systems.

Conflict of interests

The authors declare that they have no conflict of interests.

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