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Effect of thermal cycling on optical properties of e-beam deposited hafnia thin film

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Abstract

HfO_2 thin films have gained much significance in recent years as a promising dielectric material for semiconductor electronics added to their wide applications in the field of optical filters as a high index material. The resistance of HfO_2 films to impurity diffusion and intermixing at the interface as well as higher environmental stability have made these films one of the most extensively studied upon materials in laser optics, optical coatings and semiconductor domain. In the present study, Hafnium Oxide film was deposited on glass substrate using reactive oxygenated E-Beam deposition technique with in-situ quartz crystal thickness monitoring to control the film thickness and rate of evaporation. The coated substrate was optically characterized using spectrophotometer and Variable Angle Spectroscopic Ellipsometry (VASE) to determine its transmission spectra as well as optical constants. The coated sample was put under thermal stress testing in a test chamber with temperature variation from -40° to + 65° C in a cyclic manner for 7 cycles with a rate of temperature change of 5° C/minute. The coated sample was again optically characterized to investigate the effect of thermal cycling on its optical performance and physical parameters. Copyright © 2017 VBRI Press.

Keywords: Thin film, optical filters, thermal cycling, ellipsometry.

Introduction

Hafnia thin films are one of the most widely used high index materials in optical thin film filter fabrication due to their hardness, mechanical stability as well as broad transparency in the infrared (IR) to UV wavelength ranges. HfO_2 thin films have been extensively used in antireflection coatings [**1**], IR optical filters [**2**], UV mirrors [**3**], wide bandpass filter [**4**], heat mirrors for energy efficient windows [**5**], laser mirrors [**6**] etc. The optical properties (n and k) of hafnia thin films are dependent on the deposition conditions and method as has been reported in various prior arts **[2, 4, 7-10**]. Various researchers have deposited HfO2 thin films using Electron Beam (EB) evaporation [**5, 11**], ion assisted deposition **[3, 10**], atomic layer deposition [**12**], chemical solution deposition [**13**], reactive DC magnetron sputtering [**14**], chemical vapour deposition [**15**] for various applications ranging from semiconductor to optical filters.

For application requiring deployment of optical filters and multilayer thin films in harsh environmental conditions as well as in high precision military applications, thermal fatigue and stress testing of such films becomes one of the key assessment criteria of the ruggedness and durability of such films. Such kind of thermal fatigue testing of metallic thin films [**16, 17**] and metal oxides [**18**] have been reported earlier to check the mechanical and physical stability of thin films. As hafnia is used as a constituent material in fabrication of multilayer thin film optics with potential applications in space and harsh weather conditions, its behavior after undergoing thermal cycling needs to be studied with respect to its optical constants and spectral performance.

In the present study, HfO_2 thin film was deposited on BK7 glass substrate using E-beam deposition technique at a substrate temperature of 250˚ C. The thickness during deposition was controlled and monitored by quartz crystal thickness monitor. The coated sample was characterized before and after subjecting it to thermal cycling test from -40˚ to +65˚ C to study the effect of accelerated temperature variation on the physical and optical properties of hafnia thin film. The substrate was characterized by Variable Angle Spectroscopic Ellipsometry (VASE) at incidence angles of 65˚, 70˚ and 75˚ to extract the optical constants of the hafnia thin film. VASE measurements are known to analyse optical coatings with improved accuracy compared to conventional fixed angle single wavelength ellipsometric measurements as it can acquire large amounts of data from a given sample [**19-21**].

Experimental

Materials and methods

The HfO_2 thin films for the present study was grown by Electron-beam gun evaporation technique (PLS 570 coating system, Pfeiffer Vacuum) on optical grade glass substrate (BK7, n=1.52). The substrate was initially cleaned ex-situ in an ultrasonic bath and later cleaned with acetone, ethanol and de-ionized water and then dried by hot drier. The substrates were further cleaned in-situ by glow discharge for 4-5 minutes in the presence of argon gas to make substrate free of any contamination and ensure high quality of deposited films. The material used for deposition was vacuum-grade 99.9% pure granulates of HfO_2 (procured from Umicore Thin Film Products) with a bulk material density and melting point of 9.7 g/cc and 2812˚ C respectively. The vacuum chamber was pumped down to 2.5×10^{-5} mbar pressure before carrying out the deposition in an oxygenated reactive environment with O_2 partial pressure of 2.0×10^{-4} mbar. The film thickness, the rate of deposition and the cut point were controlled using quartz crystal thickness (Intellemetrics, IL820) monitor. **Table 1** lists the deposition conditions parameters maintained during deposition.

Table 1. HfO_2 deposition parameters.

S.no.	Deposition Parameter	Values
1.	Base Pressure	2.5×10^{-5} mbar
2.	Oxygen Partial pressure	2.0×10^{-4} mbar
3.	Substrate temperature	250° C
4.	Substrate rotation	15 rpm
5.	Deposition rate	0.3 nm/sec
6.	Thickness Monitoring	Dual sensor head Quartz Crystal monitoring

The sample after deposition was characterized using spectrophotometer and ellipsometer before putting it in a thermal cycling chamber (M/s Weiss WK series Thermal cycling chamber) for almost 24 hours. The substrate was subjected to cyclic variation of temperature from -40˚ to +65˚ C with a temperature gradient of 5˚ C/min. The sample is soaked at both the temperature extremes for a period of approximately 30 minutes during each cycle. The process was continued for a total of 7 cycles as per the temperature-time diagram given in **Fig. 1**.

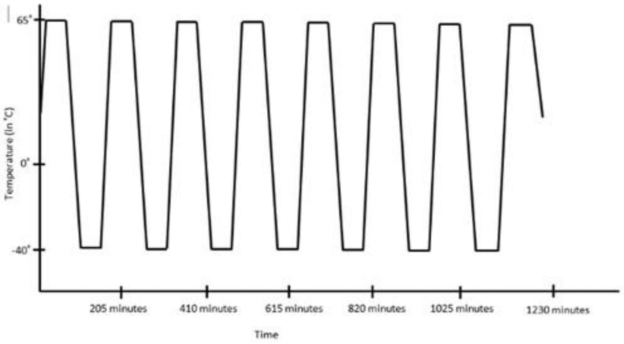

Fig. 1. Temperature Vs Time plot of the thermal cycling test.

The coated sample was characterized by spectrophotometer and VASE techniques as mentioned earlier. Ellipsometry measures the ratio of Fresnel reflection coefficients for p-polarized and s-polarized light reflected from the surface of the sample. The measured values are expressed in the form of psi (Ψ) and delta (Δ) as given in Equation 1.

$$P = Rp/Rs = \tan(\Psi)\, e^{(i\Delta)} \qquad (1)$$

As VASE is an indirect method of extracting the optical constants and thickness of the thin film based on fitting of experimental data with the modelled data, usually the quality of fit is given by a maximum likelihood estimator which is a positive quantity and tends to zero when the experimental data approaches or exactly matches the calculated data. In the present study, Mean Squared Error (MSE) shall be used as the maximum likelihood estimator which is given in Equation 2 [**20, 21**].

$$MSE = \sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{mod}-\Psi_i^{exp}}{\sigma_{\Psi,i}^{exp}}\right)^2+\left(\frac{\Delta_i^{mod}-\Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}}\right)^2\right]} \qquad (2)$$

where, N is the number of (Ψ, Δ) pairs, M is the number of variable parameters in the model and σ is the standard deviation on the experimental data points. The following section presents the results and analysis of the acquired data.

Results and discussion

The transmission spectra of the film before and after the thermal cycling test is given in **Fig. 2** which suggests that the transmission spectra shifted towards higher wavelength side by approximately 10 nm after thermal cycling which might have caused due to a combined effect of variation in film thickness and surface roughness after the thermal cycle. Moreover, the minor reduction in the transmission peaks and corresponding increase in the transmission dips suggests variation in optical constants of the film when it was subjected to thermal stress.

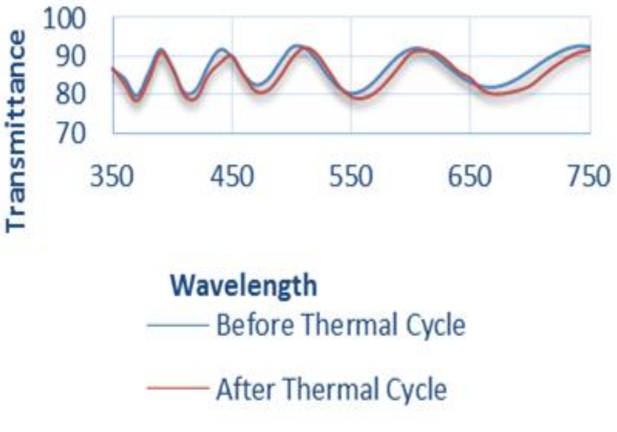

Fig. 2. Optical transmission spectra of Hafnia thin film before and after thermal cycling.

To determine the change in film thickness and its optical constants, the VASE measurements were Cauchy fitted to extract the optical constants of the film. The coated sample was characterized at room temperature in M2000 ellipsometer (rotating compensator ellipsometer, Make: J A Woollam Co. Inc.) in the wavelength range of 350-1000 nm with a step size of approximately 1.5nm at three different incidence angles of 65˚, 70˚ and 75˚. The acquired data were analysed using WVASE32 software module. As the glass substrate used for this experiment was both side polished, opaque scotch tape was applied on the second surface of the substrate so that reflection from the second surface does not affect the data acquisition from the first surface. To extract the optical constants of the hafnia thin film, the entire structure is modelled as surface roughness/HfO_2/Glass substrate.

The surface roughness layer was taken as a mixture of 50% void and 50% HfO_2 thin film. Since the Hafnia film is optically transparent in the spectral region of interest, Cauchy model of fitting was used to match the acquired data with the generated theoretical data. Cauchy dispersion model which assumes zero absorption in the spectral region of interest is given by Equation 3.

$$n(\lambda) = A + (B/\lambda^2) + (C/\lambda^4), \quad k(\lambda) = 0 \tag{3}$$

where, n (λ) and k (λ) represent the refractive index and extinction coefficient respectively whereas A, B and C represent the Cauchy coefficients which need to be determined to know the dispersion behavior of HfO_2 thin film. The Ψ and Δ values of the hafnia thin film fitted with Cauchy model is shown in **Fig. 3**.

The optical and physical parameters extracted from this fitting is given in **Table 2**. The MSE was 42.76 for this fitting with a surface roughness value of 11.718 nm. The thickness of the film was determined to be 824.185 nm.

Table 2. Physical and optical parameters of HfO_2 thin film before thermal cycling.

Parameters	**Values**
Film Thickness	824.185 nm
Surface roughness	11.718 nm
MSE	42.76
Refractive index at 550 nm	1.8907

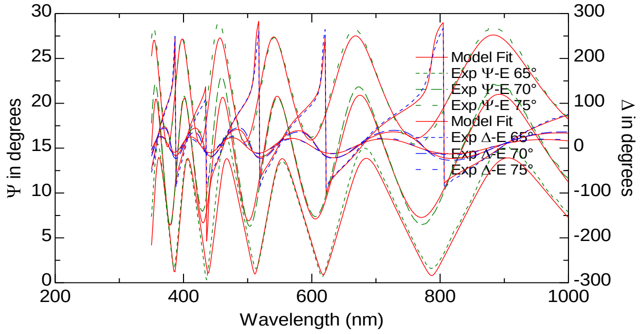

Fig. 3. Cauchy fitted Ψ and Δ values of the hafnia thin film before thermal cycling.

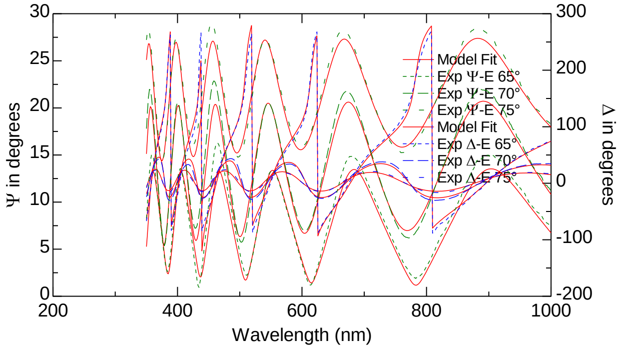

Fig. 4. Cauchy fitted Ψ and Δ values of the hafnia thin film after thermal cycling.

The Cauchy fitted Ψ and Δ values of the hafnia thin film after thermal cycling is given in **Fig. 4**. The optical and physical parameters extracted from this fitting is given in **Table 3**.

Table 3. Physical and optical parameters of HfO_2 thin film after thermal cycling.

Parameters	**Values**
Film Thickness	820.501 nm
Surface roughness	7.417 nm
MSE	34.2
Refractive index at 550 nm	1.9006

As mentioned in **Table 3**, the film thickness of the hafnia thin film decreased marginally after thermal cycling due to possible densification of the film structure which is also supported by the fact that the refractive index of the film also increased from its value before thermal cycling.

Fig. 5 shows the variation in refractive index of the film both before and after the thermal cycling. The refractive index increased from 1.8907 to 1.9006 at 550 nm after thermal cycling.

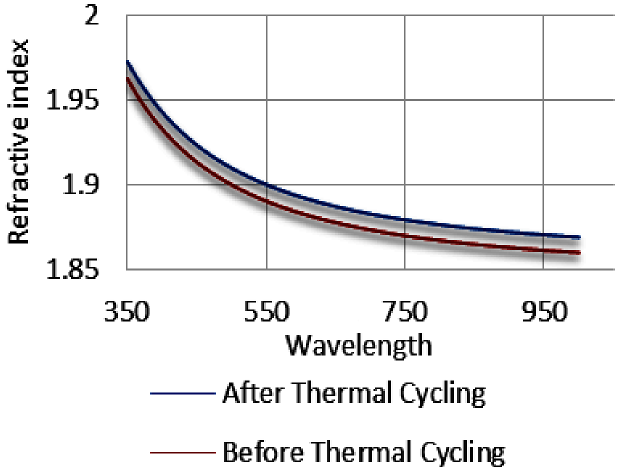

Fig. 5. Dispersive refractive index of hafnia thin film before and after thermal cycling.

Conclusion

The present study determined the optical properties of hafnia thin film deposited in reactive oxygenated E-beam evaporation technique before and after subjecting it to thermal cycles by using spectrophotometric and ellipsometric measurements. The film properties were analyzed using cauchy fitting and it was found that the refractive index of the film increased after thermal cycling with a reduction in film thickness which is attributed to densification of the film structure after thermal cycling. The surface roughness of the film also decreased after thermal cycling with reduced MSE values of the cauchy fitted model. The results of this study can be useful to compensate the shift in optical constants and transmission spectra of hafnia thin film during design of thin film multilayer optical filters involving hafnia so as to make it suitable for operations in harsh environmental conditions.

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Author's contributions

Conceived the plan: MK, ALS; Performed the experiments: MK, NK; Data analysis: VK, ALS; Wrote the paper: MK, ALS. Authors have no competing financial interests.

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