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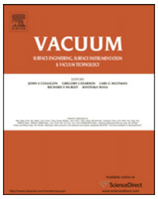

# Determination of the optical constants of $HfO_2$–$SiO_2$ composite thin films through reverse fitting of transmission spectra

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Composite thin films of $HfO_2$:$SiO_2$ with wide range of relative composition from 100:0 (pure $HfO_2$) to 10:90 have been deposited on fused silica substrates by co-evaporation technique and the optical properties of the films have been studied by measuring the transmission spectra of the samples by spectrophotometer. Different important optical parameters viz., band gap, refractive index and absorption coefficients of the samples have been obtained by fitting the measured optical spectra with theoretically generated spectra and the variation of the optical constants as a function of $SiO_2$ content in the films have been obtained. Two different dispersion models viz., the single effective oscillator model and the Tauc–Lorentz model have been used to generate the theoretical spectra in the above fitting procedure. X-ray reflectivity (XRR) measurement technique has been used to find the densities of the films in order to explain the observed variation in optical properties of the films with increase in $SiO_2$ content.

## 1. Introduction

Design and development of optical multilayer devices are constrained by the optical constants such as refractive index or band gap of available materials. The design of an ideal antireflection coating may require refractive index values unavailable with standard coating materials and must be simulated by a number of thin layers of different dielectric materials [1]. The situation becomes even more difficult in designing a narrow-band filter or a rejection filter, where it is necessary to increase the number of layers to achieve the desired characteristic that often compromises its spectral performance and durability. Hence it is necessary to find new methodology which gives desired index values for developing optical devices.

In recent years novel properties have been obtained in composite oxide films prepared by vapor phase mixing of different dielectric materials or by solid solution based techniques [2–4]. Solid solution based methodology, where the composite film is deposited from a precursor of desired composition synthesized using a solid state route, however, suffers from a drawback that only limited number of materials show solid solubility over a wide composition range. The vapor phase mixing of materials on the other hand exploits the advantage of thin films deposition technology which, when applied with controlled and optimized parameters, can synthesize new phases or materials which may otherwise not stable or impossible to prepare through the conventional solid state route [5]. Co-evaporation of two oxide materials, for example, can give rise to films having a range of properties that is not available from a finite number of discrete materials. These properties are not only intermediate to those of the constituents of the alloy but often are also unique and unavailable in any single material.

Hafnium oxide is one of the most widely used high index coating materials for the fabrication of multilayer optical devices [6,7] because of its favorable optical properties like transparent spectral range from the infrared to the ultra violet, high refractive index, hardness, thermal, mechanical and chemical stability and higher damage threshold compared to other coating materials [8,9]. $SiO_2$ is the most compatible low index material used with $HfO_2$ for developing multilayer devices. Use of $HfO_2$–$SiO_2$ composite film in lieu of pure $HfO_2$ has also been explored [10,11] for tuning the band gap and refractive index of the high index layer which ultimately leads to the development of multilayer optical coatings with relatively smaller number of layers and also helps in extending the range of its application to deep UV. Since it has been observed in several cases that properties of the composite

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films do not always obey a linear interpolation between the properties of the two extreme materials over the whole composition range, exact knowledge of the optical properties of these materials is extremely important for their application in multilayer optical devices. Though the structural and morphological properties of the $HfO_2$:$SiO_2$ composite films have been reported earlier [10–12], including in two of our communications [11,12], with a brief mention about the variation of refractive index over composition, the details of the optical properties over the whole compositional range have not been reported yet.

In the present work, composite thin films of $HfO_2$:$SiO_2$ with wide range of composition from 100:0 (pure $HfO_2$) to 10:90 have been deposited on fused silica substrates by co-evaporation technique and the optical properties of the films have been studied by measuring the transmission spectra of the samples by spectrophotometer. Two different dispersion models viz., the single effective oscillator [13,14] model and the Tauc–Lorentz model [15] have been used for describing the dispersion relations of the optical constants of the $HfO_2$:$SiO_2$ composites in fitting the transmission spectra of the samples. Film densities have been obtained using X-ray reflectivity (XRR) measurements and the density values have been used in explaining the observed variation of the optical properties as a function of composition.

## 2. Experimental details

The $HfO_2$:$SiO_2$ composite thin films have been deposited on quartz substrates kept at 350 °C, by reactive electron beam co-deposition technique in a fully automatic thin films deposition system. The system is equipped with two 8 kW electron beam guns with sweeps and automatic emission controls. The rate of deposition of individual material is controlled and measured by independent quartz crystal monitors. Typical rates of deposition maintained for a pure $HfO_2$ or a pure $SiO_2$ film is $\sim 10$ Å $s^{-1}$. The change in composition is achieved by changing the deposition rates of individual materials. Optical thickness of the composite film is measured by Leybold's OMS-2000 optical thickness monitor. The total working pressure inside the chamber during co-deposition was kept at $1 \times 10^{-4}$ mbar. The deposition process is controlled by a software enabling simultaneous automatic measurements and acquisition of parameters (deposition rate, pressure inside the chamber, temperature, etc.). All these films studied here are having optical thickness of 6–8 quarter wave thick at the wavelength of 600 nm in order to have appropriate numbers of interference fringes for spectrophotometric analysis.

Optical constants of the films were obtained by transmittance measurements of the composite thin films from 190 nm to 1200 nm on a Shimadzu UV-3101PC UV–VIS-NIR spectrophotometer. The measured transmission data have been fitted with appropriate model generated theoretical spectra for obtaining optical constants of the films. Densities of the films have been measured by X-ray reflectivity (XRR) technique carried out in an X-ray reflectometer (SOPRA, France). The measurements have been carried out with a Cu $K_\alpha$ (1.54 Å) source with grazing angle of incidence in the range of 0–2° and with an angular resolution of 0.001°. Rocking curve measurements have been done prior to each measurement for aligning the sample.

Our earlier investigation on crystal structure shows that [12], the grazing incidence X-ray diffraction (GIXRD) spectrum of the $HfO_2$ film, though having few distinctive peaks, does not correspond preferentially to any of the crystalline phases, viz., monoclinic, tetragonal or orthorhombic structure and thus indicates mixed-phase or random polycrystalline nature of the sample. GIXRD spectra of the $HfO_2$–$SiO_2$ composite films, on the other hand, show amorphous-like broad features.

## 3. Modeling and fitting procedure

### 3.1. Spectrophotometric analysis

The optical constants of the films have been obtained by fitting the measured transmission data with a theoretically generated spectrum under the following assumptions [16]:

i. A thin isotropic dielectric layer covers a thick, weakly absorbing substrate, and the optical system is immersed in air.
ii. Optical radiation of mean wavelength $\lambda$ and spectral half width $\Delta\lambda$ is incident normally on the sample.
iii. Interference of internally reflected radiation occurs in the thin films [$\Delta\lambda \ll \lambda^2/2nt$] and is negligible in the substrate [$\Delta\lambda \gg \lambda^2/2nt_s$] where $n$, $t$, $t_s$ are the refractive index, thickness of the film, thickness of the substrate, respectively.
iv. The refractive index of the film ($n$) is larger than refractive index of the substrate ($n_s$) i.e., $n > n_s$.
v. The film and the substrate are weakly absorbing in the studied spectral region i.e. $n^2 \gg k^2$ and $n_s^2 \gg k_s^2$, where $k$ and $k_s$ are the extinction coefficients of the film and the substrate, respectively.

With the above assumption and further assuming that the thickness of the dielectric film is uniform, the transmittance of such a two-layer system can be expressed as follows [17]:

$$T(\lambda; n, t, n_s, k_s) = T_1(\lambda; n, k, t, n_s, k_s)/T_2(\lambda; n, k, t, n_s, k_s) \quad (1)$$

where,

$$T_1 = (1 - R_1)(1 - R_2)(1 - R_3)xx_s \quad (1a)$$

$$T_2 = 1 + R_1R_2x^2 - R_1R_3x^2x_s^2 + 2r_1r_2\left(1 - R_3x_s^2\right)x\cos(\psi) \quad (1b)$$

$$R_1 = r_1^2, R_2 = r_2^2, R_3 = r_3^2 \quad (1c)$$

$$r_1 = \frac{1-n}{1+n}, r_2 = \frac{n-n_s}{n+n_s}, r_3 = \frac{n_s-1}{n_s+1} \quad (1d)$$

$$\alpha = 4\pi k/\lambda, x = \exp(-\alpha t) \quad (1e)$$

$$\alpha_s = 4\pi k_s/\lambda, x_s = \exp(-\alpha_s t_s) \quad (1f)$$

$$\psi = 4\pi nt/\lambda \quad (1g)$$

Using above mentioned relation and assuming a suitable dispersion model for the wavelength variation of the optical constants of the substrate and the film, as discussed in detail in the next section, the experimental transmittance spectra of the film are fitted with theoretically generated spectra. The fitting has been carried out by minimizing the squared difference ($\chi^2$) between the measured and calculated values of transmission given by:

$$\chi^2 = \frac{1}{(2N-P)}\sum_{i=1}^{N}\left[\left(T_i^{\mathrm{Exp}} - T_i^{\mathrm{Cal}}\right)^2\right] \quad (2)$$

where $T_i^{\mathrm{Exp}}$ and $T_i^{\mathrm{Cal}}$ are the experimental and theoretical transmittances, respectively. $N$ is the number of data points, $P$ is the number of model parameters and the minimization has been carried out using the Levenberg–Marquardt algorithm.

For the optical constants ($n_s$ and $k_s$) of the substrate we have assumed a Cauchy–Urbach type dispersion relation as given below: