Electronic properties of hafnium oxide: A contribution from defects and traps

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ABSTRACT

In the present article, we give a review of modern data and latest achievements pertaining to the study of electronic properties of oxygen vacancies in hafnium oxide. Hafnium oxide is a key dielectric for use in many advanced silicon devices. Oxygen vacancies in hafnium oxide largely determine the electronic properties of the material. We show that the electronic transitions between the states due to oxygen vacancies largely determine the optical absorption and luminescent properties of hafnium oxide. We discuss the role of oxygen vacancies as traps that facilitate charge transport in hafnium oxide films. Also, we demonstrate the fact that the electrical conductivity in hafnium oxide is controlled by the phonon-assisted tunnelling of charge carriers between traps that were identified as oxygen vacancies.

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1. Introduction

Currently, dielectrics with high dielectric permittivity, or high-κ dielectrics, such as hafnium oxide (hafnia) HfO$_2$, zirconium oxide ZrO$_2$, aluminium oxide Al$_2$O$_3$, tantalum oxide Ta$_2$O$_5$, and titanium oxide TiO$_2$, gradually replace the traditional dielectric, silicon oxide SiO$_2$, in many silicon devices.

Among the high-κ dielectrics, hafnium oxide attracts the greatest interest because it combines a large band-gap energy $E_g = 5.6$–5.8 eV [1–3], high dielectric permittivity $\kappa = 16$–25 [3,4] (for comparison, the silicon oxide permittivity is $\kappa_{\text{SiO}_2} = 3.9$), high thermal stability (melting point $T_{\text{melt}} \approx 2780$ °C), high thermodynamic stability in contact with silicon, and high energy barriers for electrons and holes with respect to silicon (respectively, 2.0 and 2.5 eV) [1,5]. In recent years, HfO$_2$ has been given an extensive study, mainly because of its potential applications as high-κ gate dielectric in metal-oxide-semiconductor (MOS) field-effect transistors [6–8]. In 2007, the Intel Corporation has implemented high-κ hafnium oxide HfO$_2$ as the gate dielectric in silicon devices of Intel® Core™ family instead of silicon oxide SiO$_2$ [9]. This event was widely recognized as a cornerstone in microelectronics. Currently, hafnium oxide replaces silicon oxide in memory devices. Hafnium oxide (pure, doped, or oxygen-deficient material) attracts additional interest as a promising candidate for use in non-volatile resistive random access memory (ReRAM) [10–12] and ferroelectric random access memory devices (FeRAM) [13–15]. Also, hafnium oxide is widely used for preparation of optical and protective coatings in the production of special types of glass for fibre optic products, as well as for obtaining high-quality optical products. Hafnium-based ceramics are used in teeth prosthetics [16,17].

Hafnium oxide has many polymorphic modifications. Under standard conditions, HfO$_2$ has a stable monoclinic prismatic crystalline form m-HfO$_2$ of the P2$_1$/c crystal system (baddeleyite). At higher pressures, the monoclinic HfO$_2$ transforms into an OI orthorhombic phase (o-HfO$_2$) (space group Pnma). Further increase of pressure leads to a transformation of HfO$_2$ into an OII orthorhombic phase (space group Pnma, structural form of cotunnite) [18]. Under atmospheric pressure and high temperatures ($T \gtrsim 1700$ °C), the monoclinic HfO$_2$ transforms in a tetragonal HfO$_2$ phase (t-HfO$_2$) (space group P4$_2$/mnc). Further heating (up to 2600 °C) leads to a transformation of HfO$_2$ into cubic c-HfO$_2$ (structural form of fluorite, Fm3m). It is not possible to obtain the pure t-HfO$_2$ and c-HfO$_2$ phases at room temperature (under standard conditions) even though with ultra-fast quenching. However, the formation of the cubic modification c-HfO$_2$ was observed in several reported studies of thin HfO$_2$ films (as well as ZrO$_2$ films of thickness 10–50 nm) at temperatures 200 °C [19,20]. Formation of a tetragonal phase with properties differing from those of the high-temperature bulk structure was observed in 10–50 nm thick films at temperatures of 300–600 °C. Formation of the stable monoclinic phase was observed in films of thickness $d > 50$ nm.

The crystalline phases of hafnium oxide have a higher dielectric permittivity compared to the amorphous phase. By means of quantum-chemical simulation, it was shown that the tetragonal phase t-HfO$_2$ has the highest dielectric permittivity ($\kappa_{\text{t-HfO}_2} \approx 70$) and it exhibits the highest anisotropy. Monoclinic m-HfO$_2$ has the lowest dielectric permittivity and relatively weak anisotropy ($\kappa \approx 17$). The permittivity of cubic c-HfO$_2$ is $\kappa = 27$ [21].

In spite of numerous theoretical investigations of the electronic structure of defect-free crystalline HfO$_2$ modifications, the effective mass of charge carriers was calculated from ab initio principles only in Refs. [22,23]. This mass in crystalline HfO$_2$ is anisotropic, and it differs from the mass in the crystalline modifications. The cubic phase c-HfO$_2$ has the lowest theoretically predicted effective mass of charge carriers equal to $0.6m_0$ ($m_0$ is the free electron mass), whereas the effective mass of charge carriers in the monoclinic phase, which is structurally closest to the amorphous phase, is $1.1m_0$. The tunnelling effective masses of charge carriers in amorphous HfO$_2$ as obtained from transport measurements are significantly lower than the predicted values: 0.1$m_0$ [24], 0.17$m_0$ [25], 0.18$m_0$ [26], 0.22$m_0$ [27], (0.15–0.23)$m_0$ [28], 0.4$m_0$ [29].

Real HfO$_2$ films normally contain many defects. These defects largely define the electronic properties of hafnia, including its optical and charge transport properties. The defects act as electron and hole traps, and they play a dual role in silicon devices. In cases in which HfO$_2$ is used as the gate dielectric layer in MOS transistors or as blocking elements in flash memory cells, the electrons (or holes) injected into the oxide layer get captured on traps in HfO$_2$, and the conductivity via traps plays a negative role: an electric charge accumulates in the dielectric layer, the leakage current shows an increase, the threshold voltage exhibits instability, and the electron devices suffer substantial degradation with reduced functioning reliability.

At the same time, using hafnia as a storage medium in flash memory cells requires location of electrons and/or holes at traps to store information. In the latter case, the dielectric layer should have a high density of traps ($\gtrsim 10^{19}$ cm$^{-3}$) in order to ensure a large memory window, or difference between the signals corresponding to logical “0” and “1”. Also, the traps in the storage medium of flash memory cells should have a sufficiently high ionization energy ($\gtrsim 1$ eV) to provide for desired retention characteristics of the material intended for fabrication of non-volatile memory device elements (the standard requirements here are $\geq 10$ years at 85 °C).

In recent years, a new generation of flash memory devices, Resistive Random Access Memory (ReRAM), has been developed. ReRAM devices are based on the switching back and forth from a High-Resistance State (HRS) of the insulating medium to a Low Resistance State (LRS) when a current flows through, or a voltage pulse is applied across, a metal–insulator–metal structure. Various high-κ dielectrics can be used as the functional medium in ReRAM cells: TiO$_2$ [30], HfO$_2$ [31], ZrO$_2$ [32], Ta$_2$O$_5$ [33], SiO$_2$ [34], GeO$_2$ [35]. HfO$_2$-based ReRAM devices offer much promise in commercial applications. The switching mechanism of ReRAM from HRS to LRS and vice versa is the subject of extensive current research. However, many details of this phenomenon still remain poorly understood. A most attractive hypothesis to explain the switching phenomenon in ReRAM devices (and, in particular, in HfO$_2$-based ReRAM devices) implies generation and recombination of oxygen vacancies in the material [36].
Recently, the orthorhombic crystalline phase of high-$\kappa$ HfO$_2$ thin films was reported to exhibit ferroelectric properties, thus offering a promising material for application in another new generation of flash memory devices, Ferroelectric Random Access Memory (FeRAM) [13–15]. Despite the fact that FeRAM devices have many advantages over other types of FeRAM devices, their retention characteristics, presenting the key properties of non-volatile memory devices, seriously suffer from the depolarization effect. Possible cause for the depolarization effect is the charge leakage via defects in the crystal lattice of the ferroelectric that act as traps for electrons and holes.

Presently, it is widely recognized that the most thermodynamically favourable defects in hafnium oxide are oxygen vacancies (VO) [1,4,5,36]. That is why, for determining the characteristics of traps in hafnium oxide (such as the density of traps, the localization energy of charge carriers at traps, and the capture cross-section), understanding of the atomic and electronic structure of oxygen vacancies is necessary. The electronic structure of oxygen vacancies in HfO$_2$ was extensively studied using theoretical quantum-chemical simulations [37–44], photoelectron spectroscopy [44], optical absorption [45], luminescence [46–52], and electron and hole transport experiments [24,53–55].

In the present publication, we give a review of modern data on the electronic structure of oxygen vacancies in hafnium oxide, the key high-$\kappa$ dielectric for modern silicon devices.

2. Electronic structure of oxygen vacancy in hafnium oxide

The oxygen vacancy in hafnium oxide can be obtained by two methods. The first method is the synthesis of non-stoichiometric oxygen-lean (or metal-rich) HfO$_x$ ($x < 2$) [51]. The second method employs the irradiation of stoichiometric HfO$_2$ with inert-gas ions. In HfO$_2$, each Hf atom is coordinated with eight O atoms, and each O atom is coordinated with three or four Hf atoms. An oxygen vacancy in HfO$_2$ can be formed by breaking four Hf–O bonds, whereas eight such bonds should be broken for forming a Hf vacancy. It is clear that the formation of oxygen vacancies in ion-irradiated HfO$_2$ samples is more energetically favourable a process in comparison with hafnium vacancies. Traditionally, for the introduction of oxygen vacancies into hafnium oxide, irradiation of samples with Ar$^+$ ions with energy in the range 1–5 keV is used [44,56].

The subject of this section is the electronic structure of the oxygen vacancy in hafnia. The first subsection (Section 2.1) summarizes the most recent results on study of hafnium oxide using XPS techniques after bombarding by Ar$^+$ ions. The following subsection (Section 2.2) presents the results of ab initio quantum-chemical simulations of VO in HfO$_2$.

2.1. Results of X-ray photoelectrons spectroscopy

Experimental X-ray photoelectron spectra (XPS) of the Hf4f$_{7/2}$−Hf4f$_{5/2}$ atomic level and the valence band of stoichiometric HfO$_2$ or non-stoichiometric hafnium oxide (HfO$_x$) [57] are shown in Fig. 1. Violation of stoichiometry causes the formation of a low-energy shoulder at the Hf4f$_{7/2}$−Hf4f$_{5/2}$ doublet due to metallic hafnium. A similar shoulder is also observed in the XPS spectra of hafnium oxide whose stoichiometry was violated using argon ion irradiation [44]. This shoulder can be identified as one arising due to hafnium in metallic state and due to hafnium sub-oxides HfO$_{x-2}$. Thus, presence of oxygen vacancies in non-stoichiometric hafnium oxide films can be assumed.

XPS spectra of the Hf4f$_{7/2}$−Hf4f$_{5/2}$ atomic level in HfO$_2$ films obtained by atomic layer deposition (ALD) and irradiated with different fluencies of Ar$^+$ ions are shown in Fig. 2 [58]. Irradiation with argon is accompanied with a reduction of the amplitude of the peaks due to hafnium oxide and with the emergence of additional peaks due to metallic hafnium. Such a behaviour is indicative of the formation of non-stoichiometric HfO$_x$ in which the density of VO increases with increasing the irradiation time, or irradiation dose.

Independent evidence for the presence of oxygen vacancies in HfO$_x$ can be obtained via a comparison of experimental XPS spectra of the valence band of HfO$_2$ with the spectra obtained in ab initio calculations of monoclinic hafnium oxide (Fig. 1(b)). The calculated data rather adequately represent experimental spectra if one takes into account the fact that, here, it is XPS spectra of HfO$_2$ in amorphous and crystalline phases that are compared. The main discrepancy consists in that the experimental XPS spectrum of the valence band of hafnia involves two symmetric peaks [44], whereas the theoretical XPS spectrum exhibits two asymmetric peaks. Fig. 1(b) shows that the violation of stoichiometry in hafnium oxide films leads to the appearance of electronic states at energy 3 eV over the valence-band ceiling energy $E_v$. A similar result has also been demonstrated by the theoretical spectra of cubic HfO$_2$ with hosted neutral VO [51].

2.2. Quantum-chemical simulations

The electronic structure of oxygen vacancies was extensively studied theoretically. Oxygen vacancies were predominantly examined in the monoclinic modification of HfO$_2$ [37–44]. Foster et al. [37] have for the first time performed an ab initio simulation of VO in HfO$_2$ within the classical density functional theory (DFT) with a basic wave-function set chosen in the form of plane waves. Some approximations were used for the pseudopotentials that defined the electronic structure of oxygen vacancies and other intrinsic defects. Neutral, and singly and doubly charged positive, oxygen vacancies in three-fold and four-fold coordination were calculated. The neighbour Hf atoms were found to experience insignificant spatial displacements ((0.5%–1%) of the bond length) towards the neutral oxygen vacancy, this result being indicative of complete
screening of the vacancy by the two remaining electrons. Positively charged vacancies were found to feature even stronger a relaxation. The energy required for the formation of a neutral oxygen vacancy was estimated as follows:

$$E_{\text{form}} = E_{V\Omega} - \left( E_i - \frac{1}{2} E_{\Omega_2} \right),$$  \hspace{1cm} (1)$$

where $E_{V\Omega}$ is the total energy of the relaxed supercell with the hosted neutral defect, $E_i$ is the total energy of the defect-free supercell, and $E_{\Omega_2}$ is the total energy of an isolated oxygen molecule. The formation of a four-fold coordinated vacancy (9.34 eV) requires a somewhat lower energy in comparison with the three-fold coordinated vacancy (9.36 eV).

Foster et al. [37] have found that the neutral oxygen vacancy introduces an energy level, filled with two electrons, into the band gap of HfO$_2$. They have also proposed a method for evaluating the energy position of the oxygen-vacancy levels with respect to the valence-band ceiling of HfO$_2$ as the gain in energy $\chi_h$ that occurs when a hole from the valence band ceiling
gets captured by the vacancy. In a similar way, the energy position of oxygen–vacancy levels with respect to the bottom of the conduction band of HfO$_2$ was evaluated as the gain in energy $\chi_e$ achieved when an electron at the conduction-band bottom undergoes a capture at an oxygen vacancy. The energies $\chi_e$ and $\chi_h$ for oxygen vacancies with a charge $q$ were evaluated as follows:

$$\chi_e(V^q) = E^- + E_{\chi}^q - E^0 - E_{\chi}^{q-1} + k_2,$$

$$\chi_h(V^q) = E^+ + E_{\chi}^q - E^0 - E_{\chi}^{q+1} + k_3. \quad (2)$$

In Eqs. (2) and (3), the quantities $E^0$, $E^-$, and $E^+$ are, respectively, the total energies of the defect-free neutral, and negatively and positively charged, supercells; the quantities $E_{\chi}^{q+1}$, $E_{\chi}^q$, and $E_{\chi}^{q-1}$ are the total energies of the supercells with the variously charged vacancies, and $k_2$ and $k_3$ are the additives to the energy position of the oxygen-vacancy-induced state with respect to the conduction-band edge which must be introduced because of the much underestimated band gap energy of hafnium oxide.

The obtained positive values of $\chi_e$ and $\chi_h$ show the trapping of an electron or a hole at an oxygen vacancy to be an energy favourable process. The position of the trap levels in the band gap of m-HfO$_2$ with respect to the conduction-band bottom of silicon proves that positively charged oxygen vacancies can readily capture electrons. Nonetheless, the results obtained in Ref. [37] are just qualitative results.

In [38], the energy position of the defect states due to oxygen vacancies was evaluated for c-HfO$_2$ using DFT approaches capable of yielding a band-gap-energy value close to the experimentally evaluated band gap width of c-HfO$_2$. Both positively and negatively charged oxygen vacancies were calculated. It was shown that an oxygen vacancy could capture one or two electrons, and it introduced respectively singly or doubly filled levels into the forbidden band of c-HfO$_2$ (Fig. 3(a)).

Fig. 3(a) shows that the oxygen vacancy levels occupied by electrons lie above the valence-band ceiling of silicon, so that the transition of an electron from an oxygen vacancy in c-HfO$_2$ into silicon (for instance, at an acceptor state) presents an energetically favourable process. According to the results of Ref. [38], the conductivity of HfO$_2$ is the electron one due to the electron transport via traps. The energy level due to the traps is about 1–1.5 eV below the conduction-band bottom.

Although the energy positions of the trap levels obtained in Refs. [39] and [41] are close to each other, the differences, most likely resulting from the use of different theoretical models are noteworthy. It was found that the spin–singlet state of the doubly charged oxygen vacancy is energetically more preferable (by 0.2 eV) than the spin–triplet state. A change of the VO charge state leads to a substantial, almost symmetrical displacement of neighbour Hf atoms: by 11% and 8% from vacancy respectively for V$^{+2}$ and V$^{+1}$, and by 8% and 4% towards vacancy respectively for V$^{-2}$ and for V$^{-1}$. The displacements of the nearest oxygen atoms are much smaller [39]. The calculations of VO forming energy have showed that a positively charged VO is more stable when a triply coordinated oxygen vacancy, whereas a negatively charged oxygen vacancy is more stable when a four-fold coordinated oxygen vacancy [41]. A doubly negative charged oxygen vacancy is thermodynamically unstable. The obtained result is consistent with the data obtained in [42].

Gavartin et al. [41] have reported an estimate of the optical ionization energy of oxygen vacancy which was obtained as follows:

$$W_{\text{opt}}(V^0) = E_{\chi}^{q+1} + E^+ - E_{\chi}^0 - E^0. \quad (4)$$

In Eq. (4), the meaning of involved terms is the same as in Eqs. (2) and (3), except for the quantity $E_{\chi}^{q+1}$ now being the energy of the supercell with an oxygen vacancy in the charge state $q + 1$ calculated on the assumption of equilibrium geometry for the supercell with charge $q$.

Besides, the values of the thermal ionization energy of oxygen vacancy were calculated:

$$W_t = W_{\text{opt}} - (E_V - E_{\chi}^{\text{relax}}), \quad (5)$$

where $E_V$ and $E_{\chi}^{\text{relax}}$ are the total energies of non-relaxed and relaxed supercells with oxygen vacancies in identical charge states. The calculated values are given in Table 1.

The values of $W_{\text{opt}}$ proved to be close to the energy position of the levels due to the single-electron states shown in Fig. 3(b) and (c). However, as it will be shown in the next sections, the energies $W_{\text{opt}}$ for V$^-$ are twice smaller than the values of 2.5 eV obtained in the experiment. The energy positions of the levels due to the neutral and positively charge oxygen vacancies,

<table>
<thead>
<tr>
<th>$q$</th>
<th>$W_{\text{opt}}$ (eV)</th>
<th>$E_{\chi}^{\text{relax}}$ (eV)</th>
<th>$W_t$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>3.33</td>
<td>1.01</td>
<td>2.32</td>
</tr>
<tr>
<td>0</td>
<td>3.13</td>
<td>0.80</td>
<td>2.33</td>
</tr>
<tr>
<td>-1</td>
<td>1.24</td>
<td>0.48</td>
<td>0.76</td>
</tr>
<tr>
<td>-2</td>
<td>0.99</td>
<td>0.43</td>
<td>0.56</td>
</tr>
</tbody>
</table>
which proved to lie deep in the band gap of HfO$_2$, point to the fact that the vacancies cannot play part of shallow traps for electrons. The results of Gavartin et al. [41] and the agreement of those results with experimental data are consistent with the common assumption that it is oxygen vacancies that are defects most likely acting as traps in HfO$_2$. Accordingly, negatively charged oxygen vacancies are defects causing threshold-voltage instability in HfO$_2$-based MOS transistors.

Muñoz Ramo et al. [43] gave an analysis of previously reported data on the electronic structure of oxygen vacancies in m-HfO$_2$, and they performed calculations of optical transitions using the Time-Dependent Density Functional Theory (TDDFT). Among the five charge states of oxygen vacancy, the thermodynamically stable ones were identified to be the states due to the neutral and doubly charged positive (fully ionized) oxygen vacancies (depending on the density of electrons in the system). Nonetheless, under non-equilibrium conditions other charge states of oxygen vacancies may also play a substantial role.

Finally, Perevalov et al. [44] performed an ab initio numerical simulation of oxygen poly-vacancies in hafnium oxide. According to calculated data, each subsequent removal of one oxygen atom from the material leads to the appearance of an additional energy level occupied by an electron in the band gap of hafnium oxide. The induced defect states are distributed rather non-uniformly over the gap of HfO$_2$. With the growth of poly-vacancy size (or the number of removed oxygen atoms) in the band gap of hafnia, the defect-induced peak grows in amplitude, with the energy position of this peak being roughly identical to that of the peak due to oxygen monovacancy. From here, a conclusion can be drawn that the oxygen monovacancy features an electron density distribution typical of oxygen poly-vacancies HfO$_2$.

3. Luminescence of the oxygen vacancy in hafnium oxide

Identification and control of the density of oxygen vacancies in HfO$_2$ is a problem of much significance for optimization of various technological processes. A highly efficient non-destructive technique for studying defects in dielectrics is luminescence. In HfO$_2$, a 2.7 eV blue luminescence band is normally observed [46–52]. Until recently, the atomic structure of the defects responsible for the 2.7 eV luminescence remained unclear. Kaichev et al. [48] put forward a hypothesis that the 2.7 eV blue luminescence band observed in HfO$_2$ was due to oxygen vacancies. Quantum-chemical calculations of the radiative transitions between the oxygen-vacancy-induced states in HfO$_2$ can prove or discard this hypothesis. Yet, ab initio calculations of luminescence transitions present extremely difficult a problem. Simultaneously, it was found that the excitation energy for luminescence in several dielectrics coincides with the absorption energy of the materials [59–61]. The excitation energy of the blue luminescence in HfO$_2$ was estimated to roughly equal 5.2 eV [46]. Yet, the experimental absorption spectra for HfO$_2$ yield a large scatter of values for the spectral position of the absorption peak, from 3.5 to 5.2 eV [45,62]. The origin of the absorption band is most likely due to oxygen vacancies. The state-of-the-art theoretical methods and computing means permit calculation of optical absorption spectra in solids from the first principles.

The cathodoluminescence spectrum of a HfO$_{1.9}$ film shown in Fig. 4 exhibits a feature peaking at energy 2.65 eV. The photoluminescence spectrum of HfO$_3$ shown in the same figure (this spectrum was borrowed from Ref. [46]) involves an additional peak at 2.7 eV. A photoluminescence excitation spectrum for photoluminescence spectra monitored at 2.7 eV is shown in Fig. 4. A maximum intensity of the 2.7 eV luminescence band was observed under excitation with 5.2 eV quanta. In amorphous and polycrystalline HfO$_2$, an absorption band peaking at an energy of 5.2 eV was observed (see Fig. 5) [63].

The spectral position of the maximum of the latter band fairly well agrees with the spectral position of the optical-absorption maximum (at energy 5.3 eV) in the cubic modification of hafnium oxide with oxygen vacancies as obtained in ab initio calculations. Thus, since a most intense 2.7 eV photoluminescence band in hafnium oxide was observed under the same excitation that induced a most intense optical absorption due to oxygen vacancies, it can be concluded that both the
Fig. 4. (1) Photoluminescence spectrum (taken from Ref. [46]) and (2) photoluminescence excitation spectrum for photoluminescence spectra monitored at 2.7 eV for HfO$_{x}$. (3) Cathodoluminescence spectrum for HfO$_{1.9}$ films and (4) calculated optical absorption spectrum of c-HfO$_{2}$ with oxygen vacancy. Source: Adapted with permission from Ref. [51]. © 2014, American Institute of Physics.

2.7 eV blue luminescence band and the 5.2 eV excitation band were due to oxygen vacancies. Note that the calculations also predict the emergence of a broad absorption band at 4.7 eV. Earlier, absorption in the latter spectral region in HfO$_{x}$ was theoretically predicted in [39] and experimentally observed in [45].

Interestingly, in SiO$_{2}$ [64–67] the observed 2.7 eV luminescence band with half width at half maximum (HWHM) 0.34 eV was interpreted as one due to oxygen vacancies. In SiO$_{2}$, the blue band was observed in samples excited with energies 5.0 eV and 7.6 eV [61,64]. According to our data, the luminescence band due to oxygen vacancies in HfO$_{2}$ peaks at the same energy 2.7 eV, yet it exhibits a much greater HWHM value (see Fig. 5). The excitation energy of the oxygen vacancy in HfO$_{2}$, 5.2 eV, is close to that of the oxygen vacancy in SiO$_{2}$, which is equal to 5.0 eV.

A configuration diagram of the neutral oxygen vacancy in HfO$_{2}$ is shown in Fig. 6(a). The lower term refers to the filled ground state, and the upper term, to the empty excited state. The vertical transition with energy 5.2 eV refers to an optical excitation of the electron from the equilibrium filled ground state into the empty excited state. The relaxation from the excited state into the ground state corresponds to a transition with energy 2.7 eV. Further is will be shown that the charge transport in HfO$_{2}$ proceeds via tunnel hops of charge carriers over traps [7,8,53,68]. A quantum-chemical simulation study shows that the traps in HfO$_{2}$ are oxygen vacancies [39]. The trap thermal energy $W_{t}$ of oxygen vacancy in HfO$_{2}$ is equal to half the Stokes luminescence shift.
4. Charge transport in hafnium oxide

This section is dedicated to experiments on the charge transport through HfO$_2$. The first subsection (Section 4.1) introduces the most recent results on study of charge transport mechanisms in hafnium oxide. The following subsections (Sections 4.2 and 4.3) present results on study of electron and hole interactions with traps and each other; their contributions into charge transport processes in HfO$_2$ are represented. We will discuss a role of oxygen vacancy in the charge transport also.

4.1. Charge transport mechanisms in HfO$_2$

A key problem in the physics of dielectric materials is the identification of the operating charge transport mechanism, which underlies the electrical conduction in a particular material. In many applications, a critical property of a dielectric material is a low density of leakage currents through the material in strong electric fields [69]. In case of low density of traps, an isolated trap gets ionized due to the emission of trapped electron into the conduction band. Two ionization mechanisms for isolated traps are presently known, one mechanism being the Frenkel effect $\lg J$-$\sqrt{F}$ [70], and the other mechanism, multi-phonon trap ionization [71–76] (here and below, $J$ is the current density and $F$ is the electric field in the dielectric). The Frenkel effect is observed when the energy barrier for the emission of charge carriers from charged traps shows a reduction in the electric field. In the pioneering work by Frenkel, thermal ionization of traps in an electric field was only considered [70]. In [76,77], thermally enhanced tunnelling ionization of Coulomb traps was analysed.

If the density of traps is high, the overlap of the Coulomb potentials due to neighbour traps and a transition from Frenkel to Poole law $\lg J$-$\sqrt{F}$ will be observed [76,78]. Of the multi-phonon ionization of closely spaced traps (phonon-assisted tunnelling between traps), the Poole law is also characteristic [79,80]. Below, we describe experiments that were performed to study the charge transport mechanism in amorphous HfO$_2$ films and to compare the experimental data with various trap ionization models.

The mechanism that underlies the charge transport in hafnium oxide was examined quite extensively. However, in their reported studies most authors interpreted their data within the framework of the Frenkel model. The authors of [81] gave an analysis of the current–voltage characteristics of a n-Si/HfO$_2$/Ni structure at positive potentials applied to the metal contact on the assumption of various models of charge transport in HfO$_2$. The synthesis process of the HfO$_2$ films was described in [81]. The measured current–voltage characteristics of a n-Si/HfO$_2$/Ni structure are shown in Fig. 7 (symbols). Evidently, the electric current increases exponentially with growth of voltage and/or temperature. The current injected out of the electrode into the dielectric can be the Schottky thermionic current [82]:

$$J = A T^2 \exp \left( - \frac{\Phi_0 - \beta_{Sh} \sqrt{F}}{kT} \right).$$

(7)

In Eq. (7), $A = \frac{4\pi m^* e^2}{h^2} = 120 \text{m}^2 \text{K}^{-2}$ is the Richardson–Dushman constant, $T$ is temperature, $\Phi_0$ is the height of the triangular potential barrier for electrons at the semiconductor–dielectric interface (2.0 eV [2]), $\beta_{Sh} = \sqrt{\frac{e^3}{4\pi \varepsilon_0 \varepsilon}}$ is the Schottky constant, $k$ is the Boltzmann constant, $m^*$ is the effective tunnelling mass, $e$ is the elementary (electron) charge, $h$ is the Planck constant, $\varepsilon$ is the high-frequency dielectric permittivity of hafnium oxide, and $\varepsilon_0$ is the electrical constant. For a uniform electric field, we have $F = U/d$, where $U$ is the voltage applied between the contacts and $d$ is the dielectric-film thickness. The best agreement between the experimental data and the current–voltage curves as predicted by the Schottky
model is achieved on the assumption of $\varepsilon = 2.5$, the latter value being notably smaller than the high-frequency dielectric permeability of hafnium oxide, $\varepsilon_{\text{HfO}_2} = 4.4$.

The tunnelling emission that proceeds by the Fowler–Nordheim mechanism [83]

$$ J = A F^2 \exp \left( -B \sqrt{m^* \Phi_0} \frac{3/2}{F} \right), $$

$$ A = \frac{e^3}{8\pi \hbar \Phi_0}, \quad B = \frac{8\pi \sqrt{2}}{3 \hbar e}, $$

weakly depends on temperature, and it therefore fails to offer an adequate description to the experimental data.

An analysis of the experimental data within the Frenkel model [70]

$$ J = e N^{2/3} P, $$
$$ P = \gamma \exp \left( -\frac{W - \beta_F \sqrt{F}}{kT} \right), $$

shows the Frenkel law to be capable of providing a qualitatively adequate description to the experimental data. Hereinafter, $N$ is the trap density, $P$ is the rate of trap ionization per second, $\gamma$ is the frequency factor, $W$ the trap ionization energy, and $\beta_F = \sqrt{e^3/\pi \varepsilon_0 \varepsilon} / e$ is the Frenkel constant. Fitting the experimental data with the theoretical dependences plotted in Frenkel plate in $J$-vs-$\sqrt{U}$, the authors of [81] were able to obtain a satisfactory agreement between the experimental and theoretically predicted data; such an agreement, however, could only be achieved on the assumption of $\varepsilon = 10$, the latter value being much in excess of the high-frequency dielectric permeability of HfO$_2$. The obtained trap-energy value proved to be $W = 0.3$ eV. On the assumption of $\gamma = W/h \sim 10^{14}$ s$^{-1}$, the trap density proves to be extremely low, equal to $N \sim 4$ cm$^{-3}$. For such a trap density, the mean distance between traps is $s = N^{-1/3} \sim 6$ mm. Thus, in a sample provided with 140 $\mu$m diameter contacts we have just one trap per 2600 contacts. The latter value being unrealistic, one can conclude that the Frenkel model fails to provide an adequate quantitative description to the data obtained while investigating charge transport in hafnium oxide in spite of the achieved qualitative agreement between the measured and calculated current–voltage characteristics.

Like the Frenkel model, the model of overlapped Coulomb centres, or the Hill model, [78]

$$ J = e N^{2/3} P, $$
$$ P = \gamma \exp \left( -\frac{W - e^2 / \varepsilon_0 \varepsilon s}{kT} \right) \sinh \left( \frac{eF s}{2kT} \right), $$

offers a qualitatively adequate description to the experimental data. Fitting the measured current–voltage characteristics with calculated data yields the following values for involved parameters: $N = 2.5 \times 10^{20}$ cm$^{-3}$, $W = 0.9$ eV, $\varepsilon = 4$, $\varepsilon_0 \varepsilon = 4$, $e = 1.6 \times 10^{-19}$ C, $\Phi_0 = 10^{-3}$ V, $m^* = 0.1 m_0$ (where $m_0$ is the electronic mass).

**Fig. 7.** Current–voltage characteristics of $n$-Si/HfO$_2$(20 nm)/Ni structure with the negative voltage applied to the Ni gate at different temperatures. Characters show experimental data, lines represent simulations by phonon-assisted tunnelling between traps (12). Source: Reprinted with permission from Ref. [81]. © 2014, American Institute of Physics.
\( \gamma = 2 \times 10^4 \text{s}^{-1} \). Evidently, the latter model also fails to provide an adequate description to the charge transport in hafnium oxide because of the too small value of the frequency factor \( \gamma \ll W / h \).

The multi-phonon ionization model for a neutral trap [71] assumes that delocalized charged carriers can be captured by neutral defects in the dielectric. In this model, the conduction is controlled by the rate of the phonon-assisted ionization of traps. Since the typical phonon energies \( W_{\text{ph}} \) are generally much smaller than the trap ionization energies, an electron or hole can escape from a trap by interacting with a large number of phonons. In the latter case, the dependence of the electric current on the field and temperature is the following:

\[
J = eN^{2/3}P,
\]

\[
P = \sum_{l=1}^{\infty} \exp \left( \frac{W_{\text{ph}}}{2kT} - Z \coth \frac{W_{\text{ph}}}{2kT} \right) I_l \left( \frac{Z}{\sinh(W_{\text{ph}}/2kT)} \right) P_l(W_t + IW_{\text{ph}}),
\]

\[
P_l(W) = \frac{eF}{2\sqrt{2m^*W}} \exp \left( -\frac{3\sqrt{2m^*W}}{4} W^{3/2} \right), \quad Z = \frac{W_{\text{opt}} - W_t}{W_{\text{ph}}},
\]

where \( l \) is the total number of the phonons having interacted with the charge carrier, \( I_l \) are the modified Bessel functions, and \( P_l(W) \) is the rate of the tunnelling penetration across a triangular potential barrier of height \( W \). Like the previous models, the model of (11) provides a qualitatively adequate description to measured current–voltage characteristics. It is worth noting that an analysis of the equations of (11) shows that the highest trap ionization probability corresponds to the total number of the phonons absorbed by the charge carrier which ranges from \( \sim 10 \) to \( \sim 30 \) depending on the particular proportion between the energies \( W_{\text{ph}} \) and \( W_t \).

The best coincidence between the calculated and measured current–voltage characteristics was achieved with the following values of involved parameters: \( N = 2 \times 10^{20} \text{ cm}^{-3}, W_t = 0.5 \text{ eV}, W_{\text{opt}} = 1.0 \text{ eV}, W_{\text{ph}} = 40 \text{ meV}, m^* = 0.2m_0 \). Here, like in the model of overlapped Coulomb centres, the trap density also proves to be too low (that is, the mean separation between traps \( s \approx 20 \mu \text{m} \) turns out to be three orders of magnitude larger than the thickness of the examined films).

On decreasing the distance between traps, the tunnelling probability between the traps increases in value. With the involvement of phonons in the process taken into account, the charge transport in dielectrics can be treated using the model of phonon-assisted tunnelling of charge carriers between traps [79,80]:

\[
J = eN^{2/3}P,
\]

\[
P = \frac{\sqrt{2\pi hW_t}}{m^*W_{\text{opt}} - W_t} \exp \left( -\frac{W_{\text{opt}} - W_t}{2kT} \right) \exp \left( -\frac{2\sqrt{2m^*W_t}}{h} \right) \sinh \left( \frac{eF}{2kT} \right), \quad \text{where} \quad h = h/2\pi.
\]

The current–voltage characteristics of hafnium oxide simulated by the model of the photon-assisted tunnelling between traps are shown in Fig. 7 with various dashed lines. Evidently, like all the previous models of charge transport in dielectrics, the latter model well represents the qualitative regularities demonstrated by the experimental data. The best coincidence between the calculated and experimental dependences was obtained with the following values of involved parameters: \( N = 2.5 \times 10^{25} \text{ cm}^{-3}, W_t = 1.25 \text{ eV}, W_{\text{opt}} = 2.5 \text{ eV}, m^* = 0.8m_0 \). The obtained value of the thermal ionization energy, 1.25 eV, is close to the previously obtained values of the trap energy in HfO\(_2\), 1.2 eV [45] and 1.36 eV [53], and it coincides with half the Stokes shift of the blue luminescence (6) (Fig. 6(a)).

The optical ionization energy of the trap, \( W_{\text{opt}} = 2.5 \text{ eV} \), is close to the calculated value, \( W_{\text{opt}} = 2.35 \text{ eV} \), for the negatively charged oxygen vacancy in hafnium oxide [43]. It should be noted here that, with the obtained trap-energy values, the relation \( W_{\text{opt}} = 2W_t \) holds. The configuration diagram of a negatively charged trap in HfO\(_2\) is shown in Fig. 6(b). The lower term corresponds to the state of the trap filled with an electron, and the upper term is due to an excited empty state. The vertical transition with energy 2.5 eV refers to the optical excitation of the trap, and the transition with energy 1.25 eV refers to the thermal trap ionization energy \( W_t \).

The above-mentioned experiments were carried out on amorphous HfO\(_2\) films. Very often, high-\( \kappa \) dielectrics are obtained as polycrystalline materials. In this connection, there arises a question about possible realization of excessive leakage currents along grain boundaries in polycrystalline films in comparison with amorphous films. Kim et al. [84] examined the current–voltage characteristics of amorphous HfO\(_2\) films in comparison with those of polycrystalline films having monoclinic or tetragonal structure (Fig. 8). The transition from amorphous to polycrystalline state was achieved after annealing of HfO\(_2\) films in nitrogen atmosphere at temperatures 500–900 \(^\circ\text{C}\). It was found that the annealing at temperatures 500 and 600 \(^\circ\text{C}\) resulted in a transition of the film from amorphous to polycrystalline state. This transition, however, was not accompanied with an increase of the electrical conductivity of HfO\(_2\). Thus, the presence of grain boundaries due to polycrystallites does not lead to an enhanced conductivity of the dielectric in comparison with the amorphous state. Annealing at temperatures 700, 800, and 900 \(^\circ\text{C}\) resulted in a conductivity value that decreased in comparison with the conductivity of the initial amorphous film.

The phonon-assisted tunnelling between traps provides a quantitatively adequate description to the exponentially large scatter of conductivity values in hafnium oxide films synthesized under various conditions. Fig. 9 shows the current–voltage characteristics of hafnium oxide films obtained through oxidation of thin metal hafnium layers at various temperatures [45]. A decrease in oxidation temperature results in an increase of the electric current at fixed voltage \( -1 \text{ V} \) by six orders. The
Fig. 8. Current–voltage characteristics of HfO$_2$ films after annealing at different conditions. Source: Reprinted with permissions from Ref. [84]. © 2003, American Institute of Physics.

Fig. 9. Experimental current–voltage characteristics (symbols) and results of simulations by phonon-assisted tunnelling between traps (12) (lines) in hafnia films, produced by metal hafnium films oxidation at different temperatures: 1–500 °C, 2–600 °C, 3–600 °C. Source: Adapted with permission from Ref. [45]. © 2004, American Institute of Physics.

Current–voltage characteristics shown in Fig. 9 can be well fitted with the curves predicted by the phonon-assisted tunnelling model with the following adopted values of model parameters: thermal trap energy $W_t = 1.25$ eV, optical trap energy $2.5$ eV, effective-mass value $m^* = 0.2m_0$. In the phonon-assisted tunnelling model, in samples with a high density of traps the increase in the electric current is explained by the tunnelling rate between neighbour traps being enhanced due to a smaller distance between the traps. In the films obtained at temperature 700 °C, the trap density was $N = 2.5 \times 10^{19}$ cm$^{-3}$. In the films obtained at lower temperatures, namely at 600 and 500 °C, the trap density amounted to $N = 6 \times 10^{20}$ cm$^{-3}$ and $N = 1.1 \times 10^{21}$ cm$^{-3}$, respectively.

The difference between the effective-mass values obtained for different sets of HfO$_2$ films can be attributed to the presence of space charges due to trapped electrons and holes in the bulk of the dielectric material. The presence of an electric charge leads to local fluctuations of the field around its mean value. To allow for the presence of the space charge, one has to solve the Poisson equation and the Shockley–Reed–Hall equations for filled electron and hole traps, equations which allow for the recombination of free electrons with localized holes, and free holes with localized electrons [76].

The spectral dependence of the absorption coefficient $\alpha$ in hafnium oxide films obtained at various temperatures in the fundamental absorption edge region and at the energies of light quanta lower than the band gap energy is shown in Fig. 10 in $(ahv)^{1/2}$-vs-$h\nu$ plate [45] (here $h\nu$ is photon energy, n is the refraction coefficient). A decrease in synthesis temperature is accompanied by a shift of the fundamental absorption edge towards lower energies. At quantum energies smaller than the band gap energy, an optical absorption peak is observed (Fig. 10). The amplitude and width of the peak both decrease in
Fig. 10. Optical absorption spectra in hafnia films, produced by metal hafnium films oxidation at different temperatures. 
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Fig. 11. Optical absorption dependency on annealing time in oxygen at different annealing temperatures. Absorption coefficient at photon energy lesser than the band gap (see Fig. 10) is integrated as shown in the inset. 
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Thus, the charge transport experiments show that an increase in the film synthesis temperature leads to a reduced density of traps in hafnium oxide films. A similar behaviour was also observed for the optical absorption at quantum energies below the fundamental absorption edge (Fig. 10). These data indicate that the optical absorption in hafnium oxide in the subthreshold region is the absorption due to oxygen vacancies.

Fig. 12 shows a band diagram that illustrates the optical transitions from the top of the valence band of HfO$_2$ to the empty states due to oxygen vacancies [45]. The ionization energy of the filled energy levels due to oxygen vacancies is 1.2 eV, the latter value being close to the thermal trap ionization energy, $W_t = 1.25$ eV.

4.2. Electron and hole traps, Wigner crystallization of electrons in HfO$_2$

Fig. 13(a) shows a hysteresis observed in the capacitance–voltage ($C$–$V$) characteristics of an $n$-Si/HfO$_2$(20 nm)/Ni structure whose current–voltage characteristics were presented in Fig. 7 [81]. Application of the positive voltage $+5$ V to the metal shifts the $C$–$V$ characteristics towards positive potentials by $2.1$ V. Application of the negative voltage $-5$ V to the metal results in a $0.3$ V shift of the $C$–$V$ characteristics towards negative potentials. The shifts of the $C$–$V$ characteristics towards positive or negative potentials point to the accumulation of either positive or negative charges at electron or hole
traps, in a way that is the case in silicon nitride [86]. On an assumption that the electron traps in the dielectric were uniformly filled with electrons, the shift of the C–V characteristics towards positive potentials implies that the density of filled electron traps in the material was \( n_e^f = 5 \times 10^{18} \text{ cm}^{-3} \). The density of filled hole traps proved to be approximately 5 ÷ 7 times lower. The latter is due to the fact that, with the silicon substrate being in depletion, in the silicon there formed a Schottky space-charge region due to positively charged donors because of the injection of minority carriers (holes) into the dielectric; across the latter layer, an appreciable fraction of the total potential applied to the MOS structure dropped. This phenomenon will be discussed in detailed in the next section. Lu et al. [85] examined a hysteresis observed in the capacitance–voltage characteristics of MOS structures on p-type silicon substrates (Fig. 13(b)). In the latter case, at a positive potential applied to the metal, the silicon is in accumulation with majority charge carriers, and the voltage drop across the silicon substrate can be neglected. Under such conditions, accumulation of a positive charge in HfO₂ due to trapped holes was observed. The estimated density of filled hole traps proved to be \( n_p^f = 5 \times 10^{18} \text{ cm}^{-3} \). The effect of the voltage drop across the space-charge region in silicon was not observed under both signs of the metal potential providing that an MOS transistor is used. E.g., in flash memory elements with hafnium oxide used as the storage medium, the accumulated negative or positive charges had comparable values (Fig. 14) [87]. The latter result points to roughly identical concentrations of electron and hole traps in hafnium oxide, \( n_e^f = n_p^f = 5 \times 10^{18} \text{ cm}^{-3} \).

The cross-section for the capture of electrons by oxygen vacancies in HfO₂ was evaluated while analysing the accumulation kinetics of injected charge trapped in HfO₂ (Fig. 15) [88]. The capture cross-section proved to be \( \sigma_e = 3 \times 10^{-13} \text{ cm}^{-2} \). The cross-section for the capture of holes by oxygen vacancies as deduced from the experimental data proved to be \( \sigma_h = 1.5 \times 10^{-14} \text{ cm}^{-2} \) [85].

Engaging attention is the fact that the density of filled electron traps in the dielectric as determined from the accumulation of injected charges, \( n_e^f = 5 \times 10^{18} \text{ cm}^{-3} \), proved to be smaller than the total density of empty (neutral) electron traps,
N = 2.5 × 10^{20} \text{ cm}^{-3}, as determined from charge transport experiments performed on the same HfO$_2$ samples (see Fig. 7). Most likely, the point here is that, in the charge accumulation experiments, the density of filled traps, $n_t$, is measured, whereas the results of the charge transport experiments are defined by the total density of neutral (empty) traps, $N$. Of course, here we have $n_t \ll N$. The small amount of filled (charged) traps in HfO$_2$ can be explained by the Coulomb repulsion of trap-localized electrons (Fig. 16(a)), in a way also being the case for silicon nitride [89]. Fig. 16(b) illustrates a two-dimensional model for the Wigner crystallization of trap-localized electrons in HfO$_2$. The small circles denote empty traps, whereas the large circles refer to filled traps. The mean distance between traps, $s = N^{-1/3} \sim 1.5$ nm, is much smaller than the mean distance between filled traps, $n_t^{-1/3} \sim 6$ nm. In Refs. [90,91], numerical simulations were performed to examine the Wigner crystallization of trap-localized electrons. It was found that the two-dimensional Wigner glass crystallizes into a hexagonal lattice (see Fig. 16(b)). The lattice constant of the glass is equal to twice the Coulomb repulsion radius $R_q$ in the medium, defined as follows:

$$W_{\text{ph}} = \frac{1}{4\pi \kappa \varepsilon_0} \frac{e^2}{R_q^2}. \quad (13)$$

4.3. Bipolar conductivity in HfO$_2$

For gaining a better insight into the mechanism of charge transport in dielectric materials, the type/sign of mobile charge carriers should be identified. In semiconductors, the sign of mobile carriers can be determined by measuring Hall effect or thermoelectric power. In dielectrics, both methods cannot be used because of the negligibly low density of mobile carriers. In dielectrics, the sign of mobile carriers can be determined in experiments on the injection of minority carriers from n- and p-type silicon into dielectric in a MOS structure [92,93] or in experiments on the separation of electron and hole current components in an MOS field-effect transistor (MOSFET) [94].
Localized electrons are distributed in a hexagonal lattice structure.

The conductivity in dielectrics can be either monopolar (with particles of one type participating in charge transport) or bipolar (with electrons and holes both participating in charge transport). E.g., the conduction in an MOS structure with thermal SiO$_2$ [95] and, also, the conduction in Al$_2$O$_3$ [74] and Ta$_2$O$_5$ [96] is the monopolar conduction due to electrons. At the same time, the conduction in Si$_3$N$_4$ [93,94], ZrO$_2$ [97] and TiO$_2$ [98] is a bipolar process.

As for the sign of mobile charge carriers in HfO$_2$, the reported data are contradictory. In Refs. [24,53,99,100], the presence of electron traps in HfO$_2$ was assumed. While examining the conduction mechanism in HfO$_2$, Zhu et al. [24] and Jeong et al. [53] have found that the trap energy in the material ranged in the interval from 1.36 to 1.5 eV. An assumption that the trap energies evaluated from charge-transport data refer to electron traps requires an experimental substantiation. Below, we describe experiments on the determination of the sign of mobile carriers in HfO$_2$ by a technique based on the injection of minority carriers into HfO$_2$ films out of n- and p-type silicon substrate.

The current–voltage characteristics of a p-Si/HfO$_2$/Ni structure in accumulation and depletion modes are shown in Fig. 17(a) [54]. In accumulation, with the nickel contact being biased negatively, almost the entire voltage applied to the
structure drops across the dielectric layer, and the electric current increases exponentially with the growth of the electric field. At a positive potential applied to the nickel contact, i.e. in depletion, at low voltages the electric current exponentially increases in magnitude with bias voltage. At sufficiently large bias voltages, the electric current shows saturation. The saturation level increases in samples exposed to illumination. The saturation of the electric current and the increase of the saturated-current level in illuminated samples indicate that, in the depletion mode, minority carriers, that is, electrons, are injected out of silicon into hafnium oxide. Independent evidence for the injection of minorities is provided by the transition of capacitance from the inversion to non-equilibrium depletion mode (Fig. 17(b)).

A band diagram of a p-Si/HfO$_2$/Ni structure suggested by measured photoemission and photoconduction data [2] is shown in Fig. 18(a). The height of the potential barrier for electrons at the Si/HfO$_2$ interface is 2.0 eV, and that for holes is 2.5 eV. The band gap energy of HfO$_2$ is 5.6 eV. The height of the potential barrier for electrons at the HfO$_2$/Ni interface is 2.5 eV. At a positive bias voltage applied to the nickel contact, the electrons in the inversion layer are injected into silicon (current component $J_e$ in Fig. 18(b)). An incremental field due to the positive charge at the nickel contact is screened by the charge due to the negatively charged acceptors in the depletion layer rather than by the charge due to the electrons in the inversion layer. That is why the increment of the total bias voltage turns out to be screened due to the growth of the potential drop across the depletion layer rather than due to the growth of the potential drop across the dielectric. Illumination causes additional photogeneration of electron–hole pairs (the bent arrow in Fig. 18(b)). Under the action of the electric field, the holes move into the bulk of Si while the electrons (minority carriers) are injected into HfO$_2$, which process leads to an increase of the electric current that flows through the dielectric. Thus, at a positive potential applied to Ni, the conduction in
HfO$_2$ is (at least partially) due to the electrons injected out of the silicon substrate. If the conduction at a positive potential applied to the nickel contact were due to holes ($J^*_h$), then no non-equilibrium depletion effects in silicon would be observed.

Current–voltage and capacitance–voltage characteristics of $n$-Si/HfO$_2$/Ni structures are shown in Fig. 17(c) and (d). In accumulation, i.e. at a positive potential applied to the nickel contact, the electric current exponentially increases with increasing the potential applied to the metal. In the depletion mode, i.e. at a negative potential applied to the Ni contact, the electric current comes to saturation, with the saturation level increasing under illumination in a way it was in the $p$-Si/HfO$_2$/Ni structures (in depletion mode).

The saturation of the electric current in the $n$-Si/HfO$_2$/Ni structures in depletion points to the injection of minorities (holes) out of the silicon substrate into HfO$_2$ ($J_h$ in Fig. 17(c)). An independent support to the latter statement is provided by the transition of capacitance from inversion into non-equilibrium depletion mode (Fig. 17(d)).

Thus, like in Si$_3$N$_4$, ZrO$_2$, and TiO$_2$, the conduction in HfO$_2$ proved to be bipolar. The latter conclusion agrees with the experiment on the separation of electric current components in MOS transistors [101]. In such transistors, electrons are injected into HfO$_2$ out of the negatively biased contact (see Fig. 19(a)), while holes are injected out of the positively biased contact (see Fig. 19(b)). Like in Si$_3$N$_4$, recombination of free electrons with trapped holes and/or recombination of free holes with trapped electrons in the near-contact regions can be observed.

The authors of Refs. [24,53,85,99,100], who evaluated the trap ionization energies in HfO$_2$, assumed that the traps under study were electron traps. Since it was shown in [54] that the conduction in HfO$_2$ was a bipolar one, there arises an uncertainty whether the obtained data referred to electron or hole traps. One can assume that the ionization energies of electron and hole traps in HfO$_2$ have values identical to those in Si$_3$N$_4$ [77]. However, additional experiments are required to validate this hypothesis.

### 5. Summary and outlook

In the present publication, a review of presently available data on the electronic structure of the key intrinsic defect in hafnium oxide, the oxygen vacancy, is given. The defect is responsible for the 2.7 eV blue luminescence band, normally excited within the 5.2 eV absorption band of HfO$_2$. Oxygen vacancies are responsible for localization of electrons and holes in HfO$_2$ and, also, for charge transport in the material. The charge transport in HfO$_2$ is a process controlled by the phonon-assisted tunnelling of electrons between traps. The thermal energy of the traps, $W_t = 1.25$ eV, is equal to half the Stokes shift of the luminescence band due to oxygen vacancies. The optical energy of the traps is $W_{opt} = 2.5$ eV. The conduction in HfO$_2$ is a bipolar process, the electrons and holes being injected respectively out of the negatively biased and positively biased contact.

Among the still unresolved material-science problems for hafnium oxide, the most important one is the determination of characteristics of the electron and hole traps in the material. Solution of this problem will permit the development of an adequate theory for charge transport in hafnium oxide. Revealing the conduction mechanism in non-stoichiometric hafnium sub-oxides HfO$_x$ with $x \ll 2$ presents a separate important problem.

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