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# The Optical Absorption and Photoluminescence Characteristics of Evaporated and IAD HfO<sub>2</sub> Thin Films

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**Abstract:** HfO<sub>2</sub> thin films are extensively applied in optical coatings and microelectronic devices. However, film defects, which are vital to the performance of the thin films, are still under intense investigation. In this work, the absorption, photoluminescence, and crystallization characteristics of HfO<sub>2</sub> films prepared by electron-beam evaporation and ion-assisted deposition are investigated in detail. Experimental results showed that high-temperature thermal annealing in air resulted in a reduced absorption coefficient, an increased bandgap width, and an increased degree of crystallization. After thermal annealing, an absorption shoulder near 5.8 eV was caused by excitons in the films, which were independent of oxygen vacancy defects and crystallization. Under 6.4 eV (193 nm) laser excitation, the photoluminescence spectrum showed five emission peaks for HfO<sub>2</sub> films both with and without thermal annealing. The emission peak near 4.4 eV was generated by the self-trapped exciton, and the peak near 4.0 eV was related to the OH group in the film. The oxygen vacancy defect-induced absorption of HfO<sub>2</sub> films in a broad spectral range significantly increased when HfO<sub>2</sub> film was re-annealed in Ar gas after first being annealed in air, while the photoluminescence spectrum showed no significant change, indicating that the emission peaks at 2.3, 2.8, and 3.4 eV were not related to oxygen vacancy defects.

**Keywords:** HfO<sub>2</sub> thin films; optical absorption; photoluminescence; electron-beam deposition; ion-assisted deposition (IAD)

# 1. Introduction

 $HfO_2$  is a dielectric material with a wide band-gap, high dielectric constant, high refractive index, and high thermal stability that is widely used in the preparation of optical coatings and microelectronic films [1–3]. For optical thin-film applications, it is widely used in the preparation of optical films with low absorption and high damage threshold for high-power pulsed laser systems [4–8]. For microelectronic applications,  $HfO_2$  is the most promising alternative to  $SiO_2$  in metal-oxide-semiconductor (MOS) microelectronic devices [9]. Studies have shown that there are various defects in  $HfO_2$  films, such as oxygen vacancies and charge traps [9–16]. These defects affect the absorption loss and laser damage threshold of the optical coatings, and the leakage current and carrier mobility of the MOS. The investigation of the defects in  $HfO_2$  films is therefore of great significance for the preparation of high-performance laser optical thin films and microelectronic films.



Defects in HfO<sub>2</sub> films are difficult to measure directly. When defects are present, localized states are generated between the valence band and conduction band. When electrons at lower energy levels absorb photon energy, they may jump to higher energy levels, and when electrons at higher energy levels return back to lower energy levels via radiation relaxation, photon emission may occur. Therefore, the optical absorption spectrum and the photoluminescence emission spectrum of  $HfO_2$  films can be used to analyze the defect states in the films. There has been some past research studying both the absorption and photoluminescence of HfO<sub>2</sub> optical films. Ciapponi et al. found that HfO<sub>2</sub> films prepared by electron-beam deposition (EBD) showed significant luminescence, but the luminescence of ion-assisted films could not be distinguished from the uncoated substrate [15]. Papernov et al. studied the optical properties of oxygen vacancies in HfO<sub>2</sub> thin films by absorption and luminescence spectroscopy [13]. They only investigated the luminescence for EBD films since no measurable luminescence was detected in the films prepared by ion-beam sputtering (IBS). In this paper, we present the absorption, photoluminescence, and crystallization properties of two kinds of HfO<sub>2</sub> films prepared by EBD and ion-assisted deposition (IAD), respectively. The optical absorption and photoluminescence characteristics of the films as deposited and after thermal annealing were investigated in detail in combination with the crystallization of the films, and the causes of the films' absorption and photoluminescence were analyzed. These results will be very helpful in the preparation of high-performance HfO<sub>2</sub> films with low absorption and high damage threshold that are essential for high-power laser applications.

#### 2. Materials and Methods

EBD and IAD are the major techniques for preparing low-absorption  $HfO_2$  optical films [16]. Both techniques were employed to prepare the  $HfO_2$  film samples in our experiment. The samples were prepared with a Syruspro 1110 coating plant from Leybold Optics, Alzenau, Germany. The raw material for the coating was a high-purity hafnium metal with purity higher than 99.9%, which was oxygenated to form the HfO<sub>2</sub> films during the coating process. Two sets of samples were prepared by EBD and IAD, respectively. The starting vacuum pressure for deposition was  $3 \times 10^{-6}$  mbar. The film deposition rate was 0.2 nm/s, and the substrate temperature was 120  $^\circ$ C. The O<sub>2</sub> flow rate was 45 sccm (standard cubic centimeters per minute). The ion source used for the IAD process was an advanced plasma source (APS, Leybold Optics, Alzenau, Germany) operated with 100 V bias voltage and 50 A beam current. The deposition rate and film thickness were controlled by a quartz crystal. The transmittance and reflectance spectroscopy of the film samples were measured with a Lambda 950 spectrophotometer (Pekin Elmer, Waltham, MA, USA). The photoluminescence (PL) spectra of the film samples were excited by an ArF excimer laser at 193 nm (IndyStar 1000, Coherent, Santa Clara, CA, USA). The laser repetition rate was 100 Hz, and the pulse width was 10.5 ns. The excimer laser beam was approximately normally incident onto the sample surface. PL was collected at a 45° detection angle from the incident laser beam with a lens coupling the PL emission into an optical fiber that was connected to the entrance of a high-resolution spectrometer (iHR320, Jobin Yvon, Paris, France, grating grooves: 300–2400 line/mm, spectral resolution: 0.79–0.02 nm) equipped with an intensified charge-coupled device (ICCD). A 193 nm filter was placed in front of the entrance of PL collection optics to avoid interference from the 193 nm laser-excited fluorescence of the optical fiber. The samples were placed inside an adiabatic chamber purged with high-purity  $N_2$  gas. The measurements were performed at room temperature and in an  $N_2$  atmosphere to avoid the influence of the oxygen absorption of the 193 nm excitation on the PL measurements. The XRD of the film was performed with a X'Pert3 Powder X-ray diffractometer (XRD, PANalytical, Almelo, The Netherlands) with a  $2\theta$  scan range of  $10^{\circ}$ – $70^{\circ}$  and a step of  $0.03^{\circ}$ . Thermal annealing was carried out in a tube furnace with a maximum temperature of 400 °C. The furnace temperature was first increased linearly from room temperature to the treatment temperature (400 °C) in one hour, then stabilized at 400 °C for 1 h, and then decreased back to room temperature (around 25 °C). High-purity Ar gas (>99.999%) was introduced into the tube furnace when needed. The substrates used for depositing the  $HfO_2$ 

films were fused silica and silicon wafers, respectively, with diameters of 25 mm. The film coated on fused silica was used for transmittance and reflectance measurements in the wavelength range of 190–800 nm and for XRD. Considering that fused silica has a strong photoluminescence under 193 nm laser irradiation and silicon substrate does not [17], the  $HfO_2$  film coated on silicon was used to measure the PL spectrum in order to avoid the influence of the substrate emission.

## 3. Results and Discussion

#### 3.1. Optical Absorption

The EBD and IAD HfO<sub>2</sub> film samples presented a significantly lower transmission at wavelengths shorter than 250 nm compared to bare fused-silica substrate, as presented in Figure 1a, indicating that the HfO<sub>2</sub> films had a strong absorption at the short wavelength range, as presented in Figure 1b. After thermal annealing at 400 °C in air, the transmittance in the short wavelength range improved with decreasing absorption. In the meantime, the refractive index and physical thickness of the films were calculated via a method proposed by Swanepoel [18]. The EBD and IAD films had refractive indices of 1.93 and 2.05 at a wavelength of 400 nm and physical thicknesses of 252 and 227 nm, respectively. After annealing, the refractive indices increased to 1.98 and 2.06, and the thicknesses reduced to 245 and 226 nm, respectively. Unlike the ideal crystal, there were many mesoscopic voids in both the EBD and IAD HfO<sub>2</sub> films. Thermal annealing reduced the void density and volume in the film samples, increasing the refractive index and thickness of the IAD film were smaller than that of the EBD film. On the other hand, the weak absorption of the HfO<sub>2</sub> films at a wavelength greater than 250 nm was calculated by the method proposed by Swanepoel [18]. The absorption coefficient  $\alpha$  of a strong absorption at a wavelength shorter than 250 nm was calculated by the formula [12]:

$$T = (1 - R)\exp(-\alpha d) \tag{1}$$

where *T* and *R* are the transmittance and reflectance of the film, respectively, and *d* is the physical thickness of the film. The relationship between the calculated absorption spectrum presented in Figure 1b shows that the IAD film had a higher absorption than the EBD film. After annealing in air, the absorption of the  $HfO_2$  film at a photon energy level higher than 5.5 eV (225 nm) was significantly reduced, which could be related to the reduction of oxygen vacancy defects in the film.



**Figure 1.** (a) The transmission of the prepared  $HfO_2$  film samples and the substrate; (b) The absorption of the prepared  $HfO_2$  film samples. EBD: electron-beam deposition; IAD: ion-assisted deposition; Sub: bare fused-silica substrate.

As HfO<sub>2</sub> film is an indirect bandgap material [12,19], the absorption coefficient  $\alpha$  related to band edge and the photon energy satisfy the following formula:

$$\alpha h v = B \left( h v - E_g \right)^2 \tag{2}$$

where hv is the energy of the incident photon, *B* is the absorption edge width parameter, and  $E_g$  is the band gap.

The optical band gap width  $E_g$  of the HfO<sub>2</sub> film could be determined by the Tauc patterning method, and the results are shown in Figure 2 and Table 1. The bandgap data were consistent with the reported values of 5.25–5.8 eV [14]. The smaller bandgap of the IAD film compared to the EBD film may be related to the increase of the microscopic defects in the film caused by ion bombardment. The absorption spectrum of the EBD film after thermal annealing showed a significant shoulder around 5.8 eV. This shoulder appeared after annealing in air, indicating that it was not caused by oxygen vacancies. Hoppe et al. showed the same results and thought it was intrinsic to monoclinic HfO<sub>2</sub> [12], and Aarik et al. indicated it might have originated from excitonic absorption [19].



Figure 2. Tauc patterning calculated from the absorption spectra of (a) EBD and (b) IAD thin films.

**Table 1.** The optical bandgap  $E_g$  of the HfO<sub>2</sub> films.

Coating Method	As-Deposited (eV)	Annealing in Air (eV)	Re-Annealing in Ar (eV)
EBD	5.56	5.66	5.64
IAD	5.49	5.55	5.54

### 3.2. Crystalline Structure

A comparison of the crystalline structures of the  $HfO_2$  films before and after thermal annealing (as shown in Figure 3) indicated that the EBD film was amorphous and the monoclinic-phase  $HfO_2$  appeared after annealing. The as-deposited IAD film contained a monoclinic phase, and the diffraction peak became stronger after annealing. According to the Scherrer formula, the crystal size D (nm) can be evaluated as:

$$D = K\gamma / (B\cos\theta) \tag{3}$$

where K = 0.89 is the Scherrer constant, *B* is the half-maximum width of the diffraction peak (radians),  $\theta$  is the diffraction angle, and  $\gamma$  is the X-ray wavelength (0.154056 nm). Defects may have contributed to line broadening and thus caused errors when we used the Scherrer formula. For a rough estimation, we ignored the error and directly used the Scherrer formula to calculate the crystallite sizes of thin films. The crystallite sizes of the EBD and IAD HfO<sub>2</sub> films after annealing were 14.90 and 14.40 nm, respectively. The small difference in crystallite size but the significant difference in the absorption shoulder near 5.8 eV after annealing for both the EBD and IAD films, as well as the fact that no absorption shoulder was present for as-deposited and partially crystallized IAD films, clearly indicated that the absorption shoulder was not related to the film crystallization.



Figure 3. The XRD patterns of the prepared HfO<sub>2</sub> films.

# 3.3. Photoluminescence

PL is a sensitive and effective tool for the defect characterization of films. In our experiment, a 193 nm (6.4 eV) excimer laser was used as the excitation source for PL measurements. The laser energy density was 2 mJ/cm<sup>2</sup>. The measured PL spectra of the as-deposited and thermally annealed EBD and IAD HfO<sub>2</sub> films are presented in Figure 4. The PL spectra could be decomposed into five PL bands, with corresponding peak positions of approximately 2.3, 2.8, 3.4, 4.0, and 4.4 eV, respectively, as shown in the insets of Figure 4. The PL bands may have originated from self-trapped excitons, radicals, defects, etc. For both the EBD and IAD samples in general, annealing caused increases in peak intensities. The peak intensity increase was much more significant for the EBD film than for the IAD film, which was believed to be related to the annealing-induced crystallization. As the as-deposited IAD film was already partially crystallized, the annealing-induced peak intensity change was relatively small.



**Figure 4.** Photoluminescence (PL) spectra of (**a**) the EBD  $HfO_2$  films and (**b**) the IAD  $HfO_2$  films, excited by 193 nm laser irradiation. The insets are the multi-band fits.

In recent years, PL of HfO<sub>2</sub> film has been intensively investigated [13,15,19–23]. Aarik et al. [19] assigned the PL band near 4.4 eV to self-trapped excitons, which caused the absorption shoulder near 5.8 eV. Our absorption and PL measurements confirmed the correlation between the 4.4 eV PL band and the absorption shoulder near 5.8 eV. From Figures 1 and 4, thermal annealing induced the obvious absorption shoulder near 5.8 eV and a significant increase in PL intensity at 4.4 eV for the EBD film, while the influence of annealing on the absorption shoulder near 5.8 and the 4.4 eV PL band of the IAD film was much less significant. For the PL band near 4.0 eV, Rastorguev et al. [20] correlated it to the OH radical in the film. Our experimental results support this assignment. From Figures 1 and 4, thermal annealing induced a smaller change in the refractive index for the IAD film than for the EBD film, which indicated a smaller change in H<sub>2</sub>O content for the IAD film than for the EBD film, as well as

a smaller change in PL intensity near 4.0 eV. On the other hand, the assignments for the 2.3–3.4 eV PL bands of  $HfO_2$  film are still disputable: Kiisk et al. [23] and Aarik et al. [19] assigned them to oxygen vacancy defects, while Ito [21] studied  $HfO_2$  and  $ZrO_2$  with different oxygen contents and concluded that these PL bands were independent of impurities, oxygen vacancies, and interface defects. It was suggested that these PL bands were most likely due to the radiative recombination between localized states at the band tails.

To investigate the correlation between PL and the oxygen vacancy defects in HfO<sub>2</sub> films, the sample annealed in air was re-annealed under an Ar gas environment in a tube furnace. The annealing process was the same as in air in order to create only oxygen vacancy defects in the film. After re-annealing in Ar gas, the transmittance of the HfO<sub>2</sub> film in the range of 190–400 nm was significantly reduced (Figure 5a). The film absorption (Figure 5b) showed that the oxygen vacancy defects led to an absorption increase over a wide spectral range of 4.0–6.5 eV, and the bandgap of the film was also slightly reduced (Table 1). The changes of the 2.3–3.4 eV PL bands were very small, as presented in Figure 6, indicating that these PL bands were not related to oxygen vacancy defects, in opposition to Kiisk and Aarik's assumptions [19,23]. Therefore, their assignments need further investigation.



**Figure 5.** The (**a**) transmission and (**b**) absorption of EBD HfO<sub>2</sub> films before and after annealing under Ar gas.



**Figure 6.** The PL spectra of the EBD  $HfO_2$  film before and after re-annealing in Ar gas, excited by 193 nm laser irradiation.

# 4. Conclusions

In summary, absorption and photoluminescence measurements were employed to investigate defects in EBD and IAD HfO<sub>2</sub> films widely employed in optical coatings and microelectronic devices, which were of great significance for understanding the laser damage mechanism of optical films for high-energy laser applications and the performance improvement of MOS. Experimental results

showed that high-temperature thermal annealing in air reduced the absorption of HfO<sub>2</sub> films while re-annealing in Ar gas significantly increased the absorption, demonstrating that the absorption loss of the film was closely related to the oxygen vacancy defects. The PL spectra of the HfO<sub>2</sub> films showed five bands at approximately 2.3, 2.8, 3.4, 4.0, and 4.4 eV. The experimental results confirmed the assignments of 4.4 and 4.0 eV PL bands to self-trapped excitons and the OH radical, respectively, but refuted the assignments of 2.3–3.4 eV PL bands to oxygen vacancy defects. Further research on correlation between the photoluminescence and localized states of the film is still needed.

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