Journal of the Korean Ceramic Society
Vol. 53, No. 5, pp. 563~567, 2016.

http://dx.doi.org/10.4191/kcers.2016.53.5.563

# Structural and Optical Properties of $HfO_2$ Films on Sapphire Annealed in $O_2$ Ambient

**Jong-Chan Park*, Yung-Sup Yoon*, and Seong-Jun Kang**,†**

**Department of Electronic Engineering, Inha University, Incheon 22212, Korea*
***Department of Electrical and Semiconductor Engineering, Chonnam National University, Yeosu 59626, Korea*

(Received July 12, 2016; Revised August 22, 2016; Accepted August 24, 2016)

**ABSTRACT**

The structural properties of $HfO_2$ films could be improved by thermal treatment owing to their crystallization. We deposited $HfO_2$ films on sapphire by radio frequency (RF) magnetron sputtering, whose base vacuum pressure was lower than $4.5 \times 10^{-6}$ Pa, RF power was 100 W, working temperature was 200°C, working pressure was 3 mTorr, and the density of the active gas (Argon) was 20 sccm. After depositing the $HfO_2$ films, the samples were thermally treated by rapid thermal annealing (RTA) in $O_2$ ambient at different temperatures. Subsequently, the measured physical properties (structural, morphological, and optical) indicated that the crystallite size, refractive index at a wavelength of 632 nm, and packing density increased with rising temperatures. In particular, an $HfO_2$ film thermally treated at 800°C in $O_2$ ambient had the highest refractive index of 2.0237 and packing density of 0.9638. The relation between optical and structural properties was also analyzed.

***Key words : $HfO_2$, Thin film, High-k, Passivation, Sputtering***

## 1. Introduction

With the increasing degree of integration of electronic devices in recent years, their sizes have become progressively smaller. Consequently, the thickness of gate oxide of metal-oxide-semiconductor field effect transistors (MOSFETs) became small, inducing tunneling current.[1-3] To avoid this effect, research has been conducted to replace conventional $SiO_2$ gate oxide materials with hafnia ($HfO_2$), which has a high dielectric coefficient.[1-5]

In addition to displaying a high dielectric coefficient, $HfO_2$ possesses a wide band gap, high refractive index, distinguished thermal and mechanical stability, excellent adhesiveness, and low stress.[6,7] It is necessary to study how to apply $HfO_2$ to state-of-the-art semiconductor devices. Research is currently being conducted for applications such as optical coating requiring a high damage threshold, optical filter, beam splitter, non-reflective coating, and phase-shifting mask.[7-9]

Owing to its dielectric property, the application of $HfO_2$ in electrical devices has been studied often, but its use in optical applications has been insufficiently described. Therefore, this study focuses on the optical properties of $HfO_2$, investigating the variation of its structural and optical characteristics after post-deposition annealing in $O_2$ ambient, and the relationship between them.

†Corresponding author : Seong-Jun Kang
E-mail : ferroksj@chonnam.ac.kr
Tel : +82-61-659-7317 Fax : +82-61-659-7319

## 2. Experimental Procedure

Ultrasonic cleaning was used for eliminating the particles that could degrade the properties of thin films deposited on the sapphire substrates. These substrates were cleaned in acetone, isopropyl alcohol, and de-ionized water for about 15 minutes, respectively. Subsequently, 10 minutes of ultrasonic cleaning were again carried out in new de-ionized water. The substrates were then rinsed with de-ionized water and dried out by $N_2$ gas.

After the cleaning, $HfO_2$ thin films were deposited by radio frequency (RF) magnetron sputtering using a two-inch-diameter sintered ceramic target (Cerac, purity 99.99%). RF magnetron sputtering was carried out following the depositing conditions of $HfO_2$ films presented in Table 1. Before the depositing process, pre-sputtering was conducted in plasma for 10 minutes.

For the crystallization of $HfO_2$, the films were thermally treated by rapid thermal annealing (RTA) at 400, 600, and 800°C in $O_2$ ambient for approximately 120 seconds.

The structural and optical properties of the $HfO_2$ films

**Table 1.** Depositing Conditions of the $HfO_2$ Films

| | |
|---|---|
| Base vacuum pressure | $4.5 \times 10^{-6}$ Pa |
| RF power | 100 W |
| Active gas density | 20 sccm |
| Working pressure | $3 \times 10^{-3}$ Torr |
| Substrate temperature | 200°C |
| Depositing time | 20 minutes |

were analyzed. Structural properties, such as crystallinity and crystallite size, were measured by X-ray diffraction analysis (HR-XRD, Xpert-pro, MRD). Morphological properties, such as surface roughness and their configurations, were analyzed by atomic force microscopy (AFM, SII Nano Technology, SPA400). Additionally, a UV–Vis spectrometer was used to analyze the optical properties, transmittance and reflectance. These optical properties were input in the thin film design software Essential Macleod to calculate the refractive indexes of the $HfO_2$ films. The refractive indexes were fitted by the Sellmeier dispersion formula; therefore, the graph of the refractive index was described as a function of wavelength. The packing density also was calculated.

## 3. Results and Discussion

Figure 1 describes the X-ray diffraction (XRD) patterns of various $HfO_2$ films on sapphire substrates. All films have a polycrystalline structure regardless of the RTA temperatures. The peak intensity of M(–111), representing the hafnium's crystalline direction, has a tendency to increase with the RTA temperature; however, the width displays the opposite tendency. This indicates that the crystal structures are generated in their direction, M(–111), intensively. Additionally, the sub-peaks, such as M(111), M(021), M(–211), are more clearly detected with increasing temperatures than the XRD pattern of the as-grown sample. In the case of the as-grown $HfO_2$ film, the peak of M(–111) was detected at 28.25° of diffraction angle $2\theta$. The annealed $HfO_2$ films have the tendency of increasing the diffraction angle of each peak with rising annealing temperatures, 28.47°, 28.49° and 28.51° at 400, 600, and 800°C, respectively. These increasing diffraction angles and decreasing width of the peaks indicates that the crystallite sizes become lager.[5)]

Through the analysis of the XRD patterns in Fig. 1, the full width at half maximum (FWHM) of the hafnium crystalline and its crystallite size are described in Fig. 2. The FWHM was measured as 2.07° in the case of the as-grown film. By increasing the annealing temperature from 400 to 800°C, the FWHM gradually decreased from 1.27° to 0.75°. By inserting these results into the Scherrer equation, Equation (1), the crystallite size was calculated:

$$D = \frac{0.9 \times \lambda}{\beta \times \cos\theta} \quad (1)$$

where $D$ is crystallite size, λ is the X-ray wavelength (0.1541 nm), and $\beta$ is the FWHM. Additionally, $\theta$ is the Bragg diffraction angle, from the angle $2\theta$ of the detected peak. As a result, the as-grown $HfO_2$ on sapphire has a crystallite size of 3.96 nm and this value is increased to 6.46 nm after annealing at 400°C, 7.81 nm at 600°C, and 10.93 nm at 800°C. As expected from Equation (1), it the shapes of the XRD patterns became intensively high and sharp, crystallization was focused in a specific direction, and the crystallite size increased with raising the annealing temperature. Considering these facts, the tendency of constructing dense films with high annealing temperatures could be expected.[10,11)]

AFM images of the $HfO_2$ films and their surface roughness are described in Fig. 3(a) without annealing, and with annealing at (b) 400°C, (c) 600°C, and (d) 800°C. It was confirmed by morphological images that all the $HfO_2$ films were deposited successfully without pin-holes or cracks that could cause defects, regardless of the annealing and its temperatures. The surface roughness was measured to be 6.840 nm in the case of the as-grown film. The $HfO_2$ films annealed at 400 and 800°C have a surface roughness of 5.828 and 4.907 nm, respectively; these values are considerably low. This validates the idea that the annealed films are transformed into a smooth and uniform surface compared with the as-grown film. Conversely, a film annealed at 600°C has 11.350 nm of surface roughness, indicating that its surface is rough compared with that of as-grown film. We can predict these results, which were already inferred from the XRD data of Fig. 1, because sub-crystalline directions such as M(111) and M(002) were formed in this film, and such sub-crystallization could create stress on the surface.[5)] Additionally, sub-crystallites are crystallized by generating

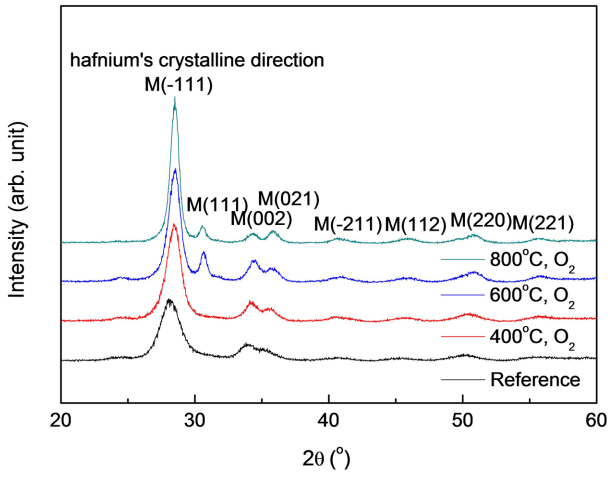


**Fig. 1.** XRD patterns of the $HfO_2$ films.

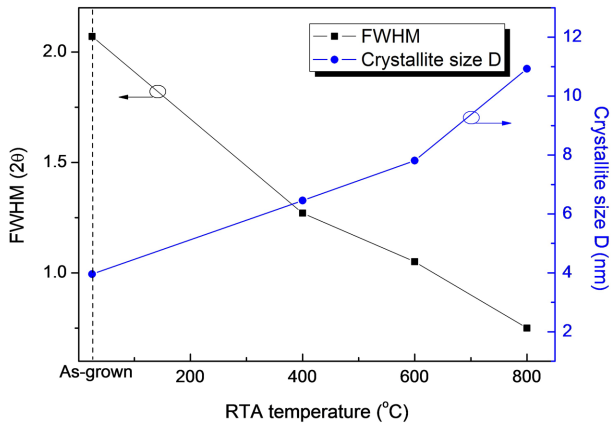


**Fig. 2.** FWHM and crystallite size of the $HfO_2$ films.

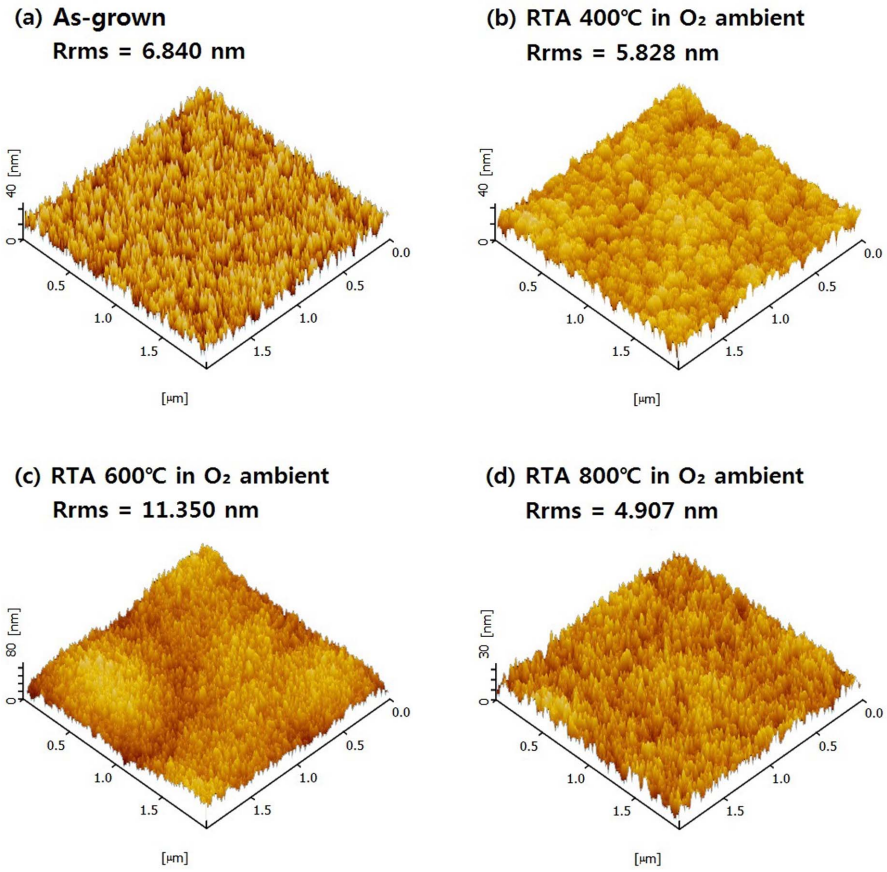


**Fig. 3.** AFM images and surface roughness values of $HfO_2$ films.

local bonding in $HfO_2$ films. It has been previously reported that oxygen vacancies were produced at this time;[10] therefore, it could be anticipated that these vacancies affect the surface roughness. In the case of the film annealed at 800°C, the intensities of the sub-peaks were reduced compared to the 600°C case, and the intensity of the M(−111) peak, representing hafnium, is increased. By considering this fact, we conclude that the crystallization was focused on specific direction and a more uniform surface was constructed.[12-14]

Figure 4 represents the transmittance and reflectance of $HfO_2$ on sapphire before and after the RTA. Considering the transmittance and reflectance curves of the as-grown film as reference, we find that the graph for films annealed at 400°C and 600°C were shifted to the short-wavelength region and that the 800°C case was shifted to the long-wavelength region. The as-grown film has a good average transmittance in the visible region (wavelength between 380–780 nm) of 80.71%. The films annealed at 400 and 600°C in $O_2$ ambient have a slightly higher average transmittance of 81.05% and 81.03%, respectively, compared to that of the as-grown film, owing to the shift to short-wavelengths. Conversely, in the case of 800°C, because of the shift to the long-wavelength region, the average transmittance was measured as 80.03%, which is slightly lower than that of the as-grown film. Nevertheless, all films have more than 80% of

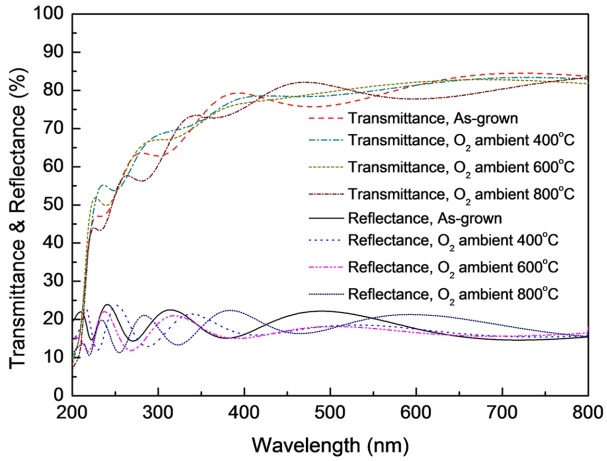


**Fig. 4.** Transmittance and reflectance of the $HfO_2$ films before and after RTA treatment.

**Table 2.** Thickness of the $HfO_2$ Films

| RTA Temperature | Film thickness |
|---|---|
| As-grown | 179.62 nm |
| 400°C | 245.57 nm |
| 600°C | 262.05 nm |
| 800°C | 265.45 nm |

transmittance and these results are mostly identical, with negligible differences.

The thickness of the films, measured by using the transmittance and reflectance results and the Essential Macleod program, are described in Table 2. $HfO_2$ films with a thickness of 179.62 nm were deposited by sputtering and became thicker up to 245.57 nm, 262.05 nm, and 265.45 nm after annealing at 400, 600, and 800°C, respectively. As the crystallite size increased, the lattice expanded by strong repulsion between surface dipoles; therefore, it could be expected that the increase of thickness was caused by this strong repulsion between the dipoles.[5)]

Figure 5 represents the refractive index at a wavelength of 632 nm for different RTA temperatures. Furthermore, Fig. 6 displays the refractive index as a function of wavelength for a film annealed at 800°C in $O_2$ ambient. The reflective indexes were obtained by using the transmittance and reflectance results in Fig. 4 and the Essential Macleod program values shown in Fig. 5. These refractive indexes were fitted by the Sellmeier dispersion formula, Equation (2) and illustrated in Fig. 6. The coefficients $A$ and $B$ used in the Sellmeier dispersion formula have been listed in Table 3.

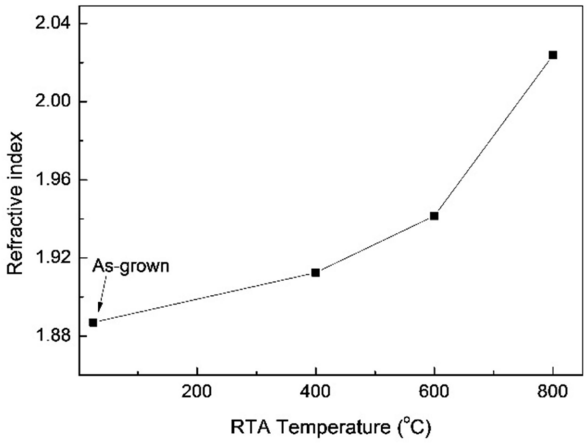


**Fig. 5.** Refractive index at 632 nm with different RTA temperatures.

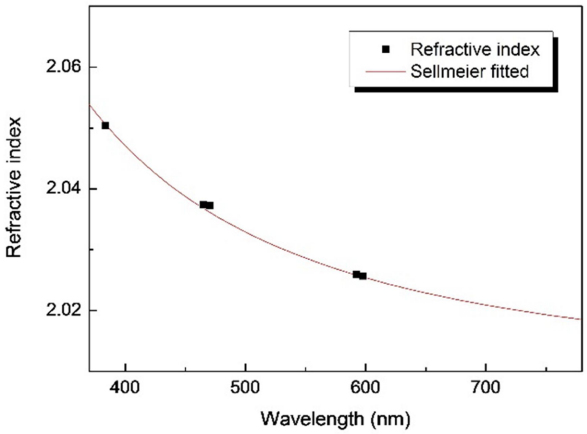


**Fig. 6.** Refractive index of $HfO_2$ annealed at 800°C and that fitted by Sellmeier dispersion equation.

**Table 3.** Calculated Coefficients $A$ and $B$ of the Sellmeier Dispersion Formula

| RTA Temp. | A | B |
|---|---|---|
| As-grown | 2.49044 | 101.91956 |
| 400°C | 2.87851 | 45.03953 |
| 600°C | 2.6493 | 35.64285 |
| 800°C | 3.03508 | 88.25695 |

$$n^2 = 1 + \frac{A\lambda^2}{(\lambda^2 - B^2)} \tag{2}$$

The refractive index of the as-grown $HfO_2$ film is 1.8870 at a wavelength of 632 nm. The annealed films have higher refractive indexes than the as-grown film: 1.9125, 1.9416, and 2.0237, when treated at 400, 600, and 800°C, respectively. This increase in the refractive index was caused by intensive crystallization with direction M(−111), which represents the hafnium crystal, generating denser films.[15,16)] Liu *et al.*[8)] had investigated the refractive index of $HfO_2$ on a quartz substrate, which was 2.008 at a wavelength of 500nm. And Puthenkovilakam *et al.*[11)] also had studied the refractive index of $HfO_2$ on silicon, which was 1.75 at a wavelength of 632nm. The results of this research have higher refractive index, 2.0237, than that of Liu *et al.*[8)] and Puthenkovilakam *et al.*.[11)]

Figure 7 shows the packing density of $HfO_2$ films before and after the annealing, for different RTA temperatures. There is a close relationship between the refractive index and packing density; this could be represented by Equation (3), which was designed by Bragg and Pippard:[17,18)]

$$n^2 = \frac{(1-p)n_v^4 + (1+p)n_v^2 n_s^2}{(1+p)n_v^2 + (1-p)n_s^2} \tag{3}$$

where $n_v$ represents the void refractive index and $n_s$ is the bulk refractive index. In this study, the void refractive index in dry air ($n_v = 1$) and the refractive index of bulk $HfO_2$

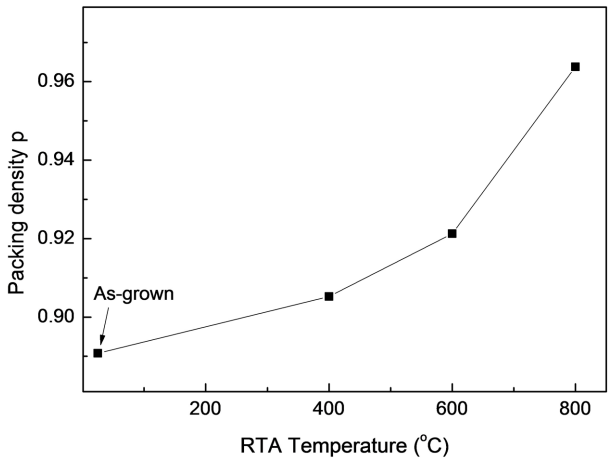


**Fig. 7.** Packing density of the $HfO_2$ films.

($n_s = 2.1$) were used. As-grown $HfO_2$ films have 0.8907 of packing density, which is a high enough value for applying to electronic device. However, the packing density of annealed films has a higher packing density, with values of 0.9053, 0.9213, and 0.9638, for RTA temperatures of 400, 600, and 800°C, respectively. It could be observed that the density has a tendency to increase with the RTA temperatures.[14–16] These results describe that optical properties such as the refractive index (which is measured by transmittance and reflectance) are related to structural properties such as packing density and crystallite size. Liu *et al.*[8] had investigated the packing density of $HfO_2$, which was measured as 0.912. This paper represents the packing density of 0.9638 which is higher than that of Liu *et al.*.[8]

## 4. Conclusions

After being deposited on sapphire substrates by RF magnetron sputtering, $HfO_2$ films were thermally treated by RTA at 400, 600, and 800°C in $O_2$ ambient. As the RTA temperatures increased, the M(−111) peak representing hafnium crystal became higher and narrower, and subcrystallites were generated such that the films presented a polycrystalline structure. In particular, in the case of a film annealed at 800°C, the average transmittance in the visible region was lowest at 80.03%, but the difference between this value and that of other films was only 1%. However, the film presented the smallest value of surface roughness, 4.907 nm, indicating that the film was uniform and smooth. Additionally, the refractive index and packing density were 2.0237 and 0.9638, respectively. These results indicate that the film annealed at 800°C has supreme properties compared to others, and that $HfO_2$ is a suitable material for applications in transparent or optical devices.

## REFERENCES


1. C. Y. Ma, W. J. Wang, C. Y. Miao, S. L. Li, and Q. Y. Zhang, "Structural, Morphological, Optical and Photoluminescence Properties of $HfO_2$ Thin Films," *Thin Solid Films*, **545** 279-84 (2013).
2. M. Alcisi, S. Scaglione, S. Martelli, A. Rizzo, and L. Vasanelli, "Structural and Optical Modification in Hafnium Oxide Thin Films Related to the Momentum Parameter Transferred by Ion Beam Assistance," *Thin Solid Films*, **354** 19-23 (1999).
3. M. Fadel, O. A. Azim M., O. A. Omer, and R. R. Basily, "A Study of Some Optical Properties of Hafnium Dioxide ($HfO_2$) Thin Films and Their Applications," *Appl. Phys. A*, **66** [3] 335-43 (1998).
4. F. L. Martinez, M. Toledano-Luque, J. J. Gandia, J. Carabe, W. Bohne, J. Rohrich, E. Strub, and I. Martil, "Optical Properties and Structure of $HfO_2$ Thin Films Grown by High Pressure Reactive Sputtering", *J. Phys. D: Appl. Phys.*, **40** [17] 5256-65 (2007).
5. K. Kamala Bharathi, N. R. Kalidindi, and C. V. Ramana, "Grain Size and Strain Effects on the Optical and Electrical Properties of Hafnium Oxide Nanocrystalline Thin Films," *J. Appl. Phys.*, **108** [8] 083529-1-5 (2010).
6. J. M. Khoshman, A. Khan, and M. E. Kordesch, "Amorphous Hafnium Oxide Thin Films for Antireflection Optical Coatings," *Surf. Coat. Technol.*, **202** [11] 2500-2 (2008).
7. G. Dai, Y. Chen, J. Lu, Z. Shen, and X. Ni, "Analysis of Laser Induced Thermal Mechanical Relationship of $HfO_2$/$SiO_2$ High Reflective Optical Thin Film at 1064 nm," *Chin. Opt. Lett.*, **7** [7] 601-4 (2009).
8. W. Liu, Z. Liu, F. Yan, T. Tan, and H. Tian, "Influence of $O_2$/Ar Flow Ratio on the Structure and Optical Properties of Sputtered Hafnium Dioxide Thin Films," *Surf. Coat. Technol.*, **205** [7] 2120-25 (2010).
9. M. F. Al-Kuhaili, "Optical Properties of Hafnium Oxide Thin Films and Their Application in Energy-Efficient Windows," *Opt. Mater.*, **27** [3] 383-87 (2004).
10. J. Ni, Q. Zhou, Z. Li, and Z. Zhang, "Oxygen Defect Induced Photoluminescence of $HfO_2$ Thin Films," *Appl. Phys. Lett.*, **93** [1] 011905-1-3 (2008).
11. R. Puthenkovilakam, Y.-S. Lin, J. Choi, J. Lu, H.-O. Blom, P. Pianetta, D. Devine, M. Sendler, and J. P. Chang, "Effects of Post–Deposition Annealing on the Material Characteristics of Ultrathin $HfO_2$ Films on Silicon," *J. Appl. Phys.*, **97** [2] 023704-1-7 (2005).
12. J. W. Park, D. K. Lee, D. Lim, H. Lee, and S. H. Choi, "Optical Properties of Thermally Annealed Hafnium Oxide and Their Correlation with Structural Change," *J. Appl. Phys.*, **104** [3] 033521-1-5 (2008).
13. C. T. Kuo, R. Kwor, and K. M. Jones, "Study of Sputtered $HfO_2$ Thin Films on Silicon," *Thin Solid Films*, **213** 257-64 (1992).
14. T. Tan, Z. Liu, H. Lu, W. Liu, and H. Tian, "Structure and Optical Properties of $HfO_2$ Thin Films on Silicon after Rapid Thermal Annealing," *Opt. Mater.,* **32** [3] 432-35 (2010).
15. M. Modreanu, J. Sancho-Parramon, D. O'Connell, J. Justice, O. Durand, and B. Servet, "Solid Phase Crystallisation of $HfO_2$ Thin Films," *Mater. Sci. Eng. B*, **118** [1-3] 127-31 (2005).
16. H. Gruger, C. Kunath, E. Kurth, S. Sorge, W. Pufe, and T. Pechstein, "High Quality r.f. Sputtered Metal Oxides ($Ta_2O_5$, $HfO_2$) and their Properties after Annealing," *Thin Solid Films*, **447** 509-15 (2004).
17. W. L. Bragg and A. B. Pippard, "The Form Birefringence of Macromolecules," *Acta. Cryst.*, **6** [11-12] 865-67 (1953).
18. S. Ben Amor, B. Rogier, G. Baud, M. Jacquet, and M. Nardin, "Characterization of Zirconia Films Deposited by r.f. Magnetron Sputtering," *Mater. Sci. Eng. B*, **57** [1] 28-39 (1998).