Oxygen Vacancy in Hafnia as a Blue Luminescence Center and a Trap of Charge Carriers

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ABSTRACT: The electronic properties of HfO2, in particular, luminescence and charge transport, are determined by defects and traps. The origin of luminescence centers and traps of charge carriers in a HfO2 crystal was studied using luminescence spectroscopy, charge transport, and quantum-chemical calculation. The 2.7 eV luminescence band and 5.2 eV absorption/luminescence excitation band are associated with an oxygen vacancy. The thermal activation energy 1.25 eV, estimated from the charge transport and thermoluminescence experiment, is equal to half of the Stokes shift in photoluminescence spectra. Hence, oxygen vacancies are supposed to operate as electron traps in HfO2, and the charge transport is described by phonon-assisted tunneling between traps.

INTRODUCTION

Hafnium oxide is a solid electrolyte with oxygen-ion conductivity. HfO2-based crystals have a higher chemical resistance in comparison with liquid alkaline metals and their vapors. This allows one to use HfO2 as a basic element of the electrochemical detector of oxygen in various aggressive media. HfO2 is widely used in silicon-based devices: as a gate dielectric in transistors and as a memory node in the new generation of resistive random access (ReRAM) flash memory.1−4 The electronic properties of HfO2 in particular, luminescence and charge transport, are determined by defects and traps. In HfO2 as a gate dielectric, electrical conductivity via traps is the undesirable and parasitic effect.5 However, when HfO2 is used as a memory medium in ReRAM, initial presence of defects is a necessary condition for resistive switching. Oxygen vacancy is a fundamental intrinsic defect in HfO2, and it was a subject of numerous theoretical studies.6−11 A luminescence band at 2.7 eV was observed in HfO2, and this emission was excited most effectively in the 5.2 eV band.12−17 The corresponding absorption near 5.2 eV was observed in refs 18 and 19. Thermoluminescence (TL) is a simple and informative technique to study charge carrier traps in dielectrics.20 However, the trap energy determined in TL experiments depends considerably on model parameters, in particular, on the frequency factor.19 The results concerning mechanisms of charge transport in HfO2 thin films were published in ref 21. The structure of luminescence centers in thin HfO2 films was studied in ref 22. The aim of the present research is to determine the atomic structure of defects responsible for the 5.2 eV absorption and 2.7 eV luminescence, as well as charge transport mechanisms in HfO2.

EXPERIMENTAL SECTION

Samples. Different types of hafnia samples are suitable in the best way for the different experiments: for photoluminescence it is 50 nm hafnia film with different stoichiometry, for thermoluminescence it is bulk hafnia, and for transport measurements it is ALD thin hafnia films.

Hafnium oxide crystals were grown by directional crystallization of the melt in a water-cooled copper crucible 130 mm in diameter. The growth installation was Kristall-407 produced by VNIITVCh, Russian Federation (frequency 5.28 MHz, maximum output power 60 kW).23 The weight of the material that was loaded into the cold container was approximately 6 kg. Hafnium oxide of the GFO-1 quality was used as a precursor. The crystals growth rate was 10 mm/h.24 The as-grown crystals, white and translucent, were several centimeters in section (Figure 1a). To produce oxygen vacancies, HfO2 crystals were annealed in the reduced medium (10−4 Torr vacuum) at 1600 °C and at 2100 °C. The treatment regime was...
4 h of heating, then 4 h of storage at high temperature, and 6 h of cooling. The pieces about $5 \times 5 \times 2 \, \text{mm}^3$ were used for luminescence experiments.

Raman spectra were collected at room temperature on a LabRAM HR800 microRaman spectrometer using a 325 nm He–Cd laser beam, with a spot size $\sim 5 \, \mu\text{m}$ and a grating with 2400 grooves/mm. Integration and accumulation times were 3 s. The measurements were replicated at five points to check reproducibility.

Hafnia is a wide gap dielectric with the band gap value 5.6 eV.25 This means that defect-free HfO$_2$ is a transparent crystal. However, real grown and annealed HfO$_2$ crystals are white-colored and nontransparent (Figure 1a). This phenomenon might be caused by transitions on electronic states in the band gap or by scattering at intrinsic defects, for example, at the crystallite boundaries. These crystals exhibit visible blue luminescence under ultraviolet (UV) excitation (Figure 1b).

The HfO$_x$ ($x \leq 2$) films were produced using ion beam sputtering deposition. Silicon substrates Si(100) with resistance 4.5 $\Omega$-cm, which undertook a deep cleaning by the RCA Co. technique, were used as substrates. The target was sputtered by the beam of Ar$^+$ ions, and, simultaneously, we delivered high-purity oxygen (O$_2$ > 99.999%) into the area near the target and substrate. The HfO$_x$ film composition ($x$-parameter) was defined by partial oxygen pressure using a gas flow controller. For our experiments, we grew two sets of HfO$_x$ samples at the partial oxygen pressures of 1.0 $\times$ 10$^{-3}$ and 3.6 $\times$ 10$^{-3}$ Pa. In these conditions, we produced nonstoichiometric ($x < 2$) films and almost stoichiometric compositions ($x \leq 2$), respectively.

The stoichiometric composition of the films was characterized using an X-ray photoelectron spectrometer (SPECs Surface Nano Analysis GmbH, Germany) using the monochromatic Al K$\alpha$ radiation under ultrahigh vacuum conditions. The [O]/[Hf] atomic ratios calculated using Scofield cross sections and integrated intensities of the O 1s and Hf 4f spectra of the stoichiometric and nonstoichiometric films were approximately 2.0 and 1.83, respectively. According to the photoelectron spectroscopy data, the impurity concentration in the investigated films is below the spectrometer sensitivity threshold.

The structure was investigated by the reflection high-energy electron diffraction (RHEED) technique on an EF-Z4 device at the accelerating voltage of 50 kV. The studied hafnia films were amorphous.

**Optical Spectroscopy.** The X-ray excited luminescence (XRL) spectra were measured at room temperature using an MDR2 diffraction monochromator and an FEU100 photomultiplier as an emission detector. The luminescence was excited using a Table 10-ray URS 1.0 setup containing a BSV 2 W tube with the W-anode. The TL curves were recorded when heating the samples at the rate of $\beta = 20 \, \text{K/min}$ after the 5 min low-temperature excitation at 85 K with unfiltered light of a 400 W deuterium discharge lamp DDS400. The spectra were recorded at $T = 300 \, \text{K}$.

The DDS400 deuterium lamp and the primary double-prism monochromator DMR-4 were used for photoluminescence (PL) excitation. The PL spectra were recorded using a secondary DMR-4 double-prism monochromator and a Hamamatsu R6358-10 type photomultiplier tube. The PL excitation (PLE) spectra were normalized to the equal number of photons incident on the sample using a yellow lumogen—a luminophore with the known energy quantum yield over the studied spectral range. The PL emission spectra were not corrected for the spectral sensitivity of the registration system.

The ab initio simulations of the optical spectra were performed in the framework of periodic supercell formalism based on the density functional theory (DFT) using a Quantum-ESPRESSO software.7 We adopted a hybrid exchange-correlation functional B3LYP to reproduce the correct band gap value 5.6 eV.25 The cubic hafnia (c-HfO$_2$) supercell containing 81 atoms was used for simulation because of its simplest structure. The simplicity of the c-HfO$_2$ crystal structure makes it the most acceptable for such kind of calculations from the point of view of computational facilities and ease of results interpretation. The comparison of the experimental spectra for crystalline hafnia with amorphous one is justified by the known fact that the type of atoms and short-range order determines most of the solids physical properties.

**Charge Transport.** To study the electronic transport mechanism in a hafnia thin film, we performed transport measurements in metal–insulator–semiconductor (MIS) structures of n-Si/HfO$_x$/Ni. To produce these structures, the 20 nm thick hafnia was deposited on a n-type Si (100) wafer by using the atomic layer deposition (ALD) technique. Tetakis dimethyl amino hafnium (TDMAHf) and water vapor were used as precursors at a chamber temperature of 250 °C for HfO$_x$ film deposition. Structural analysis shows that the resulting HfO$_x$ film was amorphous. Sample for transport measurements were equipped with round 50 nm thick Ni gates.
with a radius of 70 μm. Transport measurements were performed using a Hewlett-Packard 4155B semiconductor parameter analyzer and an Agilent E4980A precision LCR meter.

## RESULTS

### X-ray Excited Luminescence, Photoluminescence, and Optical Absorption

Raman spectra of bulk HfO2 samples as grown and annealed at 1600 °C (2100 °C) are shown in Figure 2a. One can see, the annealing does not change the crystal structure of test samples. The spectra of initial as well as annealed samples correspond to monoclinic phase. There should be 18 Raman-active modes from theoretical study. However, only 17 modes are observed in recorded Raman spectra for monoclinic HfO2: they are located at 112, 116, 140, 153, 170, 248, 261, 322, 342, 388, 403, 504, 527, 557, 566, 647, and 680 cm⁻¹ with the most intense line at 504 cm⁻¹.

The X-ray luminescence spectra of bulk crystals HfO2 before and after annealing at 1600 and 2100 °C are shown in Figure 2b. There are two broad luminescence bands centered near 2.6 and 4.4 eV. Annealing at the 1600 °C leads to a strong increase in the peak intensity of the luminescence at energy of 2.7 eV. It is explained by increasing radiative centers concentration (apparently, oxygen vacancies). At the same time, annealing at the 2100 °C results in a significant decrease of the RL intensity. This result can be explained by the significant increase in the oxygen vacancies concentration. If the defect concentration is higher than a critical value, then the luminescence intensity decreases with the concentration of radiative centers increasing, i.e., the concentration quenching effect takes place. This phenomenon is caused by nonradiative energy loss during resonant excitation transfer from one center to another.

The band at 4.4 eV was observed in both single crystals and films of HfO2 and is interpreted as autolocalized excitons luminescence. The PL and PLE spectra for HfOx≤2 and HfO1.83 are shown in Figures 3a, b. Under the HfOx≤2 excitation with quantum energy 5.25 eV, there are two PL bands observed with peak energies of about 2.7 and 3.7 eV. The PLE spectrum for band 2.7 eV has peaks with a maximal energy of about 5.2–5.4 eV. The maxima of the excitation 3.68 eV band have the energy of about 4.3 and 5.4 eV (Figure 3a). For HfO1.83, the single wide band PL peak is observed in the energies range of 2.5–3.0 eV under the excitation quanta with energy 5.2 eV (Figure 3b). The maxima of the PLE spectrum for the 2.74 eV blue emission of HfO1.83 films are at the energies of 4.5 and about 5.2 eV, whereas the maxima of PLE band 3.66 eV are at the energies of 4.4 and 5.4 eV.

In the PL spectra of HfOx≤2 and HfO1.83 under the excitation by quanta with the energy of about 5.2 eV, a blue PL band with the energy of about 2.7 eV is observed. The blue band has two excitation maxima in the range of 4.4–4.5 and 5.2–5.4 eV.

The optical absorption peak near 5.2 eV in HfO2 was observed in refs 18 and 19. The quantum-chemical simulation shows an absorption peak at 5.3 eV of the oxygen vacancy in HfO2 (Figure 3c). The calculated absorption peak for the oxygen vacancy is close to a feature of PLE for 2.7 eV emission. This means that 5.2 eV photons excite oxygen vacancies in HfO2. On the other hand, a PL emission near 2.7 eV also indicates the presence of oxygen vacancies in the bulk HfO2. The coincidence of the experimental peak position for amorphous HfO2 films from 18 with the theoretical one for the cubic-HfO2 is the justification of the correctness of mapping data obtained for the different structures.
There is another band near 3.6 eV in the PL spectrum (Figures 3a, b). This emission is excited in a PLE band near 5.3 eV. We have no data that would reveal the nature of 3.6 eV luminescence band. One can assume that the line is 3.6 eV is due to positively or negatively charged oxygen vacancy. This assumption is a subject for further investigations.

The optical transitions in the oxygen vacancy in HfO$_2$ and luminescence processes can be described using a configuration diagram in the single-band model as shown in Figure 4a. The absorption of 5.2 eV photons produces the ground-to-excited state electron transition in the oxygen vacancy (vertical up arrow). After the transition, vacancy becomes capable of emitting light. Thus, the 5.2 eV bands in the absorption and PLE spectra correspond to the same transition. Then the vacancy relaxes nonradiatively with the electron transition to a minimum of the excited state. Afterward the electron returns to the ground state (vertical down arrow) with the emission of the 2.7 eV photon, and the system relaxes to the minimum of the ground state (starting point). Polaron energy 1.25 eV corresponds to the thermal activation energy $W_1$ of the trap-capturing charge carriers. This simple single band model approach is applicable for description of the mechanism of the conductivity and luminescence of amorphous Si$_3$N$_4$ films and Al$_2$O$_3$.35,34

Taking into account the above, one can conclude that oxygen vacancies are responsible for the blue luminescence of the bulk HfO$_2$ (Figure 1b).

**Charge Transport.** Experimental current–voltage characteristics of $n$-Si/HfO$_2$/Ni structures, measured at different temperatures with a positive bias on the Ni contact, are shown in a different color in Figure 5. We found that experimental data might be qualitatively described by different models, such as Frenkel trap ionization,35,36 Hill overlapping trap ionization model,37 and multiphonon trap ionization.38 However, the fitting procedures (here we do not show their results) return the nonphysical values of the fitting parameters.

To describe the experiments quantitatively, we performed simulations in terms of the phonon-assisted tunneling between traps.39

\[
J = \frac{eP}{s}\]

\[
P = \nu \exp\left(-\frac{W_{\text{opt}} - W_1}{2kT}\right) \exp\left(-\frac{2\sqrt{2m^*W_1}}{\hbar}\right) \sinh\left(\frac{eFs}{2kT}\right)
\]

\[
\nu = \frac{\sqrt{2\pi} h W_1}{m^* s^2 \sqrt{kT(W_{\text{opt}} - W_1)}}
\]

(1)

where $J$ is the current density, $e$ is the electron charge, $s$ is the mean distance between traps, $P$ is the rate of the electron tunneling between traps, $\nu$ is the attempt to escape from the trap, $W_1$ is the trap thermal energy, $W_{\text{opt}}$ is the trap optical energy, $k$ is the Boltzmann constant, $m^*$ is the electron effective mass, $\hbar$ is the Planck constant, and $F$ is the electric field. The multiparametric fitting procedure allows us to get the values of different transport parameters, such as trap density $N = s^{-3} = 2.5 \times 10^{20} \text{ cm}^{-3}$, $W_1 = 1.25 \text{ eV}$, $W_{\text{opt}} = 2W_1 = 2.5 \text{ eV}$, and $m^* = 0.8 \text{ m}_e$. The obtained effective mass values agree with results of the quantum-chemical calculations of various HfO$_2$ allotropic modifications $m^* = (0.5-2.0)m_e$.40-42 We get a very good quantitative agreement of the experimental data with the phonon-assisted tunneling between traps. The value of 1.25 eV for the trap thermal activation energy we obtained is close to that of 1.2 eV53 and 1.36 eV5. Also, the trap optical activation energy value $W_{\text{opt}} = 2.5 \text{ eV}$ is close to the theoretically calculated value of 2.35 eV for the negatively charged oxygen vacancy in hafnia.11

A configuration diagram for the oxygen vacancy (trap) which describes the charge transport in HfO$_2$ is shown in Figure 4b. The value $W_1 = 1.25 \text{ eV}$ corresponds to the thermal activation energy of the trap, and the transition with energy $W_{\text{opt}} = 2W_1 = 2.5 \text{ eV}$ corresponds to its optical activation energy.

The similarity between the polaron energy determined from the Stokes shift in PL/PLE spectra and the thermal activation energy of the trap from the charge transport experiments indicates that oxygen vacancies operate as traps in HfO$_2$.

**Thermoluminescence.** Substituting the experimentally determined parameters $W_1$, $W_{\text{opt}}$, $m^*$, and $s = 1.7 \text{ nm}$ in the expression for an attempt to escape factor $\nu$ in the HfO$_2$ trap (1), we get the value of $\nu = 2 \times 10^{15} \text{ s}^{-1}$ at room temperature.
The shape of the thermoluminescence (TL) peak is described by the following equation,\(^{(20)}\)

\[
I(T) = n_0 \nu \exp\left(\frac{W}{kT}\right) \exp\left[-\frac{\nu}{\beta} \int_{T_0}^{T} \exp\left(\frac{W}{kT}\right) \, dT\right]
\]

where \(n_0\) is the initial concentration of trapped electrons, \(\beta\) is the rate of linear heating (K/s), and \(T_0\) is the initial temperature.

A TL curve for bulk HfO\(_2\) is presented in Figure 6. The peaks are observed at the following temperatures: 111, 158, 255, 291, 315, 372, 468, 512, and 540 K. Calculating thermal activation energies of the traps, we used a fixed value of the frequency factor \((2 \times 10^{15} \text{ s}^{-1})\), obtained for the oxygen vacancy in charge transport experiments. The thermal activation energies determined by fitting the temperatures of TL position and the decomposition results: the thin blue curves show individual peaks, whereas the thick red line is their sum. Inset: each TL peak corresponds to a value of \(W_\nu\).

![Figure 6. Experimentally obtained TL curve for HfO\(_2\) annealed at 1600 °C (thick black curve) and the decomposition results: the thin blue curves show individual peaks, whereas the thick red line is their sum. Inset: each TL peak corresponds to a value of \(W_\nu\).](image)

DISCUSSION

Frenkel proposed a way to evaluate the frequency factor for electrons localized in a trap with energy \(W\) as\(^{(36)}\)

\[
\nu = \frac{W}{h}
\]

Taking \(W = 1 \text{ eV}\) in eq 3, we get \(\nu \approx 2 \times 10^{14} \text{ s}^{-1}\). The physical meaning of \(\nu\) in this case is the electron oscillation frequency in a potential well with energy \(W\).

Alternatively, in the multiphonon trap ionization model, the value \(\nu\) corresponds to the defect oscillations frequency with an electron in the potential well. In Si\(_3\)N\(_4\) and Al\(_2\)O\(_3\)\(^{(44,45)}\) it was established that traps ionization is realized by the multiphonon mechanism from the results of charge transport experiments.

The frequency factor is equal to \(\nu \approx 5 \times 10^{13} \text{ s}^{-1}\) for Si\(_3\)N\(_4\) and Al\(_2\)O\(_3\).

The peaks with energy 2.1 eV\(^{(17,45)}\) and 1.9 eV\(^{(16,45)}\) were observed in the HfO\(_2\) cathodoluminescence. It was hypothesized that the luminescence band with energy 2.1 eV is due to the oxygen divacancy.\(^{(17)}\) It is possible to presume that the PL band centered near 1.9 eV in HfO\(_2\) is due to the oxygen trivacancy. In other words, it is suggested that PL bands with energies of band maxima less than 2.7 eV are due to oxygen polyvacancies.\(^{(36)}\) Based on this hypothesis, one should assume that thermoluminescence peaks at temperatures 255, 291, and 315 K are also caused by oxygen polyvacancies in HfO\(_2\).

In the present study, the interpretation of charge transport and TL experiments was in the supposition of only electron conductivity. On the other hand, recently it was established that the HfO\(_2\) conductivity is bipolar and is realized both by electrons and holes.\(^{(47-49)}\) The interpretation of experimental data within the bipolar model is beyond the present research.

One should note that both Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) and ZrO\(_2\) conductivities are limited by the phonon-assisted tunneling between traps.\(^{(30)}\) For Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) and ZrO\(_2\) the trap parameters, namely thermal \(W_\nu = 1.25 \text{ eV}\) and optical energies \(W_\mathrm{opt} = 2W_\nu = 2.5 \text{ eV}\), are in agreement.

CONCLUSIONS

In present work, oxygen vacancies were created at annealing bulk HfO\(_2\) crystals in a reducing atmosphere. A peak near 2.7 eV is observed in the X-ray excited luminescence spectra of bulk HfO\(_2\). This emission is excited by photons with an energy near 5.2 eV. The quantum-chemical simulation shows that the absorption peak near 5.3 eV is due to the oxygen vacancy in HfO\(_2\). Thus, the 2.7 eV PL emission is excited in the absorption/PLE band near 5.2 eV in HfO\(_2\). The polaron energy, or the chemical trap energy determined as half of Stokes shift, is equal to 1.25 eV. The thermal activation energy of the trap is determined as well as from the electron transport experiments in thin HfO\(_2\) films. Hence, oxygen vacancies are the traps in thin HfO\(_2\) films. The frequency factor value \(\nu = 2 \times 10^{15} \text{ s}^{-1}\) for the oxygen vacancy was determined in charge transport experiments. The traps parameters were calculated.

The thermal activation energy of TL peak at 372 K in bulk HfO\(_2\) was estimated to be about 1.25 eV, which coincides with half of the Stokes shift and the thermal energy determined in charge transport experiments. Thus, the TL peak at energy 372 K is related to oxygen vacancies. The low-temperature TL peaks at 315, 291, and 255 K are likely due to the oxygen polyvacancies in hafnium oxide.

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Notes

The authors declare no competing financial interest.

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