Variable angle spectroscopic ellipsometric characterization of HfO$_2$ thin film

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Abstract. Hafnium Oxide film was deposited on BK7 glass substrate using reactive oxygenated E-Beam deposition technique. The film was deposited using in-situ quartz crystal thickness monitoring to control the film thickness and rate of evaporation. The thin film was grown with a rate of deposition of 0.3 nm/s. The coated substrate was optically characterized using spectrophotometer to determine its transmission spectra. The optical constants as well as film thickness of the hafnia film were extracted by variable angle spectroscopic ellipsometry with Cauchy fitting at incidence angles of 65˚, 70˚ and 75˚.

Keywords: Optical coatings, Thin film, Ellipsometry, Cauchy fitting, Dispersion.

1. Introduction

Hafnium dioxide (HfO$_2$) films are known for their low-absorbing, hard and abrasion-resistant properties which make them useful for optical Anti-Reflection (AR), multilayer coatings as well as for fabrication of semiconductor devices [1-3]. 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 widely used and extensively studied upon materials in laser optics, optical coatings and semiconductor domain [4]. For optical coatings, HfO$_2$ is primarily used as a high index material along with SiO$_2$ as a low index material to form a High-Low (HL) multilayer stack that can have constructive interference at the interfaces to act as a reflector, band pass, band stop optical filter, polarizer and mirrors for high power laser applications [5-8]. Hafnia thin films have been deposited by various researchers using Electron Beam (EB) evaporation [9, 10], ion assisted deposition [3, 11], atomic layer deposition [12], chemical solution deposition [13], reactive DC magnetron sputtering [14], chemical vapour deposition [15] etc. to study its film structure as well as optical properties. Out of various characterization techniques, Spectroscopic Ellipsometry (SE) has been widely used to extract optical and other physical properties of hafnia films like its refractive index, absorption coefficient, band-gap, film thickness as well as defects in film structure [11, 16-19].

In this present study, hafnia thin film was deposited on BK7 substrate using reactive oxygenated electron beam gun deposition technique with in-situ quartz crystal thickness monitoring for accurate control of rate of deposition as well as film thickness. The coated sample was characterized using normal incidence spectrophotometer, variable angle spectroscopic ellipsometry (VASE) for extraction of its optical constants. 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 [20-23]. In this study, the optical constants of HfO$_2$ have been accurately extracted from the ellipsometric measurements with Cauchy dispersion model. The surface roughness between the hafnia and air exit medium has been modelled using Effective Medium Approximations (EMA).
2. Experimental Details

The HfO2 thin film was deposited on BK7 glass substrate using Electron Beam (EB) gun deposition method in Pfeiffer PLS 570 coating plant. The deposition was carried out without any ion assistance. The substrate was initially cleaned in an ultrasonic bath and later cleaned with acetone, ethanol and de-ionized water. The substrate was mounted on a spherical calotte and was rotated with a constant speed during deposition for uniform coating. The material used for deposition was vacuum-grade 99.9% pure granulates of HfO2 (procured from Umicore Thin film Products) with a bulk material density and melting point of 9.7 g/cc and 2812˚ C respectively.

During deposition, the substrate temperature was maintained at 250 ˚C by using a backside heater inside the chamber. The vacuum chamber was pumped down to 2.5 x 10^-5 mbar pressure before carrying out the deposition in an oxygenated reactive environment with O2 partial pressure of 2.0 x 10^-4 mbar. The rate of evaporation was maintained at 0.3 nm/sec and the rate was monitored and controlled by quartz crystal thickness monitor during deposition. The deposition parameters are summarized in Table 1.

| S/n. | Deposition Parameter         | Values               |
|------|-------------------------------|----------------------|
| 1.   | Base Pressure                 | 2.5 x 10^-5 mbar     |
| 2.   | Oxygen Partial pressure       | 2.0 x 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 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).

\[
P = \frac{R_p}{R_s} = \tan(\Psi) e^{i\Delta}
\]  

(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) [24].

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

(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[24]. The following section presents the results and analysis of the acquired data.

3. Result and Discussions

3.1. Spectrophotometric Measurements
The HfO2 film on glass substrate was characterized by normal incidence spectrophotometer in the wavelength range of 300-800 nm. Figure 1 shows the transmission spectra of HfO2 thin film deposited at 250° C in a reactive oxygenated environment.

![Figure 1. Normal incidence transmittance spectra of deposited hafnia thin film](image)

From the transmission spectra shown in figure 1, it is observed that the normal incidence transmittance peaks for HfO2 film is almost always close to the transmittance value of the uncoated substrate (~92% for uncoated substrate) indicating a nearly homogenous film on the substrate [25]. The continuous dip in transmission below 350 nm shows the absorption of the film structure at the onset of UV wavelength. The transmission spectra is in good agreement with earlier reported values of HfO2 being optically transparent beyond the wavelength of around 350 nm or even lower than this wavelength depending upon the specific deposition conditions and crystallinity of the film [9, 18, 19, 26].

3.2. Spectroscopic Ellipsometry
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 1.5 nm 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. The acquired VASE data for Ψ and Δ in the wavelength range 350-1000 nm are shown in figure 2 and 3 respectively for incidence angles of 65°, 70° and 75°. To extract the optical constants of the hafnia thin film, the entire structure is modelled as surface roughness/HfO2/Glass substrate. The surface roughness layer was taken as a mixture of 50% void and 50% HfO2 thin film.
Figure 2. Acquired $\Psi (\lambda)$ data of hafnia thin film on glass substrate

Figure 3. Acquired $\Delta (\lambda)$ data of hafnia thin film on glass substrate

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.

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

Here, $n (\lambda)$ and $k (\lambda)$ 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 behaviour of HfO2 thin film. The modelled data which best fits the experimental data is shown in figure 4 and figure 5 for $\Psi (\lambda)$ and $\Delta (\lambda)$ respectively. The best fit model that resulted through normal fit procedure in WVASE32 resulted in MSE of 42.76 with the Cauchy coefficients as listed in Table 2. The resultant model determined the hafnia film thickness to be 824.185 nm and the surface roughness to be of 11.716 nm.

Table 2. Best fit Cauchy coefficients of modelled data.

| Cauchy Coefficients | Values               |
|---------------------|----------------------|
| $A_n$               | 1.8482±0.00209       |
| $B_n$               | 0.012114±0.000578    |
| $C_n$               | 0.00024016±6.5e-005  |
The MSE vale can be further minimized by including an absorption model to describe the material behaviour at shorter wavelengths. Figure 6 gives the dispersion characteristics of hafnia thin film in the wavelength range of 350-1000 nm where its refractive index decreases from 1.963 at 350 nm to 1.8606 at 1000 nm following normal dispersion.

Figure 4. Measured and fitted $\Psi (\lambda)$ of hafnia thin film deposited on glass substrate

Figure 5. Measured and fitted $\Delta (\lambda)$ of hafnia thin film deposited on glass substrate

Figure 6. Cauchy fitted dispersive refractive index values of hafnia thin film
4. Conclusion
The present study determined the optical properties of hafnia thin film deposited in reactive oxygenated E-beam evaporation technique by using spectrophotometric and ellipsometric measurements. The film properties were analyzed using cauchy fitting and the refractive index of hafnia thin film was found to be 1.89 at 550 nm indicating its importance as a high index material for optical filter fabrications as well as laser mirrors. There is a further need to minimize the MSE of the fitting model by incorporating a suitable absorption function to describe the film behaviour at shorter wavelength regions.

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