Luminescence of intrinsic and extrinsic defects in hafnium oxide films

A. A. Rastorguev, V. I. Belyi, T. P. Smirnova, and L. V. Yakovkina
Nikolaev Institute of Inorganic Chemistry, 3 Lavrentiev Avenue, 630090 Novosibirsk, Russia

M. V. Zamoryanskaya
Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politechnicheskaya 26, St. Petersburg 194021, Russia

V. A. Gritsenko
Institute of Semiconductor Physics, 630090 Novosibirsk, Russia

Hei Wong
Department of Electronic Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
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Both intrinsic and extrinsic defects of hafnium oxide films are investigated based on photoluminescence (PL) and cathodoluminescence (CL) measurements. Instead of using the high-power synchrotron radiation or ArF excimer laser sources, a hydrogen-deuterium lamp (HDL) was used for the PL measurements to avoid the possible generation of active oxygen and hydroxyl ions. Results show that the HDL PL spectra generally agree with those registered using the conventional high-power excitation sources. CL spectra also agree with the PL ones. Narrow emission band at peak energy of 4.0 eV, which is ascribed to the vibronic transition of excited $OH^{\cdot *}$ radical, was found using photoluminescence excitation and at energy of 4.25 eV.

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I. INTRODUCTION

Hafnium oxide is considered as one of the most prospective candidates for high-k replacement of silicon dioxide (SiO_2) in the next generation complementary metal-oxide-semiconductor devices.[1,2] However, there are still several fundamental problems needed to be resolved.[1,2] One of the major issues is the large leakage current in the gate stack of metal-oxide-semiconductor structure due to the structural defects or trap centers in the high-k materials.

According to some theoretical studies,[3,4] electrical and thermal instabilities of hafnium oxide films can be induced by the hydrogen-containing species inherent from the film preparation processes. The precursors used for the chemical vapor deposition (CVD) processes generally contain carbon, hydrogen, and oxygen; thus, water and other by-products may contaminate the films. In the atomic layer deposition (ALD) process, water is used as one of the precursors. Infrared (IR) spectroscopy studies of the hafnia films often detect the presence of the water-related groups.[5] It was further shown that H_2O and OH groups are still detectable even after the film being annealed at 1000 °C for 30 min.[6] However, the effects of those water-related groups are still not fully explored. Some reports indicate that it can change the type of current conduction and can enhance the radiation stability by increasing the amount of OH groups.[4,7,8]

Photoluminescence (PL) is a very sensitive and effective tool for the investigation of electron structure of defect centers. It reflects the presence of the localized states in band gap. The method has also been used to investigate the electron structure of hafnium oxide and hafnium silicate films.[9–12] In these experiments, synchrotron radiation (SR) or excimer laser was used for the luminescence excitation, and it has been found that PL exists in HfO_2, Hf_xO_{2-x}, as well as $HfSi_xO_y$ film. It was further found that the gap energy of those films can vary from 4.2 to 6.8 eV depending on the synthesis conditions.[9,10,13] The H_2O molecules and OH groups in the hafnium oxide films or hafnium silicate have intrinsic defect levels in the band gap.[3,4] Upon light absorption, electrons and holes will be generated. However, the generation of some active oxygen or hydroxyl ions should not be ignored when the SR or excimer laser sources are used. It is well known that H_2O and its dissociations such as OH in excited vibronic state ($OH^{\cdot *}$) may involve in the charge energy transfer in the quenching processes and exhibit emission.[14–29] Emission of $OH^{\cdot *}$ radicals displays itself in x-ray luminescence,[20] photoluminescence,[20,21] sonoluminescence,[22–28] chemiluminescence, and bioluminescence.[29] The $OH^{\cdot}$ radical luminescence in some cases was used as an indicator for the physicochemical processes such as burning and catalysis. It was even used to replace the Hg lamp for producing ultraviolet source.[30] On the other hand, the presence of the broken links on the hafnium oxide surface can generate additional electrons and holes and should be taken into consideration. This work focuses on the investigation of the intrinsic and extrinsic defects in hafnium oxide thin films using luminescence methods. Instead of using conventional high-power source, a hydrogen-deuterium lamp was used as the excitation source to avoid the possible source-induced ion generations.

II. EXPERIMENT

Thin HfO_2 films were deposited with chemical vapor deposition (CVD) method by using hafnium dipivaloilmethanate, $Hf(C(CH)_3COCHCOC(CH)_3)_4$, as precursor. The starting material is an n-type (100) Si substrate. The thickness and refractive index of the films were measured by ellipsometry. The films were then characterized by several analytical

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techniques such as x-ray diffraction analysis, transmission electron, scanning electron microscopes, x-ray photoelectron spectroscopy (XPS), and infrared (IR) spectroscopy.

Photoluminescence measurements were conducted based on an open architecture.[32] A 400 W hydrogen-deuterium lamp (HDL), having a light intensity of 5–6 orders less than those of SR or ArF laser sources, was used as the radiation source. The light was filtered by a monochromator before being focused on the sample. The PL radiation was analyzed by another monochromator of the same type. Grating replicas for the monochromator were so selected that they have maximum reflection in the range of 4.13–6.20 eV. Operating range of the selected replicas for excitation monochromator as well as for luminescence monochromator covers the range over 2.5–6.5 eV with maximum light intensity in the first order of diffraction at 4.96 eV. Other optical components such as condensers, lenses, and quartz optical waveguides were so chosen that they have the largest transmission in the near UV region and have minimal level of luminescence. A multialkali photocathode low-noise photomultiplier (PhEU-100) was used for detecting the luminescence. The intrinsic sensitivity range of the photomultiplier is 1.5–6.5 eV. A program is developed to integrate the collected current in a window varying from 0.3 to 120 s. Photoluminescence excitation (PLE) was also conducted with the aid of lumogen-640 source, which has a constant quantum yield ranging from 2.25 to 6.20 eV.[33,34] Hydrogen lines from Balmer light sources were used for calibrating the monochromators. All PL measurements were performed in atmosphere and at room temperature.

To expand spectral range of the PL, cathodoluminescence (CL) measurement was also conducted. This work was done by attaching an optical spectrometer to a CAMEBAX electron microprobe analyzer.[35] The depth of CL generation was about 100 nm. The spectra were obtained at an energy of 5 keV and a beam current of 15 nA. The temporal delay and exposure duration are 200 ms and 0.1 s, respectively.

III. RESULTS AND DISCUSSION

It was shown that the hafnium oxide films obtained from $Hf(dpm)_4$ on silicon substrates consist of both amorphous and crystalline phases.[31] The crystalline phase is monoclinic and with nanocrystals (size in the range of 3–5 nm). An amorphous silicate interfacial layer forms between the silicon substrate and bulk HfO_2 during the film deposition. XPS measurements indicate that the bulk O/Hf ratio is about 2. Figure 1 depicts the infrared spectrum of the film synthesized at 600 °C. Gaussian deconvolution of the IR peak in the 3000–3600 cm^{-1} band is also illustrated in the inset of Fig. 1. Absorptions due to water (3450 cm^{-1}) and OH groups (3250 cm^{-1}) are obvious.[5,6] The 1500–1700 cm^{-1} absorption band is due to the organic fragments and OH groups, which arise from the decomposition of the precursors during the deposition. The 1500–1700 cm^{-1} absorption band vanishes after 800 °C annealing in atmosphere for 60 min.

Figure 2 shows PL spectra of HfO_2 film of as deposited (trace 1) and annealed at 800 °C (trace 2). Two wide bands with maxima at 4.13 and 3.35 eV are observed in the spectrum of unannealed film. The bands show maximum intensity for excited radiation with the energy in the range of 5.77–5.90 eV. The narrow bands in the spectrum are Balmer series of the HDL emission. Thermal annealing results in the redistribution of the PL intensity, peak energy shift, and variation in the value of the full width at half maximum (FWHM). The intensity of spectrum 2 rises as a result of the significant enhancement of luminescence band at peak energy of 4.43 eV, and the 4.13 eV peak is almost invisible. We believe that these changes are due to the crystal structure ordering after the annealing. Similar PL changes were observed by increasing the deposition temperature from 400 to 1200 K in the ALD process.[9,10] The band centered at 4.43 eV is a characteristic of HfO_2 monoclinic crystalline

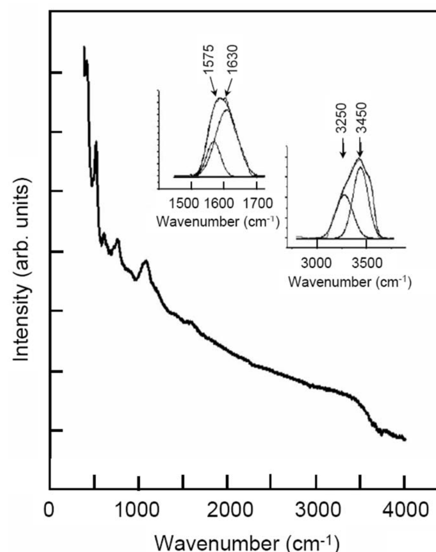


FIG. 1. Infrared spectrum of HfO_2 film deposited at 600 °C. Gaussian fits of the spectrum in the 1400–1700 and 3000–3500 cm^{-1} bands are shown in the insets.

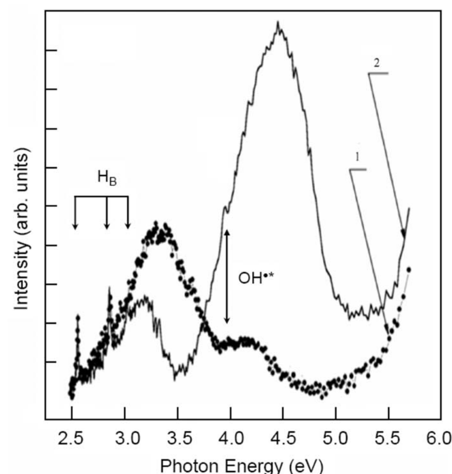


FIG. 2. Photoluminescence spectra of as-deposited sample (trace 1) and sample with 800 °C annealing for 30 min (trace 2). The excitation energy is 5.8 eV.

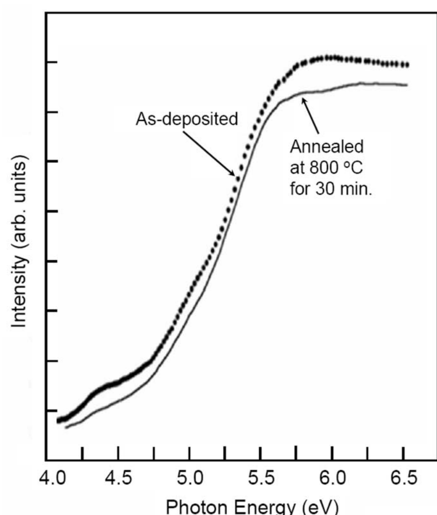


FIG. 3. Photoluminescence excitation spectra of as-deposited HfO_2 film and sample with 800 °C annealing for 30 min.

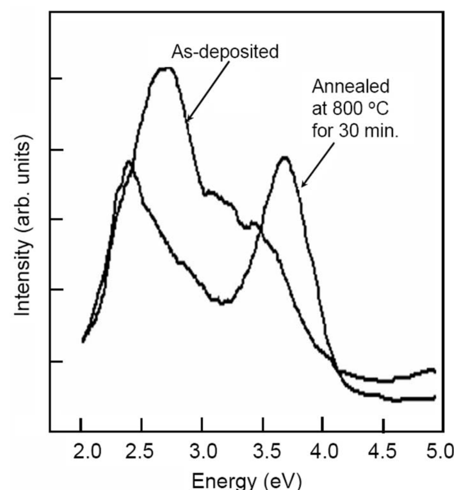


FIG. 4. Cathodoluminescence spectra of as-deposited HfO_2 film and sample annealed at 800 °C for 30 min.

phase. The nature of this band was attributed to self-trapped exciton (STE). STE is not found in the high-symmetrical oxides, such as MgO and CaO which have branched structure of the anionic excitons. It is typical for oxides with low local symmetry of oxygen center,[36,37] such as SiO_2, α-Al_2O_3, $YAlO_3$, $Y_3Al_5O_{12}$, and HfO_2, to have the same property. The change of PL spectra was also attributed to the change of charged states as the main defects in high-k materials are believed to be the oxygen vacancies.[9,10]

Figure 3 shows the PLE spectra with excitation energy of 3.75 eV. The PLE spectra are weak self-descriptiveness at the absorption band edge for oxide systems.[38] The spectra for the annealed and unannealed films differ at points of inflection, and the energy shift of the annealed sample is small. Considerable difference in the energy between the excitation and emission is mainly due to the Stokes shift. The difference between the PLE spectra is negligible, and it shows itself in the intensity of the feebly marked bands in the ranges of 5.5–6.0, 4.75–5.25, and 4.0–4.75 eV.

The PLE spectra shown in Fig. 3 are qualitatively similar to the absorption spectra of amorphous Hf_xO_{2-x} films.[12] Considering the PLE spectra of hafnium oxide and hafnium silicate films with different oxygen concentrations, correlations amongst the energy shift, intensity change, and film stoichiometry were found. Instead, the present experiment observed a good coincidence of PLE and the PL discrepancy for as-deposited and annealed samples. It suggests that the energy transport efficiency in these samples was changed. Hafnium oxide has vacancy concentration comparable with the concentration of the lattice anionic centers. That is, the "vacancy zone" may be formed below the bottom of conduction band. The PL intensity due to the electron transits from valence band to O-vacancy levels may be comparable to that due to the band-to-band transitions. Hence, the short-wave absorption edge (excitation spectrum) can be attributed to transition from valence band to the O-vacancy levels and conduction band as well. The position of the absorption edge should follow the position of the O-vacancy levels with respect to HfO_{2-x} valence band. This explanation agrees with the results reported by Ito *et al.*[11,12] In their works, the hafnium silicate shows PL spectrum similar to that of hafnium oxide. They suggest that the PL in $Hf_xSi_{(1-x)}O_y$ is most likely due to the carrier recombination in different localized states. Thus, the PL spectra in Fig. 2 should be a superposition of PL spectra in HfO_2 and in hafnium silicate. However, the contribution of hafnium silicate should be quite insignificant as hafnium silicate layer is about 2 nm thick only.

The structure, chemical composition, phase, and defect composition of the hafnium oxide films depend both on the deposition and annealing conditions.[9–12,39,40] It was found that the position of the Fermi level also varies with the deposition and annealing conditions.[41] However, the energy gap between the Fermi level and conduction band edge is less then that between Fermi level and valence band edge. Hence, the peak position of PL spectra should be slightly different for sample prepared with different precursors and annealing conditions.[42]

Cathodoluminescence (CL) measurements on the samples were also performed to probe the defect centers in a wider energy range. As shown in Fig. 4, CL bands with peaks at 2.35, 2.7, and 3.7 eV are found. Similar results were also reported previously.[9,11] The STE-related band peaked at 4.45 eV in the PL spectra is absent in the CL spectra. The band can be due to the removal of electronic states responsible for this band by the electron beam and by the heat generated during the CL excitation. It should be emphasized that our PL and CL results are qualitatively similar to each other. In addition, they are also similar to PL spectra of HfO_2 films obtained using different precursors and agree with the calculated results for the energy bands and local states position.[43–46]

As shown in Fig. 2, trace 2 has a weak peak in the range of 3.97–4.05 eV, and the peak energy is around 4.4 eV. The band, in fact, is due to the 4.0 eV peak with a FWHM of 0.08 eV, which is shown in Fig. 5. Comparing the two spectra in Fig. 3 with the high energy (>4.0 eV) portion of the spectrum for the annealed sample in Fig. 5, their major fea-

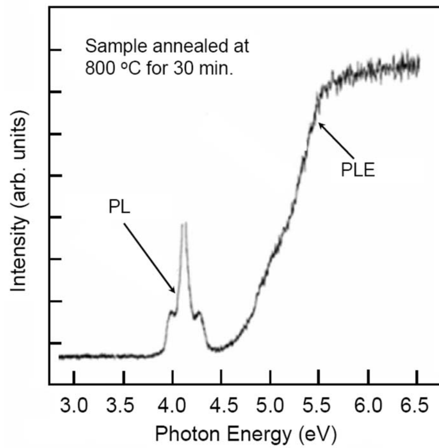


FIG. 5. Photoluminescence spectrum of hydroxyl (OH^{*}) corresponding to the $A\,^2\Sigma^+ \leftrightarrow X\,^2\Pi_i$ transition under 4.25 eV excitation and PLE spectrum of HfO_2 film annealed at 800 °C for 30 min.

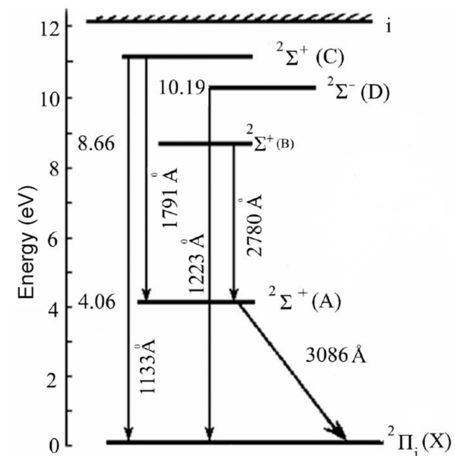
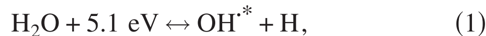


FIG. 6. Illustration of a simplified transition scheme for level deactivation of OH groups.

tures are similar. The major difference is that the 4.25 eV peak in Fig. 5 is narrower. We believe that this peak is due to OH groups in the films which have been confirmed by the IR measurement as depicted in Fig. 1.

The PL intensity of the band peaked at 4.0 eV increased remarkably by using 5.1 eV excitation. This fact is important for analyzing the power transfer mechanisms. The PL generated from the wide excitation spectrum peaked at 5.1 eV, which locates near the bottom of the conduction band, does not only support the existence of the vacancy zone but also suggests that the involvement of $OH^{\cdot *}$ radical as the excitation energy also matches the bond breaking energy of the H–OH bond in water molecule. The decomposition of water molecule in HfO_2 films upon photon absorption can be described by



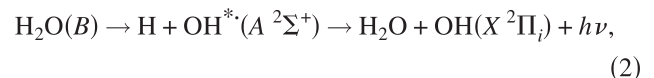
$$H_2O + 5.1\ \text{eV} \leftrightarrow OH^{\cdot *} + H, \quad (1)$$

where $OH^{\cdot *}$ is radical in electronic-excited state.

It is further noted that the 4.75–5.2 eV shoulder for the unannealed sample (see Fig. 3) is more obvious than the annealed sample (Fig. 5). We are inclined to believe that the observed luminescence center is due to the amorphous phase of hafnium oxide. This luminescence center still remains in the high-temperature annealed sample (see Fig. 5). This center should locate in amorphous phase surrounding the nanocrystals created by the thermal treatment.

Further evidences for supporting the assignment of the 4.0 eV PL band and 4.25 eV PLE band (see Fig. 5) to the OH groups can be found in some other experiments.[14–16,47] It is well known that the excited term $A\,^2\Sigma^+$ corresponds to an energy of 4.3 eV for the OH group. The main state of OH groups complies with $X\,^2\Pi_I$ term. The vibronic transition between $A\,^2\Sigma^+$ and $X\,^2\Pi_I$ is possible and gives rise to the luminescence. However, apart from ice, no report for the UV radiation from OH^{*} groups can be found. However, some indirect evidences for OH induced PL were available in large band gap oxides.[48,49] Defect centers in high-purity silica glasses were investigated using 7.9 eV photon excitation, and we observed a band at 4.25 eV.[48] Noncentral spectrum of this band was also observed with a shoulder at an energy of 4.0 eV. Theses observations were attributed to the STE effect.[48] Cathode luminescence was conducted for SiO_2/Si stack with known OH content of 2400–3000 ppm and 1–2 ppm,[49] and CL band with peak energy of 4.25 eV was observed in SiO_2 with large amount of OH groups.[49]

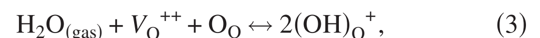
The narrow 4.0 eV radiation was also found in PL spectra of some gases.[14–16] It was identified as the vibronic transition of $A\,^2\Sigma^+ \leftrightarrow X\,^2\Pi$ in the $OH^{\cdot *}$ radical. In condensed matters, this transition is observed at lower energies.[20] The presence of this transition in the water solutions was confirmed by many investigations.[21–28] These works suggest that the narrow line radiation with energy in the range of 3.6–4.4 eV is due to the deactivation of the excited H_2O^{*} molecules. This effect can be described by the following expression:



$$H_2O(B) \rightarrow H + OH^{*\cdot}(A\,^2\Sigma^+) \rightarrow H_2O + OH(X\,^2\Pi_i) + h\nu, \quad (2)$$

where $h\nu$=3.6, 3.9, 4.0, or 4.4 eV. The narrow bands were also assigned to the appearance of $H_2O^{*}\cdot M$ excimer (M is gas atom or molecule of water),[22] and the wide band over the range of 2.0–3.25 eV can be connected with the deactivation of vibration-excited H_2O^{*} molecules.

Simplified processes for the levels deactivation of OH group (only electron states are shown) are illustrated in Fig. 6.[30,47] The lower resonant state $^2\Sigma^+(A)$ of OH group with excitation energy of 4.06 eV gives rise to the radiation band with peak energy of 4.0 eV. For hafnium oxide, we assume that the appearance of the STE is most likely due to the presence of the oxygen vacancies and OH groups. Water can enter into the films during the film deposition according to the following reaction:



$$H_2O_{(gas)} + V_O^{++} + O_O \leftrightarrow 2(OH)_O^{+}, \quad (3)$$

where V_O^{++} is oxygen vacancy and $(OH)_O^{+}$ is hydroxide with oxygen having a single negative charge; thus, it is positively charged relative to the lattice location that is previ-

ously occupied by a double negatively charged oxygen anion.

Water may also be incorporated into the film by

$$H_2O_{(gas)} + O^{2-}_{(lattice)} \rightarrow OH^{-}_{(lattice)} + OH^{-}_{(interstitial)}, \quad (4)$$

where $O^{2-}_{(lattice)}$ is from the oxygen site in the lattice, and $OH^{-}_{(lattice)}$ and $OH^{-}_{(interstitial)}$ are OH^- group in lattice and interstitial positions, respectively. As the formation of lattice OH^- bond in Eq. (4) requires significant relaxation of the lattice oxygen, it is less favorable when compared to the mechanism via the oxygen vacancy as given in Eq. (3).

Since the OH anions in the oxygen lattice points are loosely coupled with hydrogen atoms, they can hop over the defects. This assumption agrees with the works for ALD deposition of HfO_2 films with water containing system.[4,8] To sum up, the hydroxyl radical $OH^{*\cdot}$ should be the most likely emission source responsible for luminescence band with peak energy at 4.0 eV. In HfO_2 films, 4.25 eV photon excitation is enough for generating $OH^{*\cdot}$ radicals for H_2O molecules or OH groups containing film.

The absorption energy for H_2O molecules is closed to the band-to-band transition energy. This energy is able to set the water into excited state (H_2O^*) and result in the relaxation and radiation. It can also result in the dissociation of the water molecules forming O^*, H^*, OH^-, and OH^+ fragments. Excitation of OH group results in the formation of excited hydroxyl radical; when the excited radicals relax to the main state, radiative luminescence resulted. The hydroxyl radical can be readily converted into OH^- via the reaction $OH^{\cdot} + e = OH^-$. The simplest way for hydroxyl radical neutralization is the interaction with charged vacancies.

IV. CONCLUSION

Both intrinsic and extrinsic defects in hafnium oxide films are explored by using luminescence methods. The hafnium oxide films were deposited using CVD method with hafnium dipivaloilmethanate as the precursor. Photoluminescence measurements were conducted using hydrogen-deuterium lamp as the light source. Results show that the major features in the cathodoluminescence spectra agree with those in the PL ones. Narrow emission band at peak energy of 4.0 eV, which is ascribed to the vibronic transition of excited $OH^{\cdot *}$ radical (via $A\ ^2\Sigma^+ \leftrightarrow X\ ^2\Pi$), was found using photoluminescence excitation with energy of 4.25 eV. In addition, regardless of slight variations in the peak energies as a result of different band gap values and Fermi levels, similar water-related PL features are common for samples prepared at different precursors and annealing temperature.

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