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CATHODO- AND PHOTOLUMINESCENCE INCREASE IN AMORPHOUS HAFNIUM OXIDE UNDER ANNEALING IN OXYGEN

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Cathodo- and photoluminescence of amorphous nonstoichiometric films of hafnium oxide are studied with the aim to verify the hypothesis that oxygen vacancies are responsible for the luminescence. To produce oxygen vacancies, hafnium oxide was enriched in surplus metal during synthesis. To reduce the oxygen concentration, the film was annealed in oxygen. A qualitative control of the oxygen concentration was carried out by the refractive index. In the initial, almost stoichiometric films we observed a 2.7-eV band in cathodoluminescence. Annealing in oxygen results in a considerable increase in its intensity, as well as in the appearance of new bands at 1.87, 2.14, 3.40, and 3.6 eV. The observed emission bands are supposed to be due to single oxygen vacancies and polyvacancies in hafnium oxide. The luminescence increase under annealing in an oxygen atmosphere may be a result of the emission quenching effect.

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1. INTRODUCTION

An increase in the information volume and operation speed of silicon-based devices, and the attainment of a terabyte scale are underlain by scaling effects and a decrease in the channel length in metal–oxide–semiconductor (MOS) devices. That decrease is accompanied with a decrease in the thickness of the gate silicon oxide. Silicon oxide was used as a gate dielectric during four decades. The thickness of the SiO_2 layer is 1.2 nm while the designed value is 60 nm. A further decrease in the SiO_2 thickness is unacceptable because of strong tunnel currents of leakage, which lead to the heating of silicon devices and to a decrease in their reliability. A general approach to solving this problem is to replace the gate SiO_2 with alternative or high-k dielectrics with a high dielectric permeability [1–3]. Alternative dielectrics have a permittivity $k = 15$–25, to be compared with $k = 3.9$ for SiO_2. High k values allow increasing the physical thickness of the dielectric up to 5 nm, which allows suppressing the leakage current.

The most promising materials that are currently introduced instead of SiO_2 are dielectrics based on HfO_xN_y ($k \approx 15$), $HfSiO_x$ ($k \approx 15$), and HfO_2 ($k = 25$). The dielectrics based on hafnium oxide have higher thermodynamic stability on a boundary with silicon, higher permittivity, and higher barriers for holes and electrons [1–3]. The unresolved problem is high enough leakage currents due to traps and the capture of charge carriers on these traps. Therefore, studying the origin (atomic and electronic structure) of defects that operate as traps in hafnium oxide is very important.

Experimental [4–6] and theoretical [7–9] investigations of hafnium oxide show that oxygen vacancy is one

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of the main point defects. Oxygen vacancies were established to produce absorption in the spectral range 4.4–5.3 eV and to be responsible for electrical conductivity of HfO_2 [4]. The aim of this paper is the experimental study of luminescence at excitation by an electron beam (cathodoluminescence) and by synchrotron radiation (photoluminescence) in order to determine the physical nature of the luminescence center. For this, we studied a set of nonstoichiometric HfO_x ($x \leq 2$) samples enriched in surplus hafnium (in the oxygen vacancies). Two ways to affect the oxygen vacancy concentration were used: the enrichment in metal during synthesis and annealing in a reducing atmosphere (vacuum), and a decrease in the concentration of surplus hafnium (oxygen vacancy) by annealing samples in oxygen.

2. EXPERIMENTAL TECHNIQUE

The HfO_x ($x \leq 2$) films were produced using ion beam sputtering deposition (IBSD) [10]. Silicon plates Si(100) with the resistance 4.5Ω·cm, which had been subjected to a deep cleaning by the RCA Co technique [11] were used as substrates. Before mounting into the vacuum chamber, the substrates were treated in a HF solution to remove the natural oxide.

A silicon substrate was placed near the target from metallic hafnium (Williams Inc., Hf content more than 99.9 %). The target was sputtered by a beam of Ar^+ ions, and simultaneously we delivered high-purity oxygen (more than 99.999 %) into the area near the target and substrate. A beam of sputtered particles fell on the substrate surface, thus forming an HfO_x film. The films were produced at room temperature. The substrate heating by hot particles from the target did not exceed 70 °C.

The beam of Ar^+ ions for sputtering of the target material was formed by a the Kaufmann-type source [12]. The energy of Ar^+ ions was 1.2 keV, while the density of ionic current on the Hf target was 1.5 mA/cm^2. The thickness and rate of layer deposition were controlled by a quartz sensor (TM-400, Maxtec.Inc), located near the substrate. The composition (x-parameter) of the film was defined by partial pressure of oxygen using a gas flow controller. For our experiments, we grew two sets of HfO_x samples at partial oxygen pressures $9 \cdot 10^{-3}$ and $2 \cdot 10^{-3}$ Pa. In such conditions, we produced the samples of an almost stoichiometric composition ($x \approx 2$) and nonstoichiometric samples ($x < 2$).

Part of the stoichiometric and nonstoichiometric films were annealed in a vacuum with the residual pressure in the chamber less than 10^{-4} Pa at 600 °C during 1 h. The other part of the films was annealed in a flow reactor in the atmosphere of pure oxygen at $T = 600$ °C and $P = 1$ atm during 1 h.

Ellipsometric measurements on our films were carried out with an LEF-3M ellipsometer operating at $\lambda = 632.8$ nm and the incidence angle 70°C. The thickness and refractive index were calculated in the frames of the one-layer reflection system Si-substrate–HfO_x-film–atmosphere.

The conditions of film producing and annealing, as well as ellipsometric data (thickness and refractive indices) for the films are given in Table 1. Enrichment of hafnium oxide in surplus metal during synthesis and annealing or at vacuum annealing leads to an increase in the refractive index. Annealing in oxygen is accompanied by a decrease in the concentration of surplus hafnium (oxygen vacancies), and the refractive index decreases. A similar effect is observed when silicon nitride SiN_x is enriched in silicon [13, 14].

Photoluminescence (PL) and PL excitation spectra were measured at 7.5 K in both stationary and time-resolved regimes using synchrotron radiation on a SUPERLUM station of the DESYLAB laboratory (Hamburg, Germany) [15]. The time delay δt relative to the excitation pulse and the time window length Δt were chosen taking the luminescence kinetics into account. Two time windows were used: with $\delta t_1 = 2.7$ ns, $\Delta t_1 = 11.8$ ns for the fast component, and with $\delta t_2 = 60$ ns, $\Delta t_2 = 92$ ns for the slow one. The PL excitation spectra were measured at the excitation energy $E_{ex} = 4$–40 eV and normalized to an equal number of incident photons using sodium salicylate, whose quantum efficiency does not depend on the photon energy at $h\nu > 3.7$ eV.

Cathodoluminescence spectra of HfO_x samples were taken with an electron probe microanalyzer “Camebax”. This microanalyzer is equipped by four X-ray spectrometers for quantitive X-ray microanalysis and additionally by two optical spectrometers for cathodoluminescence (CL) measurements. CL spectra were recorded in the range 1.5–3.8 eV at 300 K. The sample was irradiated by a beam of 5 eV electrons at a 0.2 μm depth of electron penetration and a current density of 1.2 A/cm^2.

3. CATHODOLUMINESCENCE SPECTRA

In Fig. 1, CL spectra for a hafnium oxide film of the composition close to the stoichiometric one (sam-

Table 1. Conditions of the preparation and the ellipsometric data (thickness d and refractive index n) for the hafnium oxide films (Δd and Δn are the respective errors for d and n)

Sample number	Conditions of the sample preparation	Ellipsometric data, $\lambda = 632.8$ nm, $\Delta d \sim 1$ Å, $\Delta n \sim 0.001^*$
22	The initial HfO$_2$ film after annealing in vacuum ($P < 10^{-4}$ Pa) at 600 °C/1 h	$d = 757.6$ Å $n = 1.986$
23	The initial HfO$_2$ film after annealing in oxygen ambient ($P_{O_2} \sim 10^5$ Pa) at 600 °C/1 h	$d = 767.2$ Å $n = 1.955$
41	The initial HfO$_x$ ($x < 2$) film grown at $P_{O_2} = 2 \cdot 10^{-3}$ Pa. Nonstehiometric composition	$d = 1054.2$ Å $n = 2.010$
44	The initial HfO$_x$ ($x < 2$) film after annealing in vacuum ($P < 10^{-4}$ Pa) at 600 °C/1 h	$d = 1038.7$ Å $n = 2.013$
42	The initial HfO$_x$ ($x < 2$) film after annealing in oxygen ambient ($P_{O_2} < 10^5$ Pa) at 600 °C/1 h	$d = 1069.8$ Å $n = 2.010$

ple No. 24) are shown. We can see a single peak at 2.64 eV with an FWHM 0.92 eV (Table 2).

Annealing in oxygen (sample No. 23) leads to an increase in the CL intensity in the 2.7-eV band as well as to the appearance of new CL bands with energies 1.95, 2.16, 3.42, and 3.74 eV (see Table 2). The intensity of the 2.7-eV peak increases 7 times at annealing in oxygen. Earlier, luminescence in the 2.7-eV band was observed in Refs. [16–20]. The 2.2-eV luminescence band was observed in hafnium oxide [19, 20]. The 3.2-eV luminescence was also reported in Ref. [19], whereas the 3.7-eV emission band was observed in [20].

4. PHOTOLUMINESCENCE SPECTRA

It was established that in a hafnium oxide film with the composition close to the stoichiometric one (refractive index 1.976, sample No. 24), there is no PL at 6.7-eV excitation in the range 1.7–4.1 eV. Annealing of such a film in vacuum is accompanied by an increase in n from 1.976 (sample No. 24) in the original film to $n = 1.986$ in the film annealed at 600 °C during 1 h (sample No. 22, see Table 1). The increase in n for hafnium oxide at annealing in vacuum shows that the film is enriched in surplus Hf and indicates the formation of oxygen vacancies. The annealing of hafnium oxide in vacuum and the formation of oxygen vacancies are accompanied by the appearance of the 2.7-eV band emission (Fig. 2). It is natural to suppose that the 2.7-eV PL band is due to oxygen vacancies in hafnium oxide. This conclusion is confirmed by the PL decrease after further annealing the film in oxygen (see Fig. 2). Annealing in oxygen also results in a decrease in the refractive index to $n = 1.955$ (sample No. 23).

A further confirmation that the 2.7-eV luminescence band is due to oxygen vacancies was obtained in the experiments with nonstoichiometric hafnium oxide samples enriched in surplus metal during synthesis (see Table 1). In Fig. 3, we show the PL spectrum of the original nonstoichiometric film (sample No. 41). Such a film has the refractive index $n = 2.010$ to be compared with $n = 1.976$ for the stoichiometric sample No. 24. The HfO$_x$ film No. 41 with $n = 2.010$ demonstrates PL emission in the 2.7-eV band. The intensity of this emission is about 600 pulses/sec. Annealing in vacuum leads to an increase in surplus hafnium, which indicates the increase in the refractive index to $n = 2.013$ (sample No. 44). Annealing in vacuum is accompanied with the PL intensity weakening to 250 pulses/sec. Thus, the increase of the oxygen vacancy concentration leads to a concentration quenching of the PL emission.

Annealing in oxygen (sample No. 42) results in a decrease in the n value to 2.001, which informs us about a decrease in the surplus hafnium concentration. Annealing in oxygen produces a 6-fold increase of the PL intensity, to 3400 pulses/sec (see Fig. 2). This effect (the PL increase at annealing in oxygen) is explained by a decrease in the oxygen vacancy concentration.

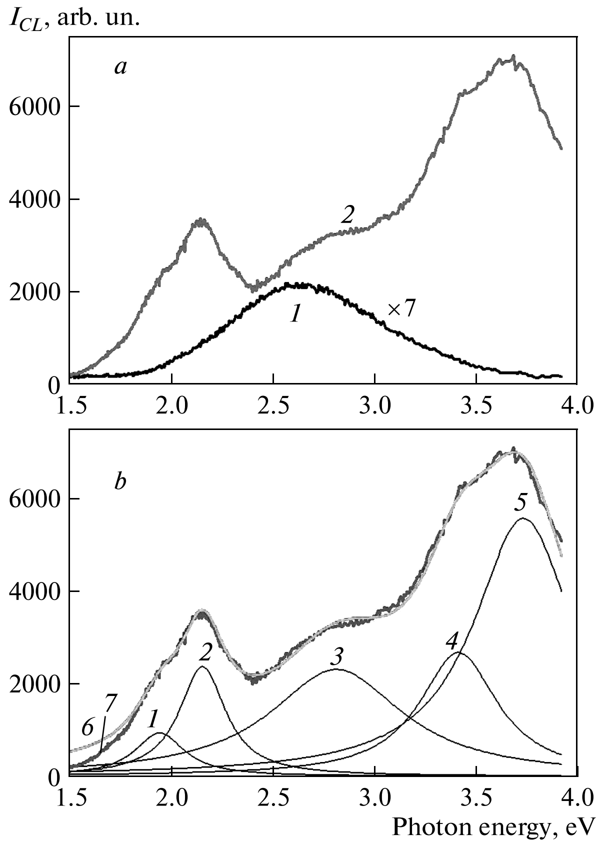

Fig. 1. (*a*) Comparison of experimental CL spectra for HfO_2 films: the original sample No. 24 (curve *1* with the intensity magnified 7 times) and after annealing in oxygen (sample No. 23, curve *2*). (*b*) Decomposition of the CL spectrum (*2* in Fig. 1*a*) into Gaussian components, shown by thin solid lines *1–5*. Curve *6* is a sum of Gaussians *1–5*, whereas gray line *7* is experimental. The parameters of Gaussians *1–5* are given in Table 2

Table 2. Results of CL spectra decomposition into Gaussian components for the HfO_2 film before and after annealing in oxygen

Component number	Maximum position, eV	FWHM, eV
1	2.64	0.92
1	1.95	0.30
2	2.16	0.29
3	2.82	0.80
4	3.42	0.47
5	3.74	0.57

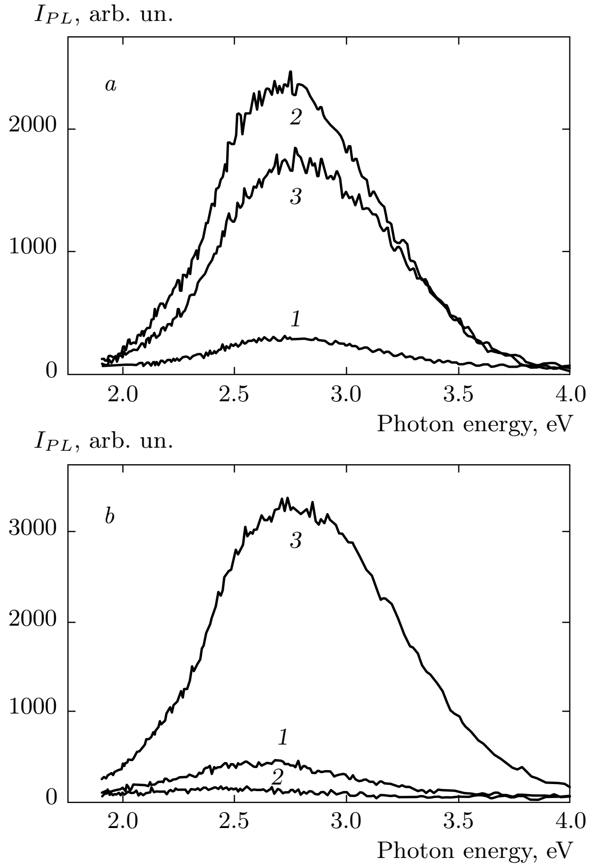

Fig. 2. PL spectra at 6.43-eV excitation for HfO_2 films of (*a*) an almost stoichiometric composition and (*b*) nonstoichiometric hafnium oxide before treatment (spectra *1*), after annealing in a vacuum (*2*), and in oxygen (*3*); $T = 7.2$ K

5. PHOTOLUMINESCENCE EXCITATION SPECTRA

The PL excitation spectrum for 2.75 eV emission in sample No. 22 annealed in vacuum is given in Fig. 4. In the PL excitation spectrum of stoichiometric hafnium oxide, there are three maximums near 6.3 and 9.5 eV. In Fig. 4, we can see three individual Gaussian components. Their parameters are given in Table 3. Maxima of these Gaussians are located at 6.33, 6.8, and 9.42 eV. The annealing in oxygen is accompanied by a minor shift of the first maximum to 6.40 eV (see Fig. 3).

6. DISCUSSION

Our interpretation assumes that the observed luminescence bands at 2.7, 3.42, and 3.74 eV are due to oxygen vacancies, whereas the 1.95- and 2.16-eV bands are

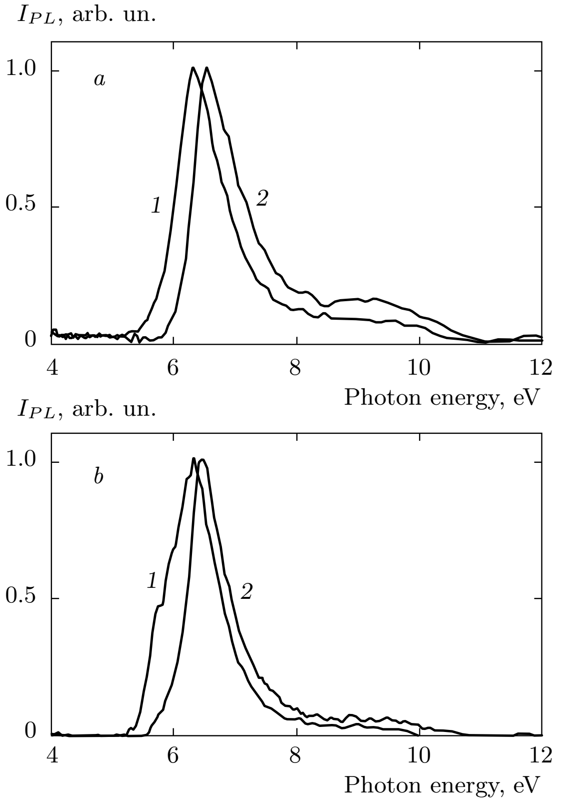

Fig. 3. PL excitation spectra for the 2.7-eV emission in (*a*) stoichiometric and (*b*) nonstoichiometric hafnium oxide films after annealing in vacuum (*1*) and in oxygen (*2*); $T = 7.2$ K. Luminescence was excited by photons of the energy 6.29 eV for sample No. 22 (*a*, curve *1*), 6.53 eV for sample No. 23 (*a*, curve *2*), 6.30 eV for sample No. 44 (*b*, curve *1*), and 6.46 eV for sample No. 42 (*b*, curve *2*)

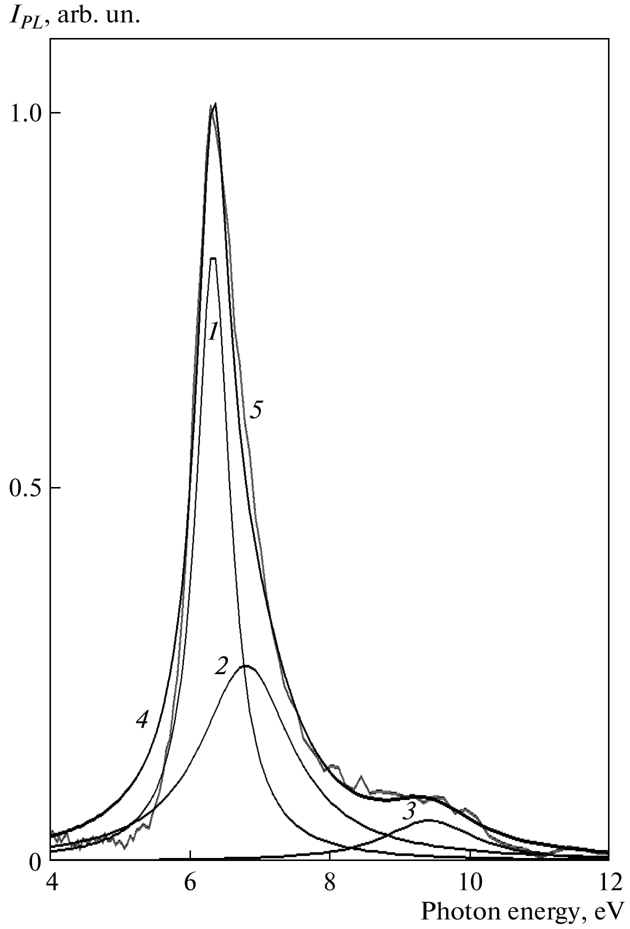

Fig. 4. PL excitation spectra for the 2.7-eV emission for sample No. 22 at $T = 7.2$ K and the results of its decomposition into three Gaussians (thin solid lines *1*–*3*). Bold line *4* shows the sum of these Gaussians *1*–*3* and line *5* is the experimental PL spectrum

Table 3. Results of PLE spectra decomposition into Gaussian components for emission 2.7 eV (sample No. 22 of HfO_2 film after annealing in vacuum)

Component number	Maximum position, eV	FWHM, eV
1	6.33	0.623
2	6.8	1.6
3	9.42	1.74

associated with oxygen divacancies in hafnium oxide. We suppose that the PL increase after annealing in oxygen is a result of a decrease in vacancies/polyvacancies (concentration quenching). The suggested interpretation of the PL and CL spectra is based on the assumption that oxygen vacancies and polyvacancies operate as recombination centers in hafnium oxide. Annealing in the reducing atmosphere (vacuum) brings forth the increase in the oxygen vacancy concentration and the decrease in the PL intensity (the effect of concentration quenching). By contrast, the annealing in oxygen results in a decrease in the oxygen concentration and the PL grows.

The luminescence intensity depends on the concentration of radiative centers as

$$I \sim n_1(N) = \frac{LJN}{LJ + \tau^{-1} + \beta N^{2/3}},$$

where n_1 is the population of the excited level, N is the concentration of luminescence centers, J is the energy density, L is a parameter independent of J, τ is the life time of the excited state, and β is a parameter that

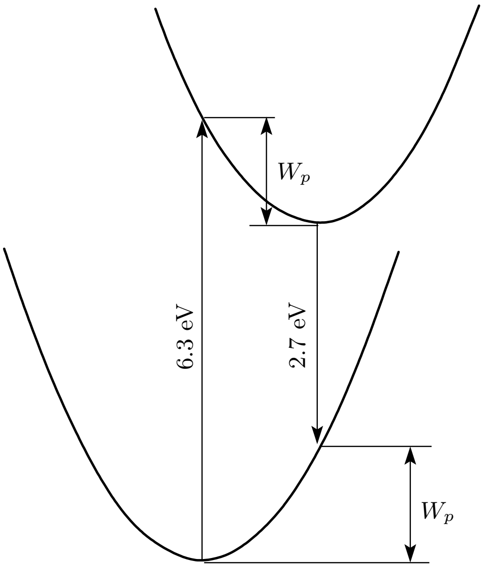

Fig. 5. Configuration diagram for the oxygen vacancy in HfO_2. The lower term corresponds to the ground (occupied) state of the defect, whereas the upper one is for the unoccupied excited state. Arrows show optical transitions at excitation, 6.3 eV, and luminescence, 2.7 eV

determines the probability of energy transfer. Here, β does not depend on the distance between luminescence centers [21].

The dependence of luminescence intensity on the concentration of luminescence centers has a maximum near the concentration value

$$N_{n_1=max} = \frac{LJ + \tau^{-1}}{[\beta(s/3-1)]^{3/s}},$$

where s is a multipolarity factor of a resonant energy transfer. The effect of the PL decrease at exceeding a certain concentration of luminescence centers is called concentration quenching. Earlier, concentration quenching has been observed in YAG doped with rare-earth ions [22].

In other versions, the increase in the PL intensity at annealing in oxygen may be due to a decrease in the concentration of centers that are responsible for nonradiative recombination. This time our data do not allow choosing between these two versions: the concentration increase of PL and the decrease in the concentration of centers responsible for nonradiative relaxation at annealing in oxygen.

The configuration diagram illustrating optical transitions at luminescence in HfO_2 is given in Fig. 5. Excitation corresponds to vertical 6.3-eV arrows directed upwards, whereas radiative relaxation (luminescence) is shown by a downward arrow 2.7 eV. The polaron energy W_p estimated based on this diagram is equal to half the Stokes shift:

$$W_p = (6.4–2.8)/2 = 1.8 \text{ eV}.$$

It is useful to recall that the trap energy determined for HfO_2 from the experiment is 1.4–1.5 eV [23, 24].

We note that the luminescence band centered at 2.6–2.8 eV was observed earlier [16–19]. In accordance with the hypothesis proposed in this paper, this PL band in HfO_2 is due to the oxygen vacancy.

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