Chapter 5: Composition Dependent Properties of HfO$_2$-SiO$_2$ Mixed Oxide Composite Thin Films

5.1 Introduction

Researches on mixed composite thin films have been the areas of intense study, because of tunable refractive indices with ability to produce continuous variation of the refractive index as well as tunable optical band gap with improved laser damage resistance [9, 139, 167]. With innovated multilayer designs, these mixed materials can be used to develop various types of graded index or inhomogeneous multilayer coatings with low mechanical stress, better tribological resistance and higher laser damage threshold than those of classical multilayer stacks [10, 168, 169]. Therefore, in order to achieve the desired performance of these gradient index optical coatings, it is prerequisite to know the dependency of the optical dispersion curves as well as laser damage threshold with mixture composition. Moreover, the determination of absorption edge as well as absorption co-efficient in weak absorption region for different mixtures is necessary to define the transparent region which can be useful for optical coatings to avoid absorption as well as radiation induced damage. Hence, predicting the effective optical properties of any mixed oxide composite material is practically of the utmost importance, but to date there is no comprehensive and universally accepted theory to account for its whole aspects. Mostly, the optical constants (refractive index and absorption co-efficient) of such mixed composite films obtained through material mixings are tackled through different models based on analytical methods or effective medium approximations (EMA) taking into account of sample geometries (grain structure) and microstructures [170]. The EMA models such as Bruggeman, Maxwell-Garnett, Lorentz-Lorentz, Linear, Drude and Looyenga model have been used to compute the compositional dependence of the refractive index as well as absorption co-efficient for different mixed films [8, 171, 172].
Recently it is observed that adding foreign oxide materials such as ZrO$_2$, Al$_2$O$_3$, SiO$_2$ etc. to pure HfO$_2$, the optical properties, mechanical properties as well as laser damage resistance of such mixed films (HfO$_2$-ZrO$_2$, HfO$_2$-Al$_2$O$_3$, HfO$_2$-SiO$_2$ etc.) have been dramatically improved [139, 173]. But, still there is a need to understand how laser damage thresholds can be increased by improving specific properties of such thin films using different optimized deposition techniques. And also there is no systematic study on the appropriateness of EMA models for hafnia-silica mixed oxide thin films so that these models can be used while designing the gradient index optical coatings using these mixtures. In the present study, HfO$_2$-SiO$_2$ mixed composite films with wide range of composition by continuous mixing of HfO$_2$ and SiO$_2$ have been deposited on fused silica substrates by electron beam co-evaporation technique. The compositional dependent refractive index as well as absorption co-efficient around strong absorption region for the mixed thin films has been analyzed using different EMA models. It is observed that the effective refractive index of the composite films with silica content more than 20% are very well modeled by the Drude model. But, when the silica contents are less than 20%, most composite films exhibit grain structure evolutions leading to better and denser microstructure and morphology, which are confirmed by grazing incidence x-ray reflectivity (GIXR) and atomic force microscopy (AFM) analysis. All EMA have failed to interpret such evolutions which dominantly controlled the effective polarizability or dielectric constant. The absorption co-efficient dependency on composition calculated by Lorentz-Lorentz model shows fair approximation to the experimental data except for lower silica content. The mixture films are found to show better surface roughness as compared to the pure hafnia resulting reduction in scattering loss. The laser induced damage threshold (LIDT) measurement for nanosecond pulse duration (Nd-YAG Laser, 2$^{nd}$ harmonic) of such mixed films has been carried out and the dependency of the damage threshold as a function of SiO$_2$ content has been investigated.
5.2 Experimental details

5.2.1 Sample preparation

The HfO₂-SiO₂ composite thin films of various compositions in the (x)HfO₂:(100-x)SiO₂ (x=0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100%) systems have been deposited on fused silica substrates by reactive electron beam co-evaporation technique in a fully automatic thin film deposition system. The fused silica substrates are properly cleaned using ultrasonic and vapour degradation cleaning method before coating. 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. The change in composition is achieved by changing the deposition rates of individual materials. Optical thickness of the composite films is measured by Leybold’s OMS-2000 optical thickness monitor. The total working pressure inside the chamber during co-deposition was kept at 1x10^{-4} mbar, while the substrate temperature was kept at 300°C. The deposition process is controlled by software enabling simultaneous automatic measurements and acquisition of parameters (deposition rate, pressure inside the chamber, temperature, etc). To suppress the unwanted fluctuation in rate of evaporation, the proportional, integration and differential (PID) parameters of the thickness as well as process control systems have been judiciously optimized. With such an accurate process control, the desired compositions of HfO₂-SiO₂ mixed films have been achieved with ±2% fluctuation in composition as measured by energy dispersive x-ray analysis [174]. The pure HfO₂ shows polycrystalline structure, while the mixed oxide films are nearly amorphous in nature. All these films studied here are having optical thickness (nd, where n is the refractive index and d is the geometrical film thickness) of 6 to 8 quarter wave thick at the monitoring wavelength of 600 nm in order to have appropriate numbers of interference fringes for spectrophotometric analysis.
5.2.2 Optical characterization

The transmission and reflection spectra of the films have been measured in the wavelength range of 190-1100 nm at almost normal angle of incidence using spectrophotometer. The relative uncertainty in the transmittance is 0.3%. In the measurement air is used as a reference. Fig. 5.1 shows the transmission as well as reflection spectra of some representative hafnia-silica mixtures in the range of 190 nm - 800 nm for the sake of clarity of the image.

![Graph showing transmission and reflection spectra](image)

**Fig. 5.1: Transmission and reflection spectra of HfO₂-SiO₂ mixed composite thin films.**

The refractive index and thickness of the films have been derived from the measured transmission spectrum using inverse synthesis method. The estimated error in thickness is negligible while that for refractive index is ±0.01. The thickness derived from the transmissions spectra is close to the in-situ measured film thickness as listed in Table-5.1, which indicates the reliability of the inverse synthesis method. Fig. 5.2 shows the refractive index spectra of HfO₂-SiO₂ composite films for whole compositions, while Fig. 5.3 shows the logarithm absorption co-efficient of the film around strong absorption region computed from the transmission (T) and reflection (R) spectra using the formula [175]
\[ \alpha_{\text{film}}(\lambda) = \frac{1}{d_{\text{film}}} \ln \left( \frac{1 - R}{T / T_{\text{sub}}} \right) \] (5.1)

where \( d_{\text{film}} \) is the film thickness and \( T_{\text{sub}} \) is the transmission of the bare substrate.

**Fig. 5.2:** Refractive index spectra of HfO\(_2\)-SiO\(_2\) mixed thin films.

**Fig. 5.3:** Absorption co-efficient spectra of HfO\(_2\)-SiO\(_2\) mixed thin films near the band edge.
The optical band gap ($E_g$) of the films has been derived from the absorption co-efficient ($\alpha$) values. Here, it is considered that the absorption co-efficient of the mixed composite films (behave like amorphous semiconductor) in the high absorption region is given according to Tauc’s relation for the allowed indirect transition [51] by the relation $(\alpha h\nu)^{1/2} = K (h\nu - E_g)$, where $K$ is constant depends on the transition probability and $E_g$ is the optical band gap, defined as the energy separation between valence band and conduction band and represents the onset of absorption related to interband transitions. The band gap is determined by plotting $(\alpha h\nu)^{1/2}$ as a function of the photon energy $h\nu$ and extrapolating the linear curve progression to zero. For mixture having more than 70% silica content, the optical band gap is not derived because the absorption edge is out of spectrophotometric measurement limits. Fig. 5.4 shows the Tauc plots for different composition of HfO$_2$-SiO$_2$ mixed composite films.

![Graph showing Tauc plots for different composition of HfO$_2$-SiO$_2$ mixed composite films.](image)

**Fig. 5.4:** Plot of $(h\nu)^{1/2}$ vs. $h\nu$ for all the HfO$_2$-SiO$_2$ mixed thin films.
5.2.3 GIXR and AFM characterization

Mass density of the mixed composite films has been measured by grazing incidence X-ray reflectivity (GIXR) technique carried out in an X-ray reflectometer. The measurements have been carried out with Cu Kα (1.54 Å) source with grazing angle of incidence in the range of 0-0.6° and with an angular resolution of 0.01°. Fig. 5.5 shows the experimental GIXR spectra for pure HfO₂ and a representative HfO₂-SiO₂ (90%-10%) mixed composite film along with the best fit theoretical spectra obtained using the formalism described elsewhere [56]. The thicknesses of the films, derived from the optical transmission spectra, have been kept invariant during GIXR fitting. By fitting X-ray reflectivity spectrum near critical angle, the film density ρ and rms roughness has been estimated and are listed in Table-5.1. The error in density measurement is approximately ±0.1 g/cm³ due to alignment of the sample position to the X-ray beam and angular resolution of the instrument.

![Graph showing X-ray reflectivity](image)

**Fig. 5.5:** Experimental X-ray reflectivity with best-fit theoretical spectrum of pure HfO₂ and HfO₂(90%)-SiO₂(90%) mixed thin films.
Table - 5.1: Parameters derived from transmission, GIXR, AFM, and LIDT measurements.

<table>
<thead>
<tr>
<th>HfO&lt;sub&gt;2&lt;/sub&gt;-%SiO&lt;sub&gt;2&lt;/sub&gt; (%)</th>
<th>Thickness Measured In Situ (nm)</th>
<th>Thickness Derived from Transmission Spectra (nm)</th>
<th>Bandgap (eV)</th>
<th>Film Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Roughness (nm) GIXR</th>
<th>Roughness (nm) AFM</th>
<th>Grain Size (nm)</th>
<th>LIDT F&lt;sub&gt;0&lt;/sub&gt; (J/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
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</thead>
<tbody>
<tr>
<td>100-0</td>
<td>521 ± 10</td>
<td>512 ± 0.3</td>
<td>5.57</td>
<td>8.42</td>
<td>3.35</td>
<td>5.62</td>
<td>196 ± 30</td>
<td>18.05 ± 2.88</td>
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<tr>
<td>90-10</td>
<td>517 ± 11</td>
<td>503 ± 0.3</td>
<td>5.62</td>
<td>8.90</td>
<td>1.53</td>
<td>1.12</td>
<td>59 ± 15</td>
<td>20.68 ± 3.30</td>
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<td>80-90</td>
<td>419 ± 08</td>
<td>438 ± 0.4</td>
<td>5.30</td>
<td>7.02</td>
<td>0.60</td>
<td>1.04</td>
<td>49 ± 17</td>
<td>19.06 ± 3.00</td>
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<tr>
<td>70-80</td>
<td>479 ± 09</td>
<td>483 ± 0.8</td>
<td>5.68</td>
<td>7.13</td>
<td>1.36</td>
<td>1.27</td>
<td>49 ± 11</td>
<td>18.71 ± 3.00</td>
</tr>
<tr>
<td>60-70</td>
<td>552 ± 10</td>
<td>563 ± 0.4</td>
<td>5.17</td>
<td>6.54</td>
<td>0.85</td>
<td>1.35</td>
<td>49 ± 16</td>
<td>20.90 ± 3.34</td>
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<tr>
<td>50-60</td>
<td>571 ± 12</td>
<td>565 ± 0.8</td>
<td>5.72</td>
<td>6.20</td>
<td>1.93</td>
<td>2.16</td>
<td>88 ± 21</td>
<td>22.00 ± 3.52</td>
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<tr>
<td>40-50</td>
<td>626 ± 13</td>
<td>615 ± 1.2</td>
<td>5.76</td>
<td>5.43</td>
<td>0.52</td>
<td>1.44</td>
<td>69 ± 14</td>
<td>23.98 ± 3.83</td>
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<td>30-40</td>
<td>694 ± 14</td>
<td>705 ± 0.8</td>
<td>5.83</td>
<td>5.34</td>
<td>0.32</td>
<td>1.52</td>
<td>69 ± 19</td>
<td>24.19 ± 3.87</td>
</tr>
<tr>
<td>20-30</td>
<td>642 ± 13</td>
<td>663 ± 0.8</td>
<td>5.62</td>
<td>6.62</td>
<td>1.48</td>
<td>1.59</td>
<td>59 ± 13</td>
<td>40.70 ± 6.51</td>
</tr>
<tr>
<td>10-20</td>
<td>590 ± 12</td>
<td>603 ± 0.4</td>
<td>5.64</td>
<td>1.50</td>
<td>1.07</td>
<td>1.51</td>
<td>94 ± 27</td>
<td>42.51 ± 6.80</td>
</tr>
<tr>
<td>0-100</td>
<td>621 ± 17</td>
<td>609 ± 0.8</td>
<td>–</td>
<td>2.60</td>
<td>1.41</td>
<td>1.51</td>
<td>81 ± 16</td>
<td>45.24 ± 7.21</td>
</tr>
</tbody>
</table>

Fused silica: – – 8.5<sup>nm</sup> – 2.46 0.20 0.60 9 ± 3 57.60 ± 9.21

Fig. 5.6: AFM surface morphology of representative HfO<sub>2</sub>-SiO<sub>2</sub> mixed thin films.
Atomic force microscopy (AFM) has been used to analyze the surface morphology of the films. AFM images were obtained in non-contact mode, under ambient conditions using silicon nitride cantilever and 3D AFM images of few representative films are shown in Fig. 5.6. The mean grain size and RMS roughness of the films have been determined from the topographic images and are listed in Table-5.1. The roughness obtained from the two techniques is different, which may be due to the scale at which measurements are performed. The roughness of all mixed films is found to be very less as compared to the pure hafnia surface, resulting less scattering loss. The possible explanation for high hafnia surface roughness is micro-crystallization of the material. In the present study, the desired film optical thickness and composition have been achieved by varying the deposition rate of constituent materials keeping other process parameters fixed. It is well known that grain growth and its structure strongly depend on the deposition conditions such as deposition rate, substrate temperature and deposition pressure. So for the mixed films, the different deposition rate of constituent materials leads to different growth structure of films, hence different grain size as well as different surface roughness as observed for the hafnia-silica mixtures.

5.2.4 LIDT measurement

The LIDTs of the HfO$_2$-SiO$_2$ composite films have been measured in the “1-on-1” mode according to ISO-11254-1 [67]. The LIDT measurement set-up is shown in Fig. 5.7. The 2$^{nd}$ harmonic (532 nm) of Q-switched Nd: YAG pulsed laser at a pulse width of 7 ns, was used for damage threshold measurement. The repetitive frequency of the laser was 10 Hz with largest pulse energy of 600 mJ. The sample was set on a motorized goniometer to give precise three-dimensional movements. The angle of incidence was slightly 2°–3° off normal to avoid interference effects due to reflection from the substrate exit surface. The energy of the laser beam is controlled with a variable attenuator using cross polarizers. The pulse energy was measured by energy meter using split-off portion of the beam by a wedge plate.
The Beam profile has been measured using “Spiricon beam profiler”. The beam spot diameter at the sample surface is 350 micron as computed from the beam analysis. Fibre optics based spectrophotometer has been used to monitor the damage event. For the present experiment, the reflection and/or transmission measurement of the sample in pump-probe mode has been used to detect damage initiation. Any physical change in the coating is reflected in the transmission/reflection spectrum. Damage onsets are verified through optical microscopy. The LIDT is defined as the pulse energy density when the damage occurs at 0% damage probability. The measurement repeatability has been verified by taking the LIDT measurement of mixed thin films deposited simultaneously on 2-fused silica substrate. The measured LIDT values for the films deposited on the 2-fused silica are almost close to each other, which confirm repeatability of the measurement. The total estimated error in the damage threshold measurement is approximately 16% due to the uncertainties in the stability of the laser system, the beam energy measurements and the beam profile measurements.

![Diagram of laser induced damage threshold measurement set-up.](image)

**Fig. 5. 7: Schematic diagram of laser induced damage threshold measurement set-up.**
5.3 Results and discussion

5.3.1 Optical properties and EMA models

The composition parameter controls the optical properties such as refractive index, absorption co-efficient and band gap of the materials, which is observed for HfO$_2$-SiO$_2$ mixed composite thin films as shown in Fig. 5.8 and Table-5.1 respectively. Both refractive index and absorption co-efficient decreases with increase of SiO$_2$ content except a certain range of mixtures which is discussed latter. Since silica has lower refractive index as well as less absorption than hafnia, so it is obvious to get lower refractive index as well as lower absorption co-efficient for mixture with higher silica content. From the GIXR measurement, it is found that the film density decreases with increasing silica content as listed in Table-5.1, as a result of which refractive index decreases. It is noticed that the refractive index of certain mixtures (90-10 and 80-20) is higher than pure HfO$_2$ film. Hence this range of mixture can be used for tailoring the high refractive index very conveniently for multilayer optical coating applications. Subsequently, the functional behaviours of the measured mixture refractive index as well as absorption co-efficient with respect to volume fraction ($f$) of SiO$_2$ have been compared to that predicted by different EMA models. The EMA models describe the mixed composite film in terms of spatially homogeneous electromagnetic response. It also requires that the individual inclusions be far from each other avoiding inclusion clustering [176]. The following widely used EMA models are chosen to compare with our experimental data:

Bruggeman model:
\[ f \frac{\epsilon_1 - \epsilon_{\text{eff}}}{{\epsilon_1} + 2\epsilon_{\text{eff}}} + (1 - f) \frac{\epsilon_2 - \epsilon_{\text{eff}}}{{\epsilon_2} + 2\epsilon_{\text{eff}}} = 0 \]  \hspace{1cm} (5.2)

Maxwell Garnett model:
\[ \frac{\epsilon_{\text{eff}} - \epsilon_2}{\epsilon_{\text{eff}} + 2\epsilon_2} = f \frac{\epsilon_1 - \epsilon_2}{{\epsilon_1} + 2\epsilon_2} \]  \hspace{1cm} (5.3)

Lorentz-Lorentz model:
\[ \frac{\epsilon_{\text{eff}} - 1}{\epsilon_{\text{eff}} + 2} = f \frac{\epsilon_1 - 1}{{\epsilon_1} + 2} + (1 - f) \frac{\epsilon_2 - 1}{{\epsilon_2} + 2} \]  \hspace{1cm} (5.4)

Drude model:
\[ \epsilon_{\text{eff}} = f\epsilon_1 + (1 - f)\epsilon_2 \]  \hspace{1cm} (5.5)
where $\varepsilon_1$ and $\varepsilon_2$ are complex dielectric functions of the material SiO$_2$ and HfO$_2$, respectively and $f$ is the volume fraction of SiO$_2$. $\varepsilon_{\text{eff}}$ is the effective dielectric function of the mixed thin film. The refractive index and absorption co-efficient of hafnia-silica mixture has been calculated according to these EMA models using the optical constants of HfO$_2$ and SiO$_2$ and the volume fraction determined from the deposition rates.

5.3.2 Theoretical refractive index of the mixed films

The experimentally determined refractive indices at 266 nm and 532 nm as a function of volume fraction of SiO$_2$ ($f$) are shown in Fig. 5.8(a), together with theoretical values calculated using different EMA model. Drude model is found to be more appropriate for explaining the effective refractive index for the hafnia-silica mixtures. This model suggests that the microstructure of the silica and hafnia phases is not point like (spherically symmetric), hence screening must be considered. The model depicts the situation where the induced dipoles were completely screened from one another so that only the external applied field induced the dipole moments. As a result the effective polarization is just simply the volume average of polarization of silica and hafnia phases, which is equivalent to capacitors connected in parallel [177, 178]. But for silica fractions < 20%, there is deviation of the EMA predicted values from the experimental values. It is because for such compositions, local structure and microstructural evolutions have played a bigger role in the effective dielectric functions. It is reported that the bond lengths of Hf-Hf and Hf-O are less for the HfO$_2$-SiO$_2$ mixed composite films with 10%, 20% and 30% SiO$_2$ content as compared to the pure HfO$_2$ film [179]. The lower bond length leads to more dense structure with smaller grains, which may be responsible for better refractive index for films having 10% and 20% silica content as observed for our mixed films. But further increase in silica concentration leads to decrease in refractive index as well as density. GIXR measurement and AFM images shows that hafnia-silica (90-10) has more density and smaller grain size as compared to the pure hafnia. For
hafnia-silica (80–20), the local structure and grain shape is expected to be responsible for its better refractive index as compared to pure hafnia.

Fig. 5.8: Experimental and computed (a) effective refractive index at wavelength of 266 nm and 532 nm and (b) effective absorption co-efficient at energy of 5.82 eV and 6.42 eV using different EMA models for HfO$_2$-SiO$_2$ mixed composite thin films.

5.3.3 Theoretical absorption co-efficient of the mixed films

The experimentally determined absorption co-efficient at 5.82 eV and 6.42 eV as a function of volume fraction of SiO$_2$ ($f$) are shown in Fig. 5.8 (b), together with the theoretical values computed using different EMA models. It has been found that for higher photon energy, Lorentz-Lorentz model shows good approximation to the experimental value except for lower silica content. Maxwell Garnett as well as Bruggeman model computed values shows good agreement with the experimental results for higher energy absorption for mixture of lower silica content. It is found that the computed absorption co-efficient values at weak absorption region using different EMA models are always higher than those observed experimentally. The discrepancies may be due to the assumptions of EMA models. The EMA model assumes
that the mixed composite material is just a mixture of materials of two separated phases with spherical, with size large enough to have the same dielectric function locally as the bulk material. This may not be the case for the presently studied silica-hafnia mixture, in which the material can mix at molecular level and therefore no clear phase separation may not exist [180]. Again the EMA models are quasi-static in nature and they are applicable for grain dimension and spacing much smaller than the wavelength of light (~0.1λ). As a result of which the EMA based effective dielectric function does not explicitly depend on the size of the grains occurring in the medium [181]. But both the absorption co-efficient as well as the absorption edge is found to be strongly affected by the grain size of the material [182, 183].

From Fig. 5.8, it is observed that, the Drude model has successfully described the refractive index of hafnia-silica mixture in both weak as well as strong absorption region as compared to the Lorentz-Lorentz model for absorption co-efficient. This is because the strong dispersion of the absorption co-efficient in weak absorption region is strongly connected to the sample microstructure, while the refractive index shows a smaller dispersion in weak absorption regions as its value is primarily influenced by the material density as compared to the microstructure [184]. By considering the possible different shape of the grain except spherical grain shape as considered in the Lorentz-Lorentz model, the absorption properties of the mixed composite films can be explained over its full range of usable volume fractions with a minimum of empirical correction factors, which would be very useful for design and development of optical filters.

5.3.4 Laser induced damage threshold

The composition parameter in mixture also controls the laser induced damage threshold (LIDT) as observed for the hafnia-silica mixture as shown in Fig. 5.9. The laser induced damage morphology shown in Fig. 5.11 shows that the damage is expected to be a mixture of thermal melting as well as internal stress generated damage.
Fig. 5.9: Variation of LIDT of HfO$_2$-SiO$_2$ mixed composite thin films with SiO$_2$ fraction. The inset plot is optical band gap vs. volume fraction of SiO$_2$.

The increasing laser induced thermal damage with silica content can be explained at the simplest level as follows. The amount of energy to produce damage is determined by the absorbed light intensity at the film surface or interfaces [185]. The absorbed power per unit volume is proportional to $(nke^2)$. From Fig. 5.8, it is clear that both refractive index ($n$) and absorption co-efficient ($\alpha$) decreases with increase of silica content, hence the absorbed power decreases. So the higher damage threshold with increase silica content may be ascribed to the lower value of the $(nke^2)$ term at the air-film interface. The increasing laser induced mechanical damage with silica content can be explained by considering the change in internal pressure $\Delta P$ in the film because of rapid heating at constant volume. The intrinsic stress generated due to this internal pressure $\Delta P$ may be directly implicated in causing mechanical damage such as surface cracks. This cracked film may absorb laser energy more efficiently, which may melt and vaporize, and damage finally occurs. Assuming $v = (E/\rho)^{1/2}$ is the velocity of elastic waves; the change in internal pressure ($\Delta P$) can be expressed as [186]:

$$\Delta P \approx A \frac{L\alpha}{C} \frac{E}{\sqrt{\rho}}$$

(5.6)
where $A = 4p^2 M (1/3(1-2v))$ is a constant [186] and depends on the laser power, laser beam diameter, reflectivity, absorption and thickness of the film, $L$ is the distance from the stressed region to the free surface (for thin films, $L$ is usually 1 μm or less), $\alpha$ is the co-efficient of thermal expansion, $E$ is the Young’s modulus and $C$ is the specific heat of the film. The effective $E$, $\alpha$ and $C$ of the mixed film has been calculated using the Reuss model [187], Turner model [187] and volume fraction mixture rule [188] respectively. The co-efficient of thermal expansion ($\alpha$) of the mixture decreases with increase of silica content (because $\alpha_{SiO_2}=0.51\times10^{-6}$ K$^{-1}$ < $\alpha_{HfO_2}=3.8\times10^{-6}$ K$^{-1}$) while the elastic modulus ($E$) decreases with increase of silica content (because $E_{SiO_2}=72$ GPa < $E_{HfO_2}=380$ GPa). But the specific heat ($C$) of the mixture increases with increase of silica content (because $C_{SiO_2}=746$ JK$^{-1}$Kg$^{-1}$ > $C_{HfO_2}=16.7$ JK$^{-1}$Kg$^{-1}$). The computed normalized internal pressure using Eq. (5.8) for different composition of the mixed films is shown in Fig. 5.10. The thermal properties used for this calculation is taken from Ref. [189]. The Fig. 5.10 shows that the internal pressure or stress $\Delta P$ decreases with increase of SiO$_2$ content. Hence the laser damage threshold due to mechanical stress increases with silica content.

![Graph showing internal stress as a function of SiO$_2$ fraction in HfO$_2$-SiO$_2$ mixed thin films.](image)

**Fig. 5.10:** Internal stress as a function of SiO$_2$ fraction in HfO$_2$-SiO$_2$ mixed thin films.
Looking at the band gap vs. volume fraction of SiO₂ plot for the mixtures up to 70% silica content in the inset plot of Fig. 5.9, it is clear that the behaviour of the LIDT is induced by other thin film property and not by the optical band gap energy [190]. But the optical band gap energy is expected to play a crucial role for the sudden transition in LIDT value as shown in Fig. 5.9. The laser induced damage threshold for mixtures with silica content equal or more than 80% is approximately double that of other mixtures, which may be due to the influence of multiphoton absorption process in the damage initiation. The rate of energy absorption from a multiphoton process is given by [191, 192]

$$\frac{dN_e}{dt} = N_0 \sigma^{(n)} (\frac{I}{h\nu})^n$$  \hspace{1cm} (5.9)

where $N_e$ is the electron density, $N$ is the initial solid atom density, $I$ is the laser intensity, $n$ is the absorption order and $h\nu$ is the photon energy. Since the transmission edge of the films of higher silica content (more than 80% silica) do not fall at wavelength equal to or less than 190 nm. So the optical band gap of these films must have value more than 6.52 eV. Hence for 532 nm laser, 3-photon absorption ($3 \times 2.33$ eV = 6.99 eV) is more probable. The Intensity ($I_e$) necessary for 3-photon absorption ($n=3$), which may occur in the mixed films, can be estimated by solving Eq. (5.9):

$$I_e = \left( \frac{N_e}{(N_0 \sigma^{(3)} \tau)} \right) E$$  \hspace{1cm} (5.10)

Where $\sigma^{(3)}$ is the 3-photon absorption cross-section ($\approx 10^{-81}$ cm$^6$ s$^2$) [193] and $\tau$ is the pulse duration. The electron density ($N_e$) necessary for rapid energy absorption would be at most the critical density ($N_c$) or at least 0.01$N_c$ depending on the size of the plasma [194]. Hence the lower and upper bound of $N_e$ are 0.01$N_c$ and $N_c$, respectively. For 532 nm laser radiation, the critical density $N_c = (1000 \text{ nm} / \lambda)^2 \times 10^{21}$ cm$^3 = 1.88 \times 10^{21}$ cm$^3$ [195]. Using Eq. (5.10) for 7 ns pulses, the lower and upper bounds of the LIDT are 294 J/cm$^2$ and 1400 J/cm$^2$, respectively. The observed LIDT ranges from 40 J/cm$^2$ to 45 J/cm$^2$ for the films having more
than 80% silica content. For very small spot sizes, damage threshold in excess of 280 J/cm² for 1064 nm wavelength [196] up to 1760 J/cm² for 532 nm wavelength [197] has been observed in fused silica for nanosecond laser, in which pure multiphoton process is expected to dominate. In the present study, the used laser beam diameter is 350 micron, which produces large spot size indicating that pure multiphoton ionization cannot be the origin of damage initiation. Hence the pure multiphoton absorption process can’t be used to estimate the damage thresholds. Instead of the pure multiphoton process, the defect assisted multiphoton mechanism [113] can be used to explain the observed damage thresholds for higher silica content films. The expected defects exist in the hafnia-silica mixed films may be localized absorbing inclusion such as Hf inclusion, Si inclusion and nonstoichiometric HfO₂ or SiO₂ inclusions, , non-bridging oxygen hole centre [198-200], defects associated with boundaries and interface, elementary point defects such as oxygen vacancies and interstitials etc [201]. These defects will be heated by absorbing the laser pulse and then transfer the heat to the host material through heat conduction, leading to decrease of the band gap of the host material as observed by K. Saito and A. J. Ikushima for bulk SiO₂ (decreasing band gap from 8.5 eV to 7 eV when the temperature is increased from 4K to 1900 K) [202]. Since such defects and the temperature dependent band gap property of the host material can potentially lower the energy required promoting an electron to the conduction band, hence reduces the order of the multiphoton process. Now depending on the laser wavelength, two or three photons absorbed by a number of neighbouring defects can lead to a sufficient population of conduction band electrons to start the localized cascade electron multiplication process responsible for damage initiation. This model accounts for the sharp transition in the LIDT.

Since for films having more than 80% silica, the expected band gap is more than 6.5 eV, so the combination of two-photon absorption followed by defect state absorption by a single photon is expected to be responsible for the improved LIDT. Hence the density of defects is
necessary to understand the damage mechanism and is determined by using this model. The overall damage thresholds as calculated for pure multiphoton process are reduced because the effective cross section for a multistep process is larger than that of a single step. For example, the cross section of a three photon process is on the order of $10^{-81}$ cm$^6$ s$^2$ while the cross section for a combination of two-photon absorption followed by excited state absorption by a single photon is estimated to have an upper bound of $10^{-61}$ cm$^6$ s$^2$ [113]. Using this modified cross section in Eq. (5.10) with the observed damage threshold of 40.7 J/cm$^2$, a lower bound to the necessary defect density is estimated to be on the order of $10^4$ cm$^{-3}$. Localized defects of this order of magnitude are comparable or less to the values reported by H. Krol et al. for fused silica surface [203], L. Gallais et al. for SiO$_2$ [204] and HfO$_2$ [198] thin films and X. Fu et al. for Niobia-Silica and Zirconia-Silica mixtures [196].

Fig. 5. 11: Laser induced damage morphology of HfO$_2$-SiO$_2$ mixed composite thin films.

5.3.5 Laser damage morphology

Moreover, a specific characteristic has been observed in the damage morphology of given representative samples as shown in Fig. 5.11. In this figure, pure HfO$_2$ film and films with silica content up to 20% shows absorption induced “melting and evaporation” type of damages, in which centre of the irradiated area has been simply removed while melted area appears on the edges and the size of the lateral damage decreases with increasing silica
content. For silica fractions above 30%, absorption induced “melting and re-crystallization” type of damage has been observed, in which moving on towards higher silica content, small separated pits appear in the damage morphology. This could be due to absorbing inclusion defects embedded in the film [67]. These absorbing inclusion defects absorb a fraction of incident energy and heat the surrounding host material causing a collapse of the band gap and plasma formation. Since this model predicts laser damage will be initiated at the site of absorbing inclusion defects, so it is reasonable to expect damage to occur at discrete localized centers, and not necessarily at the peak energy density of the laser. According to this defect-dominated damage model, for films with lower silica content, the damage sites are centered on a single defect, while for films with higher silica content, the damage sites form a connecting area composed of several defects [195]. The uncoated fused silica substrate shows higher damage threshold value and its damage morphology shows a very small single damage point indicating localized defect absorption. From the damage morphology as well as damage threshold values, it can be expected that the origin of laser induced damage mechanism may be different for certain composition of mixtures as compared to other compositions depending on the materials in the nanosecond regime.

5.4 Conclusion

HfO$_2$-SiO$_2$ mixed composite films have been prepared by electron beam co-evaporation technique. The refractive index and absorption co-efficient are found decreasing with increasing silica content except anomaly behaviour for 10% and 20%, while the optical band gap increases monotonically. The anomaly behaviour has been clarified by GIXR and AFM measurements. The experimentally observed composition dependent refractive index as well as absorption co-efficient has been compared with the theoretical computed values using different EMA models. It is observed that Drude model is more appropriate to explain the refractive index of the mixtures while Lorentz-Lorentz model computed values shows fair
agreement with experimental determined absorption co-efficient values. The mixture films are found to have better surface roughness with smaller grain size as compared to pure hafnia resulting reduction in scattering loss. The laser induced damage threshold measurement has been carried out. The improved LIDT for films having more than 80% silica content has been explained through defect assisted multiphoton ionization process, which is the primary mechanism for damage initiation in such films. This study concludes that the LIDT values and the analyzed EMA models for optical dispersion with proper logistics can be useful while designing stable optical graded index or inhomogeneous multilayer interference coatings utilizing hafnia-silica mixtures.