DEPOSITION AND CHARACTERIZATION OF REFRACTORY OXIDE THIN FILMS AND MULTILAYER OPTICAL COATINGS

By

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DECLARATION

I, do hereby declare that the research work presented in the thesis have been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other institution / university.

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LIST OF PUBLICATIONS ARISING FROM THE THESIS

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- "Correlation among microstructure, optical properties, residual stress and laser damage threshold of electron beam evaporated HfO₂ thin films", S. Jena, R. B. Tokas, S. Tripathi, K. D. Rao, D. V. Udupa, S. Thakur and N. K. Sahoo, 2017 (*Communicated*).
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DEDICATIONS

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Synopsis

Refractory oxide thin films and multilayer optical coatings have been the primary research interest in the domain of modern optics technology. The multilayer devices utilizing optical coatings such as antireflection coatings, high reflection mirrors, beam splitters, beam combiners, band pass filters etc. are indispensable for the technology development as well as experiments involving lasers, synchrotron radiations, and emission-absorption spectroscopy. Efficiency and performance of such devices depends strongly on the microstructure, optical and mechanical properties, and laser induced damage threshold (LIDT) of the thin films used to fabricate the devices. Various properties of the thin films such as refractive index, optical band gap, surface morphology, laser damage resistance, and residual stress can be tuned by varying deposition process parameters such as oxygen pressure, substrate temperature, deposition rate, and substrate rotation. Amongst all, the deposition oxygen partial pressure has the dominant effect. Therefore, study of effect of oxygen partial on different properties of thin films is very much essential for development of stable optical coatings.

Design of some challenging optical coating devices such as rugate notch filter, ripple free band pass filter, beam combiner etc. needs refractive index values which do not exist in conventional coating materials. These refractive index values can be obtained by mixing two coating materials, where one has high refractive index value and other has low refractive index value. The refractive index of the mixed oxide thin films is tailored by mixing two materials in vapor phase using co-evaporation techniques. The mixed thin films show better microstructure as compared to the individual thin film materials. These mixed oxide composite thin films enhance the scope of the optical coating designs as well as practical performances of the interference filters. HfO₂-SiO₂ mixed oxide composite thin films with different volume fraction of SiO₂ and HfO₂ are prepared and characterized to study the effect of mixing ratio on their optical properties and LIDT.

Under mechanical shocks, intense pulsed laser fields or environmental disturbances, cracking or peeling of thin coating layers may occur, which can adversely affect performance of the thin film devices. To avoid it, optimization of mechanical properties of the thin films is of great concern. The film mechanical properties such as elastic modulus, residual stress etc. are primarily related to the coating stability i.e. peeling, cracking and curling of the films. Therefore determination of residual stress and elastic modulus of thin films are very crucial for developing optical coatings. In this thesis, we have used laser Fizeau interferometer to measure substrate curvature before and after thin film coatings, from which the residual stress in the films has been estimated. Atomic force acoustic microscopy (AFAM) measurement set-up and analysis method has been utilized to derive elastic modulus of the thin films.

For high power laser applications, the multilayer coatings should withstand laser power without being damaged. Therefore, laser damage resistance test of thin films and multilayer coatings is of high importance. For that purpose, an in-house experimental facility using Nd:YAG pulsed laser has been utilized to determine LIDT value of the thin films and multilayer coatings. Laser damage mechanism and damage morphology have been analyzed. Multilayer high reflection (HR) mirrors have been developed and effort has been made to increase their LIDT. Single layer thin film properties can be improved or modified by postdeposition annealing other than process parameter tuning during deposition. The same is true for multilayer coatings. Post-deposition annealing of multilayer mirrors can significantly change their characteristics and performance. In the present thesis, post-deposition annealing effects on microstructure and LIDT of HfO₂/SiO₂ multilayer HR mirror have been investigated. The LIDT of the multilayer mirror is found increasing with annealing.

The multilayer structure can be used to fabricate omnidirectional HR mirror, which equally reflects a band of light irrespective of angle of incidence and polarization of light. This device is called omnidirectional mirror and has potential applications in the field of optical fibre power transmission, filters in solar cells, wave guide communications, and laser cavities. In the present thesis, omnidirectional HR mirror has been fabricated by depositing TiO_2/SiO_2 multilayer using sputtering technique. Asymmetric bipolar pulsed dc (ABPDC) magnetron sputtering has been used to deposit TiO_2 thin layers, which gives higher refractive index value. This ultimately leads to wider omnidirectional high reflection photonic band in the visible region as compared to literature till now for the TiO_2/SiO_2 periodic multilayer.

The most widely used refractory oxide materials for optical coating applications are hafnia (HfO₂), silica (SiO₂), zirconia (ZrO₂), titania (TiO₂) etc. All these materials are useful in the UV-VIS-NIR region of the electromagnetic spectrum except TiO₂ as it shows absorption in the visible region. SiO₂ is a low refractive index and wide band gap transparent material, while rest of the materials exhibits high refractive index. HfO2 and ZrO2 have similar kind of structure and both are useful to make coatings and devices for high power laser applications. Therefore properties of HfO₂ and ZrO₂ thin films should be investigated thoroughly. Adding low index material SiO₂, their optical properties, microstructure and LIDT can be tuned to the desired values. HfO_2 -SiO₂ and ZrO₂-SiO₂ mixed oxide thin films are useful for graded index optical filters, as one can achieve a wide range of refractive index by tuning volume fraction of SiO₂ in these mixed films. Maximum refractive index of ZrO₂ can be obtained with small addition nearly 15% of MgO to it. Therefore ZrO₂-MgO binary mixed composite thin film is important for optical coating applications. Similarly adding small amount of SiO₂ less than 20%, the LIDT of ZrO₂ get enhanced, therefore ZrO₂-SiO₂ mixed oxide thin film coating is more useful for high power laser applications. The properties of thin films are used to design multilayer coatings and devices. Multilayer consists of a stack of alternate high and low refractive index thin films. For example (HfO₂/SiO₂)^N, (TiO₂/SiO₂)^N and $(ZrO_2/SiO_2)^N$ with N= period of alternate layers, can be used to fabricate antireflection coatings, high reflection mirrors, band pass filters etc.

Though lots of studies have been carried out by several researchers on these materials and their multilayers, there exists considerable scope on these materials which needs thorough investigation to improve the properties and performance of these thin film based coatings and devices. The present doctoral research deals with the microstructure, optical and mechanical properties, and LIDT of refractory oxide thin films (HfO₂, HfO₂-SiO₂ mixed oxide, ZrO₂-MgO, and ZrO₂-SiO₂ mixed oxide) and multilayer coatings (HfO₂/SiO₂ and TiO₂/SiO₂). All the thin films and multilayer coatings studied in the present thesis are prepared by electron beam (EB) evaporation and sputtering technique. The present dissertation has been organized in seven chapters as follows:

Chapter-1 gives a brief introduction to the research background related to the refractory oxide thin films, mixed oxide thin films, and multilayers for optical coating applications. The multilayer stack design used to fabricate HR mirrors and omnidirectional reflectors are described. Finally the aim and scope of this thesis are outlined. Chapter-2 discusses the experimental techniques to deposit and characterize the thin films and multilayer coatings. The principle and working of EB evaporation, DC/RF and ABPDC magnetron sputtering techniques are discussed in detail. The optical properties and thickness of the films are derived from the transmission spectrum measured by Spectrophotometer. The crystal structure and film density are derived using X-ray diffraction (XRD) and grazing incidence Xray reflectivity (GIXR) respectively. Surface and cross-sectional morphology of the films and multilayers have been probed by atomic force microscopy (AFM) and scanning electron microscopy (SEM) respectively. The elastic modulus of the films is measured using atomic force acoustic microscopy (AFAM). Residual stress in thin films has been determined from substrate curvature measured by laser Fizeau interferometer. The LIDT of the thin films and multilayer coatings have been measured using in-house developed LIDT experimental set-up. All these techniques are described thoroughly in this chapter.

Chapter-3 deals with the study of HfO_2 thin films deposited by EB evaporation and magnetron sputtering. The chapter is described in two parts as follows.

(I) *EB evaporated* HfO_2 *thin films*: In this part, HfO_2 thin films were deposited by EB evaporation at different oxygen (O₂) partial pressure. The effect of O₂ pressure on different properties of the films has been investigated. The films are characterized to probe their structure, surface morphology, optical properties, residual stress and LIDT respectively. All the films are amorphous in nature. The refractive index and density of the films decreases with increasing oxygen partial pressure. The relation between optical band gap and refractive index follows Moss rule. Grain size and surface roughness increases with increasing O₂ pressure is correlated with the film microstructure. The decreasing LIDT with increasing O₂ pressure for 1st and 2nd harmonics of Nd: YAG laser has been explained through film porosity.

(II) *RF magnetron sputtered HfO*₂ *thin films*: In this part HfO₂ thin films have been deposited on BK7 glass substrate by RF sputtering technique at different oxygen/argon (O₂/Ar) gas flow ratios. The effect of O₂/Ar flow ratio on different film properties has been reported. The structure of the films shows that the inter-planar spacing of the films decreases with increasing O₂/Ar flow ratio causing compressive strain in the films. The dispersion of the refractive index is discussed in terms of the single-oscillator Wemple–DiDomenico model. The dispersion energy and the oscillator energy are correlated with the compressive strain in order to investigate the lattice strain effect on the optical properties. The variation of the residual stress with O₂/Ar flow ratio is explained through lattice expansion induced compressive stress and grain size dependent tensile stress in the films. The pulsed laser induced damage threshold of the films are measured and correlated with film's grain size.

Chapter-4 presents the study of several properties of EB evaporated ZrO₂-MgO and ZrO₂-SiO₂ mixed composite thin films, which are discussed in two parts as follows.

(I) ZrO_2 -MgO mixed composite thin films: In this part, a set of ZrO_2 -MgO binary mixed composite thin films have been prepared by evaporating ZrO_2 -MgO solid solution composite material using EB evaporation at different O_2 partial pressure. The effect of O_2 pressure on surface morphology, optical properties, elastic modulus and LIDT of the films has been investigated. The refractive index and density of the films are correlated. The elastic modulus of the films is determined using AFAM technique. The variation of the elastic modulus as a function of O_2 partial pressure has been studied and corroborated with the variation of density of the films. The LIDT of the films are measured with Nd:YAG pulsed laser of wavelength 532 nm. The variation of LIDT has been explained through grain size dependent thermal conductivity of the films.

(II) ZrO_2 -SiO_2 mixed composite thin films: ZrO_2 :10%SiO_2 thin films have been deposited on fused silica substrate by co-evaporation of ZrO_2 and SiO_2 using EB evaporation technique at different oxygen partial pressure. The influence of O₂ pressure on structure, surface morphology, optical properties, elastic modulus and LIDT of the films has been studied. The variation of optical band gap has been explained in terms of film crystalinity. No crystallite size or grain size effect on the optical properties of the films has been observed. The dispersion of the refractive index is discussed in terms of single oscillator Wimple-DiDomenico model. A correlation among surface morphology, dispersion energy and crystalinity has been established. The effect of grain size on the elastic modulus and LIDT of the films has been investigated.

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Chapter-6 reports the development of HfO_2/SiO_2 and TiO_2/SiO_2 multilayer mirrors, and their characterizations, which are detailed in two parts as follows.

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(II) Magnetron sputtered TiO_2/SiO_2 multilayer thin films as omnidirectional mirror: In this part, TiO_2/SiO_2 multilayer has been fabricated by sequential asymmetric bipolar pulsed DC magnetron sputtering of TiO_2 and RF magnetron sputtering of SiO_2 to achieve wide band

omnidirectional mirror. The microstructure and optical response of the multilayer has been investigated. The multilayer is considered as one dimensional photonic crystal (1DPC). The calculated band dispersion curve of the 1DPC is compared with the measured high reflection band. Wide high reflection photonic band gap ($\Delta\lambda$ =245 nm) in the visible and near infrared regions (592-837 nm) at normal incidence has been achieved. The experimentally observed omnidirectional high reflection photonic band 592-668 nm ($\Delta\lambda$ =76 nm) with band to midband ratio $\Delta\lambda/\lambda$ =12% for reflectivity R>99% over the incident angle range of 0°-70° is found almost matching with the calculated omnidirectional PBG. The omnidirectional PBG is found much wider as compared to the values reported in literature so far in the visible region for TiO₂/SiO₂ periodic multilayer 1DPC.

Chapter-7 summarizes the highlights of the research work, which are as follows: (i) Numerical code developed to determine optical properties and thickness of thin films, and spectral characteristics of multilayers, (ii) In-house built laser induced damage threshold (LIDT) measurement set-up, (iii) Use of atomic force acoustic microscopy (AFAM) measurement technique to determine elastic modulus of thin films, (iv) Utilization of laser interferometry to measure substrate curvature for determination of residual stress in thin films, (v) Influence of oxygen partial pressure on different properties of EB evaporated HfO₂, ZrO₂-MgO thin films , (vi) Structure dependent optical properties of ZrO₂-SiO₂ thin films, (vii) Correlation between residual stress and microstructure of RF sputtered HfO₂ thin films, (viii) Composition dependent optical properties and LIDT of HfO₂-SiO₂ multilayer high reflection mirror, and (x) Fabrication and characterization of TiO₂/SiO₂ multilayer one dimensional photonic crystal as omnidirectional HR mirror. Finally the chapter concludes with future directions for further studies in the field of refractory oxide thin films and multilayer optical coatings.

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Chapter 1: Introduction

This chapter gives overview about thin film coatings, mixed oxide composite thin films, multilayer thin film filters, and process parameter and post-deposition annealing effects on thin films and multilayer devices, which is based on wide literature survey on the field of refractory oxide thin films and multilayer optical coatings. It also includes aim and scope of the thesis. The detail of this chapter is described as follows.

1.1 Thin film coatings

Generally thin films are thin layers of materials ranging from fractions of a nanometer to several micrometers in thickness. It is quasi-two dimensional geometric structure. The structural, electrical, magnetic, optical, thermal, and mechanical properties of thin films may significantly differ from the bulk properties. Thin film studies have the most significant contribution technology of semiconductor devices. to the telecommunications. microelectronics, solar cells, light emitting diodes, liquid crystal display, magneto-optics memories, multilayer capacitors, transistors, rectifiers, smart windows, magnetic sensors, gas sensors, wear resistance, corrosion resistance, interference filters etc. [1]. In the present thesis the application of thin films is limited to optical coatings only. The spectral characteristics of thin film optical coatings are primarily based on principles of interference. A single layer thin film of refractory oxide can be used for different applications such antireflection coating. beam splitter, abrasion resistance etc. For example, a single layer quarter wavelength thick of silicon monoxide on both sides of silicon substrate reduces the reflection of the substrate from 31% to less than 1% at wavelength of 1.7 μ m in the infrared region [2].

Refractory oxides are very important and most widely used optical coating materials because they generally from hard, abrasion resistant, chemically and environmentally stable films with good variety of refractive indices and spectral ranges of high transmission [3] as shown in Table-1.1. ZrO_2 and HfO_2 are very common high refractive index thin film materials used for optical coatings because of their hardness, high UV transmission and higher laser damage threshold. The absorption of both hafnia and zirconia is only significant below wavelength of 250 nm; therefore they are very useful for UV coatings [4]. SiO₂ is the common low refractive index and high band gap material used for fabrication of different optical filters [4]. In addition to that, SiO₂ thin film can be used as a corrosion resistance layer of metals [5]. TiO₂ ($n \sim 2.5$) is a high refractive index material mostly used in the visible range as it begins to absorb light below 450 nm [4]. TiO₂ is very useful for applications such as self-cleaning and defogging windows [6].

Table - 1. 1: Properties of typically used refractory oxide optical coating materials [4].

Dielectric	Melting	Range of	Refractive
coating	Point	transparency	index at
material	$T_m(^{\circ}C)$	(nm)	550 nm
HfO ₂	2780	250-12000	1.95
SiO ₂	1600	200-9000	1.45-1.46
TiO ₂	1850	400-3000	2.2-2.4
ZrO ₂	2700	340-12000	1.95-2.05
Ta ₂ O ₅	1870	300-10000	2.03-2.09

1.2 Mixed oxide composite thin films

Mixed oxide dielectric thin films have been applied for more than three decades in a number of different applications. In the semiconductor industry, doping was done to create insulators and conductors from one host material. The concept of mixed oxide thin films also plays crucial role for the development of high K-materials. In the same time, topics like wide range of refractive index, amorphous structure, stress reduction and smooth surface for thin film coatings and multilayer optical filters were addressed by forming composites of two materials. Some interference optical filters need very complex multilayer structure to achieve their spectral characteristics. Because these filters requires refractive indices, which does not exist in conventional thin film materials. Two materials of different refractive index can be mixed to get the desired refractive indices. These materials are called mixed oxide composite thin films [7]. It is possible to develop more complex devices such as rugate filters, wideband antireflection coatings, non-polarizing beam splitters, minus filters etc. by using a variable refractive-index composite thin film material in the design. In the past, several research groups have reported preparation and characterization of such promising oxide dielectric thin film materials as discussed below.

The properties of mixed thin films such as structure, refractive index, composition and surface morphology depend on the deposition process and the materials. There are reports on the double EB coevaporation of mixed films of ZrO₂-MgO, ZrO₂-SiO₂, ZrO₂-MgF₂, and Ta₂O₅-TiO₂. The refractive index ranges for these films are approximately 2.05-1.7 for ZrO2-MgO, 2.05-1.45 for ZrO₂-SiO₂, 2.05-1.36 for ZrO₂-MgF₂, and 2.1-2.55 for Ta₂O₅-TiO₂ [8]. Russak et al. [9] found that the reactive dc magnetron sputtered ZrO₂-SiO₂ mixed film with 10%SiO₂ is amorphous in nature and more thermally stable than pure ZrO₂. A linear relationship between refractive index and SiO₂ content was observed. Pond et al. [10] investigated the properties of ZrO₂-SiO₂ mixed thin films evaporated from two separate ZrO₂ and SiO₂ targets using two ion guns in a IBS system . The obtained refractive index of the mixed was close to both linear and Drude models. Jensen et al. [11] reported properties of ion beam sputtered HfO₂-SiO₂ mixed thin films. They found that the mixed oxide films are amorphous in nature. The optical band gap and laser damage threshold increase with increasing SiO₂ content, while refractive index at wavelength of 355 nm decreases from 2.18 to 1.55. Kamble et al. [12] and Xing et al. [13] have investigated optical properties of EB coevaporated HfO₂-SiO₂ mixed thin film. They found that the structure of the mixed films is amorphous and the coating with SiO₂ content around 10-15% exhibits highest refractive index. Chen *et al.* [8] showed that double EB coevaporated TiO_2 -SiO₂ mixed thin films is amorphous for a SiO₂ content as low as 11% and exhibits smoother surface. The relation between refractive index and SiO₂ content follows linear and Bruggeman effective medium approximation model. Demiryont *et al.* [14] tailored refractive index of TiO₂-SiO₂ mixed thin film from 1.48 to 2.39 by co-sputtering of TiO₂ and SiO₂ simultaneously. Even now, tailoring refractive indices and tuning of band gap as well as optimizing scattering and the stability of coatings to high temperature or high laser power still keeps excitement for the researchers considering evolution of emerging functional materials.

1.3 Multilayer coatings

A multilayer thin film structure consists of thin layers of different materials stacking on top of one another with distinct interface between adjacent layers. The multilayer gives different spectral characteristics as compared to the individual layers. The spectral performance and other different properties of multilayers are determined by the structure and number of layers, the refractive index of each layer material and the optical properties of the substrate. Multilayer thin film structure has wide applications in corrosion resistance coating, thermal barrier coating, UV and x-ray mirrors, neutron super mirrors, optical filters etc.



Fig. 1. 1: Schematic of thin film and multilayer thin film structure.

Here, we will discuss mainly on multilayer structure as optical interference filters. Although the thin layers are themselves colorless, the light interference in the multilayer results in the appearance of colors at the surface, similar to as seen in a soap bubble. The basic structure of an interference filter features discrete alternating layers of high and low index materials, each having quarter wave (QW) optical thickness. The geometrical schematic of a single layer and multilayer thin films is shown in Fig. 1.1. Here, we will discuss briefly only about two optical filters i.e. high reflection mirror and omnidirectional mirror.

1.3.1 High reflection mirror

Dielectric multilayer high reflection (HR) mirrors are popularly known as Bragg mirrors. Bragg mirrors are multilayer structures consisting of periodic alternate layers of two dielectric materials with different refractive index (n_H and n_L) of optical thickness of one quarter wavelength of light ($d_H=\lambda/4n_H$ and $d_L=\lambda/4n_L$) to be reflected. The QW multilayer mirror has a characteristics high reflection (HR) region or stop band symmetric about the design wavelength λ_0 surrounded by long and short wavelength pass regions with many ripples in the pass bands as shown in Fig. 1.2. The reflectivity of such multilayer mirrors can be tuned ideally between 0 to 100 % using such stack of periodic layers. The high reflectivity is due to constructive interference of light reflected at the consecutive interfaces of a multilayer structure. The prerequisite to achieve efficient high reflection mirrors are (i) dielectric layers with minimum loss, (ii) smooth surface and sharp interfaces for least scattering, and (iii) the precise control of each layer thickness [15]. The reflectivity at the target wavelength for the periodic multilayer HR mirror is given by

$$R = \left(\frac{1 - \frac{n_H^2}{n_s} \left(\frac{n_H}{n_L}\right)^{2N}}{1 + \frac{n_H^2}{n_s} \left(\frac{n_H}{n_L}\right)^{2N}}\right)^2$$
(1.1)

The high reflectance wavelength band is given by

$$2\Delta g = \frac{4}{\pi} \sin^{-1} \left(\frac{n_H - n_L}{n_H + n_L} \right)$$
(1.2)

where g is the normalized wavelength $(g=\lambda_0/\lambda)$, n_s is the substrate refractive index, and n_H and n_L are high and low refractive index thin film layers respectively. The peak reflectivity is increased by increasing number of bilayer (N) as shown in Fig. 1.2. The width of the HR band is maximized using materials of wider refractive index contrast (n_H/n_L) .



Fig. 1. 2: Calculated reflectivity of quarter-wave stacks consisting of $N=1, 2, 3, \dots, 15$ bilayers of HfO_2/SiO_2 at centre wavelength of 650 nm.

For example, multilayers of amorphous silicon (αSi , $n_H = 3.9$) and silicon dioxide (SiO₂, $n_L = 1.45$) yield a high refractive index contrast ($n_H/n_L = 2.7$). The resulting normalized band widths are $2\Delta g = 0.6$ and $\Delta\lambda/\lambda_0 = 0.66$. Hence for $\lambda_0 = 795$ nm, $2\Delta g = 477$ nm and $\Delta\lambda = 520$ nm [16]. The high reflection mirrors are used in variety of applications such as vertical-cavity surface-emitting lasers, optical filters, solar cells, sensors etc. In addition to the above applications, the HR mirrors are important for development of high power laser systems, ring laser gyroscopes, and large-scale physics experiments like interferometric gravitational wave detectors (e.g. LIGO, VIRGO, GEO600, TAMA300, etc.) [17].

1.3.2 Omnidirectional mirrors

Omnidirectional mirror reflects both polarizations of light at all incident angles over at least some spectral band width. Dielectric multilayer QW stack can be made as omnidirectional mirror. It has advantage over metallic mirrors, of being non-dispersive and non-absorbing in the visible and NIR range. These characteristics have been used to design unprecedented control of light for several areas applications such as waveguides, biophotonic sensors, solar cells, integrated photonic chips, spontaneous emission, and biomedical optics. The condition for optimum reflection from a high and low index layer pair at a given angle and polarization is that the optical thickness must be one-half wavelength at the centre of the stop band.



Fig. 1. 3: (a) Equal omnidirectional reflection band width $(\Delta \lambda)$ contours plotted as a function of n_L and n_H , and (b) Calculated omnidirectional reflection wavelength versus angles of incidence for TE- and TM-wave for TiO₂/SiO₂ multilayer QW stack. The grey shaded are is the total omnidirectional band gap.

The pair of refractive index for which the multilayer stack will show omnidirectional reflection has been estimated by Southwell *et al.* [18] as shown in Fig. 1.3 (a). This figure shows that the QW stack with materials whose refractive index value lie above the B = 0% curve will exhibit omnidirectional reflection character. Moreover, there is an extremum value for low refractive index $n_L = 1.45$. This means that for any high index (n_H) material, the optimum value of n_L is almost 1.45. For a multilayer QW stack, the high reflection band

edges at oblique angle of incidence for both polarizations are calculated by Lekner *et al.* [19], which determines the omnidirectional reflection band. Fig. 1.3 (b) is the simulated omnidirectional band for TiO₂/SiO₂ multilayer QW stack. Several researchers have chosen different combination of high and low index material to fabricate omnidirectional mirror for different spectral region. Chigrin *et al.* [20] observed reflection of more than 99% in the range of incident angles 0-86° at the wavelength of 632.8 nm for both polarizations in a Na₃AlF₆/ZnSe multilayer. It was the first experimental report on omnidirectional reflectivity. Chen *et al.* [21] reported an omnidirectional band of 70 nm in the incident angle range of 0° -80° in a six SiO₂/TiO₂ bilayers. Park *et al.* [22] reported omnidirectional reflection in NIR region using GaAs/Al₂O₃ multilayer.

1.4 Deposition process parameters and annealing effects

Generally optical thin films and multilayer coatings are prepared by physical vapour deposition such as electron beam (EB) evaporation and sputtering. As we know, oxygen partial pressure, substrate temperature, deposition rate etc. are the important process parameters which affect the properties of EB evaporated thin film coatings, while working gas pressure, RF power and O_2/Ar flow ratio affect the properties of RF sputtered thin films. Much work has been reported to control the oxygen partial pressure during deposition to prepare high quality optical thin films. Al-Kuhaili *et al.* [23] reported the effect of oxygen partial pressure on the structure, composition, optical properties and CO-gas-sensing properties of EB evaporated HfO₂ thin film. They found that the CO-gas-sensing properties strongly depend on the film porosity, which can be controlled by oxygen partial pressure. Martinez *et al.* [24] and Toledano-Luque *et al.* [25] investigated the effect of oxygen pressure on structure, optical properties, composition, growth and morphology of HfO₂ thin films prepared using high pressure reactive sputtering. They observed that the introduction of oxygen gas into the argon glow discharge favours polycrystalline growth, while the structure

of the films deposited with pure argon plasma is amorphous. The amorphous film shows higher refractive index and smooth surface as compared to that of polycrystalline film. Shen *et al.* [26] found the refractive index and optical absorption decrease with increasing O_2 partial pressure for EB evaporated ZrO₂ thin film. The residual stress in ZrO₂ thin films changes from compressive to tensile stress by varying O_2 pressure. Ma *et al.* [27] reported that the RF Sputtered ZrO₂ thin films deposited at low O_2 partial pressure are amorphous and dense with a smooth surface.

Many researchers have tried and succeed to improve the characteristics and performance of thin films and multilayer optical coatings by post-deposition annealing. Tan et al. [28] have investigated the thermal annealing effects on the structure and optical properties of HfO₂ thin films prepared by RF reactive magnetron sputtering. They have observed that the as-deposited films are amorphous and they become polycrystalline after annealing. The optical parameters such as refractive index, extinction co-efficient and band gap are observed increasing with annealing temperature. Ramzan et al. [29] and Hakeem et al. [30] have observed similar effects of annealing on structure and optical properties of EB evaporated HfO₂ films like Tan *et al.* [28]. Ling *et al.* [31] have reported increase in refractive index, material crystallization, and phase transformation in EB evaporated ZrO2 thin films with annealing. These combined effects after the annealing leads to an increase in laser induced damage threshold of the ZrO₂ thin films. Tian et al. [32] investigated the microstructure and laser induced damage threshold of ZrO₂ coatings after annealing. They observed annealing films show higher laser damage threshold because of its monoclinic phase. Annealing also increases crystallite size or grain size of the films, as a result the thermal barrier reduces because of lesser grain boundaries. This leads to increase in laser induced damage threshold.

1.5 Aim and scope of the thesis

The most challenging issue while developing optical filters and coatings is to produce thin films of accurate optical constants and thickness. The design of the coatings is tackled through highly advanced optimization techniques to obtain the desired spectral characteristics. So the real bottleneck in this field is the manufacturing process of thin films. The physical vapor deposition process such as EB evaporation and sputtering are excellent choice to fabricate variety of optical filters. In both EB evaporation and sputtering, oxygen partial pressure plays an important role to prepare high quality thin films. Therefore, the oxygen partial pressure for deposition of HfO₂ thin films has been optimized, which is generally used as high refractive index coating material. The effects of oxygen partial pressure on different properties of such films deposited by EB evaporation and sputtering are probed. New optical and optoelectronic devices require properties of thin films which are not possible to achieve by existing materials. The mixed composite materials by mixing two or more materials have the potential to change many properties of the thin films such as refractive index, absorption co-efficient, band gap, structure, surface morphology, stress and laser induced damage threshold. Design of multilayer devices is limited by small number of available materials with suitable refractive index. For example rugate filters need sinusoidal profile of refractive index vs. thickness, which cannot be achieved through conventional coating materials. By mixing high and low refractive index materials, refractive indices which do not exist in a bulk material can be obtained. Since reports on ZrO₂-MgO, ZrO₂-SiO₂ and HfO₂-SiO₂ mixed films are scanty; therefore we have deposited and characterized these films. The effect of oxygen partial pressure on structure, surface morphology, elastic and optical properties, laser induced damage threshold of ZrO₂-MgO and ZrO₂-SiO₂ mixed thin films have been investigated. HfO₂-SiO₂ mixed films are deposited in different composition ratios and analyzed. All the mixed films are deposited by EB co-evaporation.
Long durability and wave front distortion are two main challenges faced by optical coatings in a complex optical system. Generally EB evaporated optical thin films show a columnar microstructure consisting of columns and voids. The films can absorb environmental moisture, as a result optical and mechanical instability arises in the coating. Therefore filters prepared using EB evaporation are often annealed to remove moisture from the voids. Thermal annealing is commonly used to improve the properties of thin films, consequently the multilayer thin film devices. Thermal stability of high reflection (HR) mirrors and narrow band pass filters has been improved by annealing [33]. Complete stress compensation in Nb₂O₅/SiO₂ multilayer NIR high reflectors is demonstrated [34]. A remarkable increase of the laser induced damage threshold with annealing has been observed for Ta₂O5/SiO₂ [35] and TiO₂/SiO₂ [36] multilayer HR mirror. For high power laser applications, HfO₂/SiO₂ multilayer HR mirror is most preferred. There are many reports on the effects of annealing on different properties of single layer HfO₂ thin films, but the reports that on EB evaporated HfO₂/SiO₂ multilayer is very rare. We have investigated the effect of annealing on optical properties, structure, surface morphology and laser induced damage threshold of HfO₂/SiO₂ multilayer HR mirror and also optimized the annealing process. The multilayer HR mirror shows high reflection for a wavelength range and is limited to a certain range of incidence angle only. In order to resolve this drawback, researchers recently introduced a type of dielectric reflector called "omnidirectional reflector" based on the concept of photonic crystal and photonic band gap (PBG) [22]. Bruyant et al. [37] reported an omnidirectional photonic band of 300 nm in the NIR spectrum using multilayers of microporous silicon. There are many reports on the omnidirectional mirror made of different multilayers in the visible region, but their band width is limited. For visible range, TiO₂ and SiO₂ are two well known high and low index dielectric oxide materials, respectively because of their no-absorbing and non-dispersive characteristics. Lin et al. [38] have reported omnidirectional PBG of 24 nm in the visible range in 12-pair TiO₂/SiO₂ multilayer one dimensional photonic crystal (1DPC) deposited using EB evaporation, while Chen *et al.* [21] have reported an omnidirectional PBG of about 70 nm in NIR range in 6-pair TiO₂/SiO₂ 1DPC deposited using sol-gel method. In recent years, a lot of attention has been towards achieving wider omnidirectional PBG [39-41]. An ultra wide normal PBG in visible range, which is almost triple the original width of the PBG was achieved by Lu *et al.* [41] in TiO₂/SiO₂ 1DPC by an approach, called defect-induced extension of PBGS. But spectral ripples were present within the PBG of that PC. These ripples allow light to pass within the PBG in the reflection spectra and make these devices less useful. Here TiO₂/SiO₂ multilayer one dimensional photonic crystal using magnetron sputtering technique has been fabricated, which exhibits much wider band width with free of ripples in the visible region as compared to the earlier reports. The microstructure and optical properties of the multilayer photonic crystal have been investigated to probe its layer structure, surface morphology and omnidirectional spectral characteristics. The scope of the thesis will be as follows

- (i) Effect of oxygen partial pressure on structure, optical properties, surface morphology, residual stress, elastic modulus and laser induced damage threshold of HfO₂, and ZrO₂-MgO and ZrO₂-SiO₂ mixed oxide thin films.
- (ii) Composition dependent optical properties, surface morphology and laser induced damage threshold of HfO₂-SiO₂ mixed oxide composite thin films.
- (iii) Annealing effects on microstructure, optical properties and LIDT of HfO₂/SiO₂ multilayer high reflection mirrors.
- (iv) Fabrication and characterization of magnetron sputtered TiO₂/SiO₂ multilayer photonic crystal as omnidirectional mirrors.

Chapter 2: Experimental Methods

2.1 Introduction

This chapter explains the principle and working process of thin film deposition and characterization techniques used for the thesis work. First part of the chapter presents the details of physical vapor deposition process such as electron beam (EB) evaporation and sputtering. In the second part, the characterization techniques used to probe structure, surface morphology; optical properties, residual stress, elastic modulus and laser induced damage threshold of the films are described in details.

2.2 Thin film deposition

Thin films and multilayers of the metals, alloys, ceramics, and polymers are deposited using one of several deposition techniques. Knowledge of various deposition processes enables us to deposit ultra-thin films with desired thickness/stoichiometry. Thin film deposition techniques are broadly classified under two heading such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques. Among the PVD methods, Electron beam evaporation and sputtering have been discussed in details, since all the thin films and multilayers studied in the thesis are deposited using either of the two techniques.

2.2.1 Electron beam evaporation

All non-toxic elements and alloys (including high melting point materials) can be deposited using this technique. Practically there is no reaction between the evaporation material and the crucible in these systems as the material is kept in water cooled crucibles. Because of these properties electron beam evaporation has established itself as a universal method for the deposition of high quality coatings in large quantities. Multiple materials can be deposited simultaneously or sequentially using multiple pockets crucibles.



Fig. 2. 1: Schematic of electron beam evaporation system.

The basic parts in an EB evaporation system [42] are electron gun, thermionic emitter, electron optics, high voltage DC power supply, a permanent magnet, a crucible and thickness monitoring system as shown in Fig. 2.1 (a). The electrons are produced by resistive heating of tungsten or tantalum, which are then accelerated and focused through the electron optics (deflection plates and accelerating grid). With the help of a bending magnetic, the electron beam is bent onto a water-cooled copper crucible filled with the evaporation materials. On impact with the material, the kinetic energy of electrons is transformed into heat and cause evaporation of materials. The electron temperature can be as high as 10000 K, which corresponds to the DC potential of several kV (3-10 kV). The energy of the evaporated particles is typically in the range of 0.1 eV to 0.3 eV. The VTD made Vera-902 EB evaporation coating unit present at BARC, Mumbai is shown in Fig. 2.2. The coating chamber is equipped with two 8 kW electron beam guns with sweeps and automatic emission controls, two quartz crystal monitor (Inficon's XTC/2) and optical thickness monitor (Leybold's OMS-2000). The complete deposition process is controlled by software enabling simultaneous measurements and acquisition of parameters.



Fig. 2. 2: *Multi-source electron beam evaporation system (a) External and (b) Internal view.* The mixed oxide films are prepared using EB co-evaporation method. Each of the quartz crystal monitors (QCM) has been assigned to the specified source to measure their respective rate of deposition. The rate monitors have been interfaced with sources using real time feedback techniques. The momentary composition of the mixture is given by [43]

$$C_{v} = \frac{r_{v}(t)}{\sum_{v=1}^{v=N} r_{v}(t)}$$
(2.1)

Where the concentration C_v is given in parts by volume, the evaporation rate r_v is given in nm/s and N is number of components get mixed. For the two component mixtures like HfO₂ and SiO₂, the individual concentration will be given by

$$C_{HfO_2} = \frac{r_{HfO_2}}{r_{HfO_2} + r_{SiO_2}}$$
 and $C_{SiO_2} = \frac{r_{SiO_2}}{r_{HfO_2} + r_{SiO_2}}$ (2.2)

Where C_{HfO_2} and C_{SiO_2} are concentration of HfO₂ and SiO₂ respectively.

2.2.2 Sputtering

Sputtering is a process whereby atoms are ejected from a solid target material due to bombardment of the target by energetic particles like atoms or ions (usually inert). The ejected atoms can be made to condense on a substrate to form a thin film. It is a purely momentum transfer process. The main advantages of sputtering are (a) high uniformity in film thickness, (b) good adhesion to the substrate, (c) better reproducibility of films, and (d) stoichiometric film as target [42]. The sputtered atoms have energy of few tens of eV. Based on source of discharge, sputtering can be classified into DC sputtering, RF sputtering, magnetron (DC, pulsed DC and RF) sputtering, and ion beam sputtering.

2.2.2.1 DC/RF magnetron sputtering

The magnetron sputtering process is classified as DC or RF depending on the type of power supply used as shown in Fig. 2.3(a). DC sputtering utilizes a DC gaseous discharge. The substrate and the vacuum chamber walls may be the anode, while target (deposition source) may be cathode. The power supply is simply a high-voltage DC source. DC sputtering is mainly used to deposit metals. In case of insulators, it fails because of positive charge build up on the target surface. This can be prevented by bombarding the insulator by both positive ions and electrons simultaneously. That is done by applying a RF potential to the target. The RF potential provides sufficient energy to the electrons oscillating in the alternating field to cause ionizing collisions, and a self-sustained discharge is maintained. As electrons have higher mobility compared to ions, hence the target will be self biased negatively. This repels the electrons from the vicinity of the target and forms a sheath enriched in positive ions in front the target surface. These ions bombard the target and sputtering is achieved. The RF power of few hundred watts to kilowatt is applied between the electrodes at a frequency of 13.56 MHz [44]. The most important difference between RF and DC systems is that the former requires an impedance matching network between the power supply and sputtering chamber as shown in Fig. 2.3(b). The main job of this network is to provide optimal matching of the load to the RF generator, so that sufficient power can be delivered to the sputtering chamber. The blocking capacitor C is placed in the matching network circuit to develop the all-important DC self-bias [45]. In simple DC and RF sputtering techniques, the deposition rate is low and contamination in films occurs due to the relatively high working pressure. To overcome these problems, the magnetron configuration is used as shown in Fig. 2.3(a). In the

magnetron configuration a permanent magnet (or electromagnet) with magnetic field of a few hundred gauss is added, to create lines of magnetic flux that are parallel to the surface of the target. This field makes the electrons to form a closed loop, resulting high collision rate between the electrons and the sputtering gas molecules. Therefore sputtering can be done at lower working pressure of 10^{-4} torr, which results in effectively higher deposition rates with low contamination of the deposited films.



Fig. 2. 3: Schematic of DC/RF magnetron sputtering system showing.

The DC/RF magnetron sputtering system shown in Fig. 2.4 is a homemade coating unit present at A&MPD, BARC (Vizag). The system is equipped with turbo molecular pump backed with a rotary pump. The coating chamber is equipped with two 3 inch target holder and one 6 inch target holder. Substrate rotation assembly mechanism is gear motor arrangement. The Motor is vacuum compatible and mounted inside the sputtering chamber. DC power supply of 2 kW is coupled to the system. A RF power supply (max. 1 KW and frequency 13.56 MHz) has been used to supply RF power to the cathode and an automatic impedance matching network has been used to transfer maximum power to the cathode. The anode facing the cathodes which supports the substrate is grounded. The substrate holder is water-cooled. Ar gas is used for plasma formation. A motorised movement is provided to the substrate holder for enabling sequential deposition of two materials. Vacuum chamber

Chapter 2: Experimental Methods

pressure was controlled by two mass flow controllers (MKS make) for Ar and O_2 with isolation valves and filters respectively. For controlling film thickness and pre-sputtering of targets, a shutter has been introduced between the cathodes and the anode. Two QCM have been used to monitor the rate and the total thickness deposited by respective targets. The RF power has to be switched manually from one target holder to another.



Fig. 2. 4: Multi-target sputtering coating system (a) External and (b) Internal view.

2.2.2.2 Asymmetric bipolar pulsed DC magnetron sputtering

Asymmetric bipolar pulsed DC (ABPDC) magnetron sputtering [46] has the ability to eliminate target poisoning for deposition of insulating films from conductive targets with reactive sputtering. This technique is based on the addition of a pulsed reverse bias to the normal pulsed DC waveform operating in the frequency range of hundreds of kilohertz as shown in Fig. 2.5. For example, during negative cycle of the voltage (e.g. -400 V), the argon ions strike the target and causes sputtering of aluminium. At the same time insulating Al₂O₃ film is also redeposited on the metallic target and it collects low-energy ions on its surface, which reduces sputtering of insulating films from the target surface. Even worse, as the charge builds up, the ions are repelled by the electrostatic repulsion of the Ar⁺ ions and the positive capacitor voltage. When the polarity is reversed to about +100 V, the electrons flow to the target surface and discharges ions on insulating layers resulting capacitor voltage -100 V. The reversal is typically held for 1 to 10 μ s. When the voltage returns to sputter mode (-400 V) again, the effective voltage on the plasma side of the parasitic capacitor becomes - 500 V (-400 V + -100 V). Thus, the argon ions strike the insulator with extra energy, thereby sputtering the insulators off the target first, eliminating target poisoning [46]. The effectiveness of ABPDC indeed depends on its pulse frequency, which falls in the range 25–300 kHz. A positive voltage of 25–50V is generally found to be effective and safe.



Fig. 2. 5: *Charge build-up around insulating regions leads to arc (target poisoning)* [47]. The ABPDC magnetron sputtering system present at A&MPD, BARC (Vizag) is a multi-target magnetron sputtering system in sputter up configuration. It consists of 75mm magnetrons (Angstrom Sciences make) fully compatible with bipolar PDC, DC and RF power supplies. The target to substrate distance could be varied anywhere from 75mm to 120 mm. Two 10 kW ABPDC power supplies (MKS/ENI make, model RPG-100) were used to independently power the individual magnetrons. These power supplies have a fixed reverse bias of +37V, whereas the negative voltage can be varied from 0 to-800V with programmable pulsed frequency from 50 to 250 kHz. The duty cycle can be appropriately selected during the process and has been used in a feedback control loop.

2.3 Characterization techniques

2.3.1 Spectrophotometry

The optical properties of thin films and multilayers are characterized by spectrophotometry, which measures transmission, reflection and absorption spectrum of a material. We have used UV-VIS-NIR spectrophotometer (SHIMADZU made UV-3101PC) as shown in Fig. 2.6 for the measurement of our samples. The optical properties such as refractive index, absorption co-efficient, band gap etc. and thickness of thin films can be extracted from transmission as well as reflection spectrum depending on the materials.



Fig. 2. 6: Spectrophotometer used for optical properties measurement.

The optical parameters can be extracted from only transmission spectrum by two methods i.e. "Envelope method" [48] and "Inverse synthesis method" [49]. The Envelope method is widely used technique for determination of optical constants of transparent or semiconducting thin films. This method works well for thick film having many interference fringe extremes. It fails if there are local absorption bands in between interference fringes extremes as well as for high absorption such that interference fringes are not visible unlike at absorption edge. The accuracy of the Envelope method decreases with decreasing film thickness, because the spacing between interferences extremes increases; which makes interpolation between extremes more difficult. But Inverse synthesis method works for very thin films as well as for local absorption in the samples, which is described as follows.

Inverse synthesis is a multiwavelength curve fitting method, which mainly depends on the validity of dispersion model and the fitting statistics. For simplicity, the thin film is assumed to be homogenous and uniformly deposited on transparent substrate. The substrate is perfectly smooth and thick enough to avoid the substrate surface interference effects on the measured optical spectrum of the thin film. With the above assumptions, the transmission of a single layer absorbing thin film on a transparent substrate can be expressed as follows [50]:

$$T = \frac{Ax}{B - Cx + Dx^{2}}$$
(2.3)
where $A = 16n_{s}(n^{2} + k^{2})$
 $B = [(n+1)^{2} + k^{2}][(n+1)(n+n_{s}^{2}) + k^{2}]$
 $C = 2\cos(\phi)[(n^{2} - 1 + k^{2})(n^{2} - n_{s}^{2} + k^{2}) - 2k^{2}(n_{s}^{2} + 1)] - k[2(n^{2} - n_{s}^{2} + k^{2}) + (n_{s}^{2} + 1)(n^{2} - 1 + k^{2})]2\sin(\phi)$
 $B = [(n+1)^{2} + k^{2}][(n+1)(n+n_{s}^{2}) + k^{2}]$
 $\phi = \frac{4\pi nd}{\lambda}$
 $\alpha = \frac{4\pi k}{\lambda}$
 $x = e^{(-\alpha d)}$

In the above equations, λ is the wavelength, *n*, *k*, and *d* are the refractive index, extinction coefficient and thickness of the film respectively and *n_s* is the substrate refractive index. The measured transmission spectrum gives a set of experimental data (λ_i , T_i^{Exp}), *i*=1, 2, 3,, N. From this experimental data, *n*, *k* and *d* have to be determined. For all *i*=1, 2, 3,, N, the equation must satisfy the equation: $T_i^{Cal}[\lambda_i, n_s(\lambda_i), n(\lambda_i), k(\lambda_i), d] = T_i^{Exp}$. It has three unknown $n(\lambda), k(\lambda)$, and *d*, which are obtained through optimization procedure. The initial value for *d* is taken from the in-situ measured film thickness. The functional forms of $n(\lambda)$ and $k(\lambda)$ are assumed using a suitable dispersion model. Then the fitting has been carried out by minimizing the squared difference (χ^2) between the measured and calculated values of transmission given by:

$$\chi^{2} = \frac{1}{(2N-P)} \sum_{i=1}^{N} \left[\left(T_{i}^{Exp} - T_{i}^{Cal} \right)^{2} \right]$$
(2.4)

Where T_i^{Exp} and T_i^{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 done using the Levenberg-Marquardt algorithm [12]. After the fine adjustment of model parameters, a good fitting can be achieved as shown in Fig. 2.7.



Fig. 2. 7: *Measured transmission spectrum fitted with theoretical one for a representative zirconia-magnesia thin film.*

For an example point of view, the experimental transmission spectrum along with its fitting for a thin film using single oscillator and Urbach dispersion model for refractive index and extinction co-efficient respectively is shown in Fig. 2.7. The Inverse synthesis method is very powerful and can yield very accurate values of optical constants (n & k) for thin films or even multilayer thin films with some know parameter like film thickness or material parameters as guess value. The only limitation of this method is that one has to make assumptions about the type of dispersion relation before start the fitting procedure. The optical band gap (E_g) of the films is determined from the absorption co-efficient (α) using Tauc-plot [51].

2.3.2 Atomic force microscopy (AFM)

AFM [52] is most widely used technique to investigate surface morphology of any kind of materials. It uses van der Waals force between atoms of the probe tip apex ad the surface to generate surface topography, which eliminates the resolution limit associated with optical microscopy. AFM is capable of measuring the vertical dimension (height or depth) of the sample surface, while optical and electron microscope does not have this scope.



Fig. 2. 8: Schematic diagram of AFM with beam deflection method.

A schematic diagram of a typical AFM system is shown in Fig. 2.8 and its operation is governed by three basic components (i) Cantilever tip (ii) piezoelectric scanner and (iii) feedback loop control system. A sharp tip is mounted at the end of a cantilever, which is attached at one end to a piezoelectric scanner. The force detection is based on a beam deflection method. A diode laser is bounced off from the back side of the gold coated cantilever onto a position-sensitive quadrant photodiode detector, which measures the bending of cantilever. As the tip is scanned across the sample, the tip-sample interaction force is measured by the cantilever. A feedback loop control system is used to maintain a desired force between the tip and the sample. When the measured force is larger or smaller than this

set point, the piezoelectric scanner in the z-direction moves the probe away from or towards the surface, bringing the force back to the set point. The displacement of piezo scanner directly corresponds to the height of the sample. A topographic image of the surface can be generated by recording the displacement of the piezo-scanner as a function of position. For the present thesis, NT-MDT's Solver P47H multimode scanning probe system as shown in Fig. 2.9 has been used to measure AFM surface morphology of all the samples.



Fig. 2. 9: NT-MDT Solver P47H AFM used for surface morphology analysis.

The surface roughness and grain size [53] are derived from the vertical height and the lateral size of the particles in the AFM image. Root mean square (rms) surface roughness describes the smoothness of optical surfaces. A cross-sectional line can be drawn across any part of the image to see lateral size of grains, and the vertical profile along that line gives roughness. By making several cross-sectional line profiles through different grains, it is possible to calculate the grain size. Fig. 2.10(a) & (b) show the 2D and 3D AFM topography of EB evaporated HfO₂ thin film. The grains are spherical in size with uniform size distribution. The estimated average grain size and rms roughness are found to be 58 nm and 4.2 nm as shown in Fig. 2.10(c) & (d) respectively.



Fig. 2. 10: Representative (a) 2D, (b) 3D AFM surface morphology for determination of (c) grain size and (d) surface roughness of HfO_2 thin film.

2.3.3 Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) [54] has been used to investigate the surface and crosssectional morphology of the thin films and multilayer coatings. The SEM provides information relating to surface topography, phase distribution etc. It is like conventional light microscope but the light is replaced with the electrons. The sample chamber is evacuated as the electron gun because the electrons travel in the air only very short distances. When a focused beam of electrons is scanned across the sample surface, it produces secondary electrons (SE), back-scattered electrons (BSE) and characteristics X-rays. These secondary (SE) and backscattered (BE or BSE) electrons are detected to get information about surface topography, while the X-rays gives information about composition. The resolution of a SEM is about 10 nm. The resolution is limited by the width of the exciting electron beam and the interaction volume of electrons in a solid. In the present work, all the surface and crosssectional topography images for thin films and multilayer samples were taken using a JEOL (JSM-7600F) field emission scanning electron microscope.

2.3.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) [55] is a powerful nondestructive technique, which provides information on crystal structure, phase, texture, average grain size, crystalinity, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays diffracted at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in a given material. A search of the ICDD (International Centre for Diffraction Data) database of X-ray diffraction patterns enables the phase identification of a large variety of crystalline samples.

Structure of thin films and multilayer coatings are characterized by using X-ray Bruker's D8 advanced XRD unit using Cu-K α (λ =1.5406Å) radiation. In the diffraction pattern 2 θ position represents the angle of diffraction of a particular plane from which the *d*spacing as well as lattice parameter can be derived by using Bragg's equation $2dSin\theta = n\lambda$ [55]. Where *n* is the order of diffraction, λ is the wavelength of x-ray, *d* is the distance between atomic planes and θ is the Bragg's angle. The crystallite size (*D*) is estimated from the diffraction peak using Scherrer formula as $D = 0.9\lambda/\beta Cos\theta$, where β is the FWHM of the peak. The average strain (ε) value is estimated by the change in d-spacing with respect to the d-spacing in JCPDS file by the following equation:

$$\varepsilon = \frac{\Delta d}{d} = \frac{d_{hkl} - d_{0(hkl)}}{d_{0(hkl)}}$$
(2.5)

where $d_{0(hkl)}$ is the strain-free lattice spacing. The accuracy of calculated strain largely depends on the accuracy of $d_{0(hkl)}$.

2.3.5 Grazing incidence X-ray reflectivity (GIXR)

GIXR measurement is an analytical technique which gives information on film density, layer thickness, electron density, and surface and interface roughness of thin films and multilayers. The complex refractive index (η) of an element in the X-ray region is given by [56]

$$\eta = 1 - \delta - i\beta \tag{2.6}$$

where
$$\delta = r_0 \left(\frac{N_A Z}{2 \pi A_W} \right) \lambda^2 \rho$$
 and $\beta = \frac{\mu \lambda}{4\pi}$ (2.7)

Here, r_{θ} is the classical electron radius (2.82x10⁻¹⁵ m), N_A is the Avogadro number, ρ is the density, *Z* is the atomic number and A_W is the atomic weight of the element and μ is the linear absorption coefficient of the material. The quantity [N_A (ρ Z/A_W)] actually gives the electron density of the particular element. Since refractive index of all material in hard X-ray region is less than 1, X-ray suffers total external reflection at extreme grazing angle of incidence from any surface. However, as the grazing angle of incidence value (θ) exceeds the critical angle (θ_c), X-ray starts to penetrate inside the layer and reflectivity starts to fall off rapidly. The critical angle is approximately given by the expression $\theta_c = \sqrt{\delta}$. It depends on the electron density of the material apart from the wavelength of X-ray. The reflectivity of X-ray from a thin film can be obtained using Fresnel's boundary conditions. The X-ray reflectivity gets modified for a rough surface by a 'Debye-Waller -like' factor as follows [56]:

$$R = R_0 \exp\left(-\frac{q^2 \sigma^2}{2}\right) \tag{2.8}$$

where q is the momentum transfer factor (= $4\pi Sin\theta/\lambda$), R is the reflectivity of the rough surface and R₀ is the reflectivity of an identical smooth surface and σ is the RMS roughness of the surface. Thus by fitting the X-ray reflectivity spectrum of the surface of a sample near its critical angle accurate estimation of density ρ and surface roughness σ can be made.

2.3.6 Atomic force acoustic microscopy (AFAM)

Atomic force acoustic microscope (AFAM) developed by U. Rabe *et al.* [57] is a unique tool which gives information on nano-scale surface elastic properties of materials. It is capable of giving both qualitative as well as quantitative mapping of surface elastic modulus at nanoscale using AFAM two contact resonance frequency imaging technique. The working principle of AFAM and determination of elastic modulus from the contact resonance spectrum are described below.



Fig. 2. 11: Schematic of AFAM set-up.

AFAM is a dynamical extension of AFM contact mode and its schematic is shown in Fig. 2.11. Here, the sample is placed on an ultrasonic transducer instead of the sample holder of a standard AFM set up. The transducer driven by a waveform generator emits longitudinal waves, causing out-of-plane vibrations in the sample surface. These vibrations are coupled to the cantilever by making contact between tip and the sample surface. The cantilever vibrations are detected by the photodiode using a lock-in-amplifier and recorded together with the corresponding ultrasonic frequency to obtain the contact-resonance spectrum. The frequency range employed covers the flexural modes of the cantilever from 10 kHz up to 5 MHz, with an average frequency of around 3 MHz. The basics steps for determination of elastic modulus using AFAM are: (i) Acquire the first two contact resonant modes, (ii) Using

the two contact-resonance frequencies, unique solution of k^* is derived from the intersection point of two curves of k^* vs. (L_I/L) for the two modes, and (iii) Using the Hertz contact model, E^* is calculated from k^* using known elastic properties of a reference sample.



Fig. 2. 12: (a) General case for a tip-sample interaction including lateral and vertical tipsample interaction forces and (b) Simplified case for a tip-sample interaction.

Under suitable approximation (assuming linear forces and sufficiently small vibration of the cantilever ~0.1 nm), the tip-film interaction in an AFM can be approximated by vertical and lateral spring-dashpot system [58] as shown in Fig. 2.12(a), where θ_0 is the angle between the cantilever and sample surface, while k_{lat}^* , k^* , γ_{lat} and γ are the lateral and vertical contact stiffness and damping constants, respectively. The total length of the cantilever is $L = L_1 + L'$ and the tip base is located at L_1 . It has been found that the k^* value depends mostly on the sensor tip position L_1 than on the other parameters such as θ_0 , k_{lat}^* , γ_{lat} and γ . Neglecting all these parameters and considering tip mass to be very smaller than the cantilever mass, the tip-sample coupled system reduces to the simplified system [59] as shown in Fig. 2.12(b). The characteristic equation of the simplified system is

$$k^* = \frac{\left(\frac{2}{3}\right)k_c(k_nLr)^3(1+\cos k_nL\cosh k_nL)}{P1+P2}$$
(2.9)

where $Pl = (\sinh k_n Lr \cos k_n Lr - \cosh k_n Lr \sin k_n Lr)(1 + \cos k_n L(1 - r) \cosh k_n L(1 - r))$ $P2 = (\cosh k_n L(1 - r) \sin k_n L(1 - r) - \sinh k_n L(1 - r) \cos k_n L(1 - r))(1 - \cos k_n Lr \cosh k_n Lr)$

with
$$k_n L = c_B L \sqrt{f_n}$$
 (2.10)

and

$$c_B = \sqrt{2\pi} \sqrt[4]{\frac{\rho A}{EI}}$$
(2.11)

where $r=L_1/L$, C_B is a characteristic cantilever constant, ρ is the mass density of the cantilever material, f_n is the n^{th} eigenmode mode resonance frequency of the cantilever, k_c is the spring constant or stiffness of the rectangular cantilever and k^* is the contact stiffness of the tipsample assembly. The spring constant (k_c) of the free cantilever is determined using Normal Sader method [60]. By measuring the free resonant frequency of the cantilever and substituting the measured values in Eq. (2.9), c_BL value for the cantilever is determined. The k_nL value for the surface coupled cantilever is then determined by substituting the obtained value of c_BL and the measured contact resonant frequencies in Eq. (2.9). Experimentally, the value of k^* and L_1 can be determined by using the fact that, the contact stiffness k^{*} must be the same for all cantilever eigenmode $(f_1, f_2, f_3....)$ at constant applied normal load. This leads to the conditional equation [61]

$$k^{*}(f_{1},r) = k^{*}(f_{2},r)$$
(2.12)

The solution of the Eq. (2.11) is found numerically by assuming a small range of values for L_1 , the range being found by using an optical microscope. First two contact frequencies are measured and the contact stiffness k^* obtained from Eq. (2.8) is plotted as a function of $r = L_1/L$ for the two modes and the point of intersection of the 1st and 2nd resonance curves correspond to the solution of L_1/L and contact stiffness k^* . The contact stiffness k^* is related to the elastic modulus of the probed material by Hertzian theory. According to this theory, when a hemispherical tip of radius *R* (AFM cantilever tip) indents a flat surface with a normal static load F_N , then the resulting contact stiffness k^* can be calculated as

$$k^* = 2aE^* = \sqrt[3]{6E^{*2}RF_N}$$
(2.13)

Here a is the contact radius and E^* is the reduced Young's modulus, defined as

$$\frac{1}{E^*} = \frac{1}{M_S} + \frac{1}{M_t}$$
(2.14)

Where, M_S and M_t are the indentation moduli of the sample and tip, respectively. The left equality in Eq. (2.13) is true for all geometries while the right equality of the equation can be used only for tips with hemispherical geometry [62]. The indentation modulus M_S of the sample can only be calculated after determining the tip geometry, which is very difficult to determine experimentally. Hence this can be avoided only by comparing the value of k^* obtained for the unknown sample to that of a reference sample [62]:

$$E_{s}^{*} = E_{ref}^{*} \left(\frac{k_{s}^{*}}{k_{ref}^{*}} \right)^{n}$$
(2.15)

The subscripts *s* and *ref* corresponds to the unknown sample and reference sample, respectively. The value of *n* depends on tip-sample geometry. For a spherical tip, n=3/2; while for a tip shaped like a flat punch, n=1. Now the indentation modulus of the sample M_s can be calculated from Eq. (2.13) and (2.14). For isotropic samples, Young's modulus E_s is evaluated from the indentation modulus M_s , through the relation $M_s = E_s/(1-\gamma^2)$, where v is the poisons ratio. Since the poisons ratio of our thin film samples are unknown and can vary with density of the films, therefore direct indentation modulus of these films are calculated.

2.3.7 Residual stress measurement (Substrate curvature method)

Several experimental techniques exist for measurement of residual stress in thin films. For present thesis, substrate curvature method has been used for determining residual stress. This method does not require knowledge of the film's mechanical properties such as biaxial elastic modulus, Poisson's ratio etc. Considering a thin stressed film deposited on a thick initially stress-free substrate, the residual stress in the film is determined using the substrate curvature by the Stoney's equation [63] as follows:

$$\sigma = \frac{1}{6} \left(\frac{E_s}{1 - v_s} \right) \left(\frac{1}{R_a} - \frac{1}{R_b} \right) \left(\frac{t_s^2}{t_f} \right)$$
(2.16)

Here, R_b and R_a are radii of the substrate curvature before and after film deposition, respectively, E_s and v_s are Young's modulus and Poisson's ratio of the substrate respectively, and t_s and t_f are the thicknesses of the substrate and the film, respectively subject to $t_f \ll t_s$. This treatment assumes an isotropic homogeneous stress distribution in the coating, in which deformations of the substrate are small compared to the substrate thickness. Here, tensile stress is considered to be positive, whereas compressive stress is negative.



Fig. 2. 13: Schematic of ZYGO made laser Fizeau interferometer.

The substrate curvature measurement apparatus used in this work is a ZYGO made laser Fizeau interferometer and the technique used is phase-shifting interferometry. The schematic of the system is shown in Fig. 2.13. In the laser Fizeau interferometer, a well collimated He– Ne laser illuminates the Fizeau cavity comprised of the reference transmission flat, and the test object. The reference transmission surface $S_R(x, y)$ reflects some of the laser light back into the interferometer, thus creating a reference wavefront $W_R(-x, y)$. The remainder of laser light passes through the reference transmission flat to the test surface $S_T(x, y)$ and is referred as the measurement wavefront $W_T(x, y)$. When performing surface quality tests (Flatness error), the measurement wavefront $W_T(x, y)$ reflects back to the interferometer from the test surface and recombined with the reference wavefront $W_{R}(-x, y)$ and the two wavefronts interfere with each other. The phase differences between the two wavefronts result in an image of light and dark fringes that is a direct indication of the flatness error of the test and reference surface [64]. The interference pattern is converted to electrical signals by a CCD camera enabling software acquisition and analysis. In the coordinate system of the interferometer, the combined wavefront W(x, y) is

$$W(x, y) = W_R(-x, y) + W_T(x, y)$$
(2.17)

The flatness of the surface S(x, y) is half of the wavefront W(x, y):

$$S(x, y) = \frac{1}{2}W(x, y)$$
(2.18)

During a data acquisition sequence, the computer takes several "snapshots" of the interference pattern using CCD, while introducing constant phase shift between the reference wave front $W_{\rm R}(-x, y)$ and the measurement wave front $W_{\rm T}(x, y)$. These snapshots are processed by the computer to determine the phase of the wavefront at each point. In order to estimate the surface curvature, the spherical shape component is extracted from the surface wavefront profile data by Zernike polynomial fitting analysis [65]. The mean radius of curvature (*R*) has been calculated from the curvature profile using the equation [66]

$$R = \frac{r^2}{2s} + \frac{s}{2}$$
(2.19)

Where r is the radius of circularly shaped substrate and s is the sag in the curvature profile. The very low magnitude of the sag of the substrate surface always requires optical methods which can determine the change in curvature of the substrate. Interferometry is highly accurate technique to measure the coated and uncoated substrate curvature in a controlled environment. Stress or strain in a thin film on a substrate can also be measured using x-ray diffraction technique.

2.3.8 Laser induced damage threshold (LIDT) measurement

Optical coating devices are used in many applications involving the use of high power lasers. In these cases, the coatings get damaged under these intense lasers. The laser fluence or energy, at which damage of coatings occurs, is called laser induced damage threshold (LIDT). There are many different methods of measuring LIDT. For pulsed lasers, two international standard methods are followed. One is single-shot (1 on 1 test) and other is multiple shot method [67]. The 1 on 1 test uses only one single shot on each unexposed site of the sample, whereas, the multiple shot test uses multiple shots in the same location of the sample. For both methods it is important to know the spot-size of the beam and the pulse duration. The set-up used for the LIDT measurement of our samples is shown in Fig. 2.14.



Fig. 2. 14: *Indigeneosuly developed laser induced damage threshold measurement set-up.* The LIDT measurement is done using a Q-switched Nd: YAG pulsed laser (EKSPLA NL313) having pulse width of 7 ns. The repetitive frequency of the laser was 10 Hz. It has five harmonics such as 1064 nm, 532 nm, 355 nm, 266 nm and 213 nm respectively. The laser beam is focused on the test sample using a converging lens to generate high power

density. The angle of incidence was slightly 2°–3° off normal to avoid interference effects due to reflection from the substrate exit surface. The Beam profile has been measured using "Spiricon beam profiler". The scattered radiation from thin film has been imaged by employing a CCD imaging system. Neutral density filters have been used to bring the intensity of laser light down coming from sample to the profilometer so that the detector of the profilometer does not get damaged. The measured beam profile is hat-top in nature and the spot diameter at the sample surface has been computed using beam analysis software. The representative measured laser beam profile using two different focusing lenses are presented in Fig. 2.15.



Fig. 2. 15: 3D and 2D picture of laser beam profile of Nd: YAG pulsed laser.

The energy of the laser beam is controlled with a variable attenuator using cross polarizers, which maintains uniform pulse shape. The pulse energy was measured by an energy meter (FieldMaxII-P COHERENT) using split-off portion of the beam by a wedge plate. The measured laser energy vs. polarization angle for Nd: YAG laser of wavelength of 532 nm using a variable attenuator is presented in Fig. 2.16.



Fig. 2. 16: Plot of pulsed laser energy as a function of polarization angle.

Generally optical microscopy has been used to monitor the online damage event. Damage probability plot [68, 69] has been used to quantify the LIDT value for thin film or multilayer sample. The total 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.

Chapter 3: Study of Electron Beam Evaporated and Magnetron Sputtered HfO₂ Thin Films

Hafnium oxide (HfO₂) is a refractory oxide ceramic material, which exhibits high melting point, wide band gap, high refractive index and high laser induced damage threshold with excellent thermal and chemical stability [23, 28, 70]. HfO₂ has drawn wide research interest because of its applications in variety of fields such as optical coatings, wave guides, complementary metal-oxide-semiconductor devices, memory devices, and magnetoelectronic and optoelectronic devices [71-73]. The HfO₂ thin films also exhibit hydrophobicity leading to practical applications such as self cleaning activity of windows, anticlouding effects in bathroom mirrors, car windows and fender mirrors [74]. The deposition process parameters strongly affect the properties of HfO₂ thin films. The oxygen partial pressure during deposition controls the different properties of thin films. In this context, the effect of oxygen pressure on different properties of HfO₂ thin films has been investigated in the present work. The work is presented in two parts as per the deposition process used to prepare the HfO₂ thin films. The 1st part discusses the properties of EB evaporated HfO₂ thin films prepared at different oxygen partial pressure, while the 2nd part discusses the properties RF sputtered HfO₂ thin film prepared at different O₂/Ar flow ratio.

3.1 Electron beam evaporated HfO₂ thin films prepared at different oxygen partial pressure

3.1.1 Introduction

Several studies on different properties of polycrystalline HfO_2 thin films have been reported in the literature [25, 75-77], but there is not many reports on amorphous HfO_2 thin film. Ideally, dielectric thin films for industrial applications should be amorphous in nature [71]. Because the amorphous structure contributes to a lower leakage current due to the elimination of the high-leakage paths associated with the grain boundaries in polycrystalline films [78]. The amorphous structure of the film also avoids the lattice mismatch induced stress in multilayer optical coatings or other devices. Several techniques are reported in literature to deposit HfO₂ thin films, such as electron beam (EB) evaporation, atomic layer deposition, pulsed laser deposition, sol-gel coating, magnetron sputtering etc [79]. Generally the EB evaporation technique has been preferred to deposit amorphous HfO₂ thin film. The performance of different devices based on HfO₂ thin film strongly depends on its various properties such as structure, surface morphology, optical, mechanical and laser damage threshold characteristics. Therefore understanding these properties is very much important for design and fabrication of high quality optical devices. Oxygen partial pressure during deposition is one of the crucial parameters strongly affecting the thin film properties, especially so for EB deposited films. There are very few related reports about the effect of oxygen partial pressure on various properties of EB deposited HfO₂ thin film [80-82]. There is also no systematic study of EB evaporated amorphous HfO₂ (a-HfO₂) thin film. In this study, we have investigated the effect of oxygen partial pressure on different properties of EB evaporated a-HfO₂ thin films.

3.1.2 Experimental details

HfO₂ thin films have been deposited on fused silica and soda-lime glass substrates at different O_2 partial pressure by reactive EB evaporation technique. The deposition rate of 8 Å/s and substrate temperature of 300°C was kept fixed during deposition of all the hafnia films while the O_2 pressure was varied from 1x10⁻⁴ mbar to 8x10⁻⁴ mbar. The structural characterization has been carried out by grazing incidence XRD with 20 angle in the range of 25°-80° using Cu-K_a (λ =1.5406 Å) radiation in steps of 0.1°. The surface morphology of the films has been characterized by atomic force microscopy (AFM) in non-contact mode using silicon nitride cantilever. Density and surface roughness of the films have been measured by x-ray

reflectivity (XRR) technique. This measurement has been carried out at grazing angle of incidence in the range of 0°-0.8° with an angular resolution of 0.005°. The optical transmission spectra of the films were measured using UV-VIS-NIR spectrophotometer in the range 190-1100 nm for determination of refractive index and thickness of the films. The film residual stress has been evaluated from the change in substrate curvature due to the film deposition, which is measured by a laser Fizeau interferometer. The laser induced damage threshold (LIDT) of the films have been measured in the "1-on-1" mode according to ISO-11254-1 [83]. The first harmonic (1064 nm) and second harmonic (532 nm) of a Q-switched Nd: YAG pulsed laser at a pulse width of 7 ns with focused spot size of 80 µm were used for the LIDT measurement.

3.1.3 Results and discussion

3.1.3.1 Structural properties



Fig. 3. 1: *GIXRD* pattern of HfO_2 thin films prepared at different O_2 partial pressures.

The structural characteristics of EB evaporated HfO_2 thin films deposited at various oxygen partial pressures i.e. from 1×10^{-4} mbar to 8×10^{-4} mbar have been examined by recording the XRD spectra at room temperature as shown in Fig. 3.1. Typical low glancing angle (2°) XRD pattern indicates only single and less significant broad reflection in the 20 range from 25° to 35°. Such a broad reflection is a typical indication of an amorphous phase. It means that the films are amorphous in nature. This is due to very slow surface diffusion of low energy particles during deposition in case of electron beam evaporation. Earlier report on EB evaporated HfO₂ films, showed that the as-deposited films were amorphous, whereas the annealed films were polycrystalline [29].

3.1.3.2 Film density

Film density can be simply determined from the angle at which x-rays begin to penetrate the sample, the so called critical angle for external reflection. The position of the critical angle (θ_c) is related to the dispersive correction to the refractive index (δ) as $\theta_c = \sqrt{2\delta}$ and δ is proportional to the density of the material. Thus, a higher critical angle corresponds to a denser material and vice versa [84]. The reflectivity for a rough surface gets modified by "Debye-Waller like" factor as $R = R_o \exp\left(-\frac{q^2\sigma^2}{2}\right)$, where $q \ (=4\pi Sin\theta/\lambda)$ is the momentum

transfer, *R* is the reflectivity of the rough surface, R_o is the reflectivity of an identical smooth surface and σ is the RMS surface roughness. Thus by fitting the x-ray reflectivity (XRR) spectrum of the surface of a thin film sample near its critical angle, estimation of density ρ and RMS surface roughness σ of the thin film can be made quite accurately [85]. The computational fitting has been carried out using the "IMD" code under the "XOP" software package [86] and the best fit of the spectrums are achieved by minimizing the χ^2 value. The measured and corresponding fitted XRR spectra of the HfO₂ thin films deposited at different oxygen partial pressures are shown in Fig. 3.2.



Fig. 3. 2: *Experimental x-ray reflectivity with best fit theoretical curve of* HfO_2 *thin films prepared at different* O_2 *partial pressures.*

The density and roughness of the films determined by the computer simulation are listed in Table-3.1. The film density decreases from 8.53 gm/cm^3 to 6.99 gm/cm^3 with increasing O₂ pressure from 1×10^4 mbar to 8×10^4 mbar. As the oxygen partial pressure increases, the mean free path of evaporated atoms or molecules decreases. As a result the kinetic energy of the evaporated particle reduces, which effectively reduces their surface mobility. This lower mobility of evaporated atoms leads to porous and void-rich microstructure. Thus, higher oxygen partial pressure results in lower packing density of the film and vice-versa.

3.1.3.3 Surface morphology

The two dimensional AFM images of the HfO_2 films deposited at different oxygen partial pressures are shown in Fig. 3.3(a)-(d). The root mean square surface roughness as well as the average grain size of the films have been determined from the AFM surface morphology of all the films and are listed in Table-3.1. The RMS surface roughness increases from 1.1 nm to 1.8 nm with increasing oxygen partial pressure from 1×10^4 mbar to 8×10^4 mbar as a

consequence of the increase in the grain size from 16 nm to 31 nm. The film prepared at lower oxygen pressure consists of finer grains of uniform size resulting in lower surface roughness. The film prepared at higher oxygen pressure consists of relatively larger spherical grains resulting in higher roughness. The grain morphological evolution of the HfO₂ films with oxygen partial pressure can be explained through the surface diffusion of adatoms [87]. With increasing oxygen partial pressure, the collision among evaporated atoms increases, which reduces their kinetic energy. As a result the surface diffusion of the adatoms gets lower, which favours the grain growth, resulting bigger grain size. The increasing behaviour of surface roughness with oxygen pressure is probed by both the techniques of XRR and AFM, but with slight deviation in the roughness values. The deviation is explained by the difference in lateral roughness scale that the two techniques measure [88].



Fig. 3. 3: *AFM* surface morphology of HfO_2 thin films prepared at (a) $1x10^{-4}$ mbar, (b) $2x10^{-4}$ mbar, (c) $4x10^{-4}$ mbar, and (d) $8x10^{-4}$ mbar O_2 partial pressures respectively.

3.1.3.4 Optical properties

3.1.3.4.1 Refractive index and extinction co-efficient

The measured spectral transmittance of HfO_2 thin films prepared at different oxygen partial pressures are shown in Fig. 3.4. Optical constants and thickness of the films are derived from the transmission spectrum by fitting it to the theoretical spectrum. The theoretical spectrum is generated using suitable dispersion model by formalism described elsewhere [85, 89]. The dispersion for refractive index (*n*) and extinction co-efficient (*k*) follows single oscillator [90] and Urbach model [91] respectively as follows.

$$n(\lambda) = \sqrt{1 + \left(\frac{E_0 E_d}{E_0^2 - (hc/\lambda)^2}\right)}$$
(3.1)

$$k(\lambda) = \alpha \exp\left(1240\beta\left(\frac{1}{\lambda} - \frac{1}{\gamma}\right)\right)$$
(3.2)

Where λ is the wavelength of the light, *h* is Planck's constant, *c* is the velocity of the light, E_0 is the single oscillator energy and E_d is the so-called dispersion energy. The constants α , β and γ are fitting parameters.



Fig. 3. 4: Transmission spectra of HfO₂ films prepared at different O₂ partial pressures.



Fig. 3. 5: Experimental transmission spectrum with best fit theoretical simulation of HfO_2 thin film prepared at O_2 pressure of $8x10^{-4}$ mbar.

Fig. 3.5 shows a representative experimental transmission spectrum of the film prepared at oxygen partial pressure of 8×10^{-4} mbar along with the best-fit theoretical spectrum. The obtained fitting parameters are used to determine the refractive index (*n*) and extinction coefficient (*k*) of the films as shown in Fig. 3.6. The refractive index (at 550 nm wavelength) of the film varies from 1.821 to 1.959, when O₂ partial pressure is varied in the range 1×10^{-4} to 8×10^{-4} mbar. The obtained range of refractive index for hafnia film is matching with the values reported earlier [92-94]. Both the refractive index as well as extinction coefficient of the HfO₂ film decreases with increasing oxygen partial pressure. The film packing density decreases with oxygen pressure as confirmed from XRR measurement. This decreasing density leads to decrease in refractive index. At lower oxygen pressure, the films grown may not be completely HfO₂ i.e. HfO_x, where x < 2 and the film shows little absorption due to nonstoichiometric metallic behaviour. With increasing oxygen pressure, the film transits to fully stoichiometric HfO₂ phase [95], which leads to decreasing extinction co-efficient.



Fig. 3. 6: Refractive index and extinction co-efficient spectra of HfO_2 thin films prepared at different O_2 partial pressures.

Table - 3. 1: *Physical parameters of EB evaporated amorphous HfO*₂ *thin films.*

Oxygen pressure (mbar)	Thickness (nm)	Refractive index @ 550 nm	Band gap (eV)	Film density (g/cm ³)	Grain size (nm)	RMS ro (n AFM	oughness m) XRR	Residual stress (MPa)	LID (J/cm λ=1064 nm	λ^{T} $\lambda = 532$ nm
1× 10 ⁻⁴	260	1.959	5.59	8.53	16	1.1	1.3	115	9.89	5.97
2×10^{-4}	268	1.936	5.61	8.28	18	1.2	1.4	90	9.02	4.59
4×10^{-4}	322	1.847	5.64	7.35	24	1.7	1.5	173	9.39	4.89
8×10^{-4}	350	1.821	5.67	6.99	31	1.8	1.6	139	8.83	4.52

3.1.3.4.2 Band gap

The optical band gap of the films has been estimated from the obtained values of absorption co-efficient (α). The absorption co-efficient in the high absorption region ($\alpha \ge 10^{-4}$ cm⁻¹) is given according to Tauc's relation for the allowed indirect transition [96] by the following relation (αE)^{1/2} = $K(E-E_g)$, where K is a constant that depends on the transition probability, and E_g is the optical band gap. Fig. 3.7(a) presents best fit of (αE)^{1/2} vs. photon energy E for the films at different oxygen partial pressures. The values of the optical band gap E_g were taken as the intercept of (αE)^{1/2} vs. E at (αE)^{1/2} = 0 and are listed in Table-3.1.



Fig. 3. 7: (a) Plot of (ahv) $^{1/2}$ versus hv for the HfO₂ thin films prepared at different O₂ pressures, and (b) Band gap E_g vs. refractive index n of the HfO₂ thin films.

The band gap increases from 5.59 eV to 5.67 eV with increasing oxygen pressure from 1×10^{-4} mbar to 8×10^{-4} mbar, which indicates that the optical absorption edge shifts to higher photon energy. The increment of optical band gap with oxygen partial pressure could be due to the decreasing oxygen vacancies in the film. The concentration of oxygen vacancies in oxide thin films decreases with increasing oxygen partial pressure. As a result the defect states related to oxygen vacancies become less delocalized, therefore the extended nonlocalization in valence band decreases, resulting band gap widening [97, 98]. The less the oxygen vacancy is, the larger is the band gap and vice versa. The optical band gap is plotted versus refractive index at the wavelength of 550 nm in Fig. 3.7(b). The high refractive index film exhibits lower band gap value than the low index film, which is in agreement with the Moss rule ($E_g n^4 \approx$ constant) [99]. The conclusion is that the UV transparency is better for the HfO₂ films deposited at higher oxygen partial pressure.

3.1.3.5 Residual stress

The residual stress of the films has been determined by substrate curvature. The surface profiles of the glass substrates (35 mm dia. and 1 mm thick) before and after deposition of the films prepared at different O_2 partial pressure are shown in Fig. 3.8. The mean radius of curvature has been estimated from the surface profile using procedure described in chapter-2.


Fig. 3. 8: 2D surface contour map of the substrates before and after deposition of the HfO_2 films prepared at (a) $1x10^{-4}$ mbar, and (b) $2x10^{-4}$ mbar O_2 pressure.

The residual stress (σ) in the films has been determined from the radius of curvature using the Stoney's equation. The obtained residual stress is tensile in nature and the value ranges from 90 MPa to 173 MPa for the films deposited at different oxygen partial pressure as listed in Table-3.1. The total residual stress in a thin film is composed of intrinsic stress, thermal stress and extrinsic stress. The estimated thermal stress [100] in amorphous hafnia film [101] deposited at substrate temperature of 300°C is approximately 150 MPa and compressive in nature. But the measured residual stress is tensile in nature, which indicates that the thermal stress does not play a dominant role in the overall stress. Since both the substrates as well as the thin films are amorphous in nature, hence there is no contribution from the lattice mismatch generated inherent epitaxial stress in the film [102]. The residual stress in these EB deposited hafnia thin films is therefore mostly due to the film microstructure. It is seen that the film residual stress is less for lower oxygen pressures and more for higher oxygen pressures. The variation of residual stress is not systematic with O₂ pressure and there is a correlation between stress and grain size as suggested by Nix and Clemens [103], which

predicts higher tensile stress with finer grains. This is because the overall stress in a continuous film is a competition among different stress-generating mechanisms such as grain growth, excess vacancy annihilation, grain boundary relaxation, shrinkage of grain boundary voids etc [104]. Film thickness, density, grain size, grain boundary, surface roughness, oxygen vacancy etc are the factors which influence the stress-generating mechanism. With increasing film thickness, the grain size increases which ultimately reduces the tensile stress [105]. But if the grains orients in such a way that the grain boundary energy becomes minimum, then the tensile stress increases [106]. The competition among all such stress-generating mechanisms leads to a resultant residual stress, which is observed in our case. The minimum residual stress of 90 MPa is observed to be for the HfO₂ film prepared at $2x10^4$ mbar oxygen pressure.

3.1.3.6 Laser induced damage threshold

LIDT has been determined from damage probability plot using 1-on-1 method. Fig. 3.9(a) shows the LIDT values of the HfO₂ films prepared at different oxygen partial pressure.



Fig. 3. 9: (a) LIDT of the HfO_2 thin films prepared at different O_2 partial pressures and (b) LIDT vs. density of the HfO_2 thin films.

The LIDT of hafnia films for both harmonic of the laser increases with increasing film density as shown in Fig. 3.9(b). This variation has been explained as follows. For nanosecond pulsed laser, the thermal-mechanical damage process is considered as the dominant damage process in dielectric thin films [107]. In this process, damage in dielectric thin films occurs due to an excess of thermal energy which is coupled into the optical structure by absorption of laser radiation at defect sites. When the surface temperature of the absorbing defects reaches to melting temperature, then the surface gets damaged. Examples of such defects include grain boundaries, voids, atomic and molecular contaminants, nonstoichiometric defects, inclusions, nodules etc [108]. The thermo-physical properties such as density, specific heat, thermal conductivity of the film or host matrix, etc. are of critical importance for limiting the LIDT, in case of absorbing defects driven mechanism. Based on defect originated thermal damage mechanism, the LIDT may be predicted as [109]

$$F_{th} \approx \frac{16T_c}{\pi} \left(\rho_{film} C_{film} K_{film} \tau \right)^{1/2}$$
(3.5)

where F_{th} is the damage threshold in J/cm², T_c is the melting temperature of the film, ρ_{film} is the film density, C_{film} is the specific heat at constant pressure of the film, K_{film} is the thermal conductivity of the film and τ is the laser pulse length. The relation between thermal conductivity and density is given by [110]

$$K_{film} = K_{bulk} \left(\frac{\rho_{film}}{\rho_{bulk}}\right)^3$$
(3.6)

This equation shows that the thermal conductivity is proportional to the cube of its density. The relation between specific heat at constant volume and film density [111] is given by

$$C_{film} = C_{bulk} \left(1 - \phi \right) = C_{bulk} \left(\frac{\rho_{film}}{\rho_{bulk}} \right)$$
(3.7)

The Eq. (3.6) and (3.7) suggest that the thermal conductivity and specific heat of the film increases with increasing film density, consequently the LIDT as per Eq. (3.5). Denser films

having lower thermal barriers along the film, exhibit higher thermal conductivity and hence better laser damage resistance. The LIDT of HfO₂ films for 532 nm laser is lower than that of 1064 nm laser, which is explained by multiphoton ionization (MPI) process [112]. In a pure MPI process, with decreasing laser wavelength or increasing photon energy, the LIDT drops abruptly as the number of photons (*n*) needed to bridge band gap (E_g) of material decreases and the transition takes place at photon energies of E_g/n [113]. Moreover the electrons in the conduction band absorb laser energy continuously. The absorption rate increases nonlinearly with photon energy [114], which signifies that the deposited laser energy density will be higher for shorter wavelength laser resulting lower LIDT.

3.1.4 Conclusion

The optical, microstructural, mechanical and laser induced damage threshold properties of EB evaporated HfO_2 thin films prepared at different oxygen partial pressures have been investigated. The GIXRD spectra show that the films are amorphous in nature. The optical properties of the films have been derived from the transmission spectrum measured using spectrophotometer. The refractive index and density of the films decrease with increasing oxygen partial pressure, whereas the band gap increases with it. The decreasing refractive index is mainly due to increasing porosity in films. The surface roughness as well grain size of the films are tensile in nature. The variation of residual stress with oxygen pressure has been explained through combined effect of different stress-generating mechanisms. The LIDT of the films are measured for both 532 nm and 1064 nm laser wavelength. The LIDT of the HfO₂ thin films decreases with increasing oxygen partial pressure and is explained through film porosity or density.

3.2 RF magnetron sputtered HfO₂ thin films prepared at different O₂/Ar flow ratio

3.2.1 Introduction

HfO₂ is widely used as high index and low absorption material for optical coating applications [115]. However, the overall performance of a multilayer coating not only depends on its optical properties, but also on its mechanical properties such as residual stress, elastic modulus and adhesion. Better optical properties can be achieved by maximizing the achievable refractive index of the materials with as low optical loss as possible. Film refractive index close to or higher than the bulk value because of high densification can be achieved using modern sputtering techniques [116, 117]. The densification leads to negligible porosity in the film and makes it environmentally stable. However, a disadvantage of densification is high compressive stress leading to serious structural problems like buckling or delamination of films from the substrate in optical systems of high end applications [118]. Hence control over residual stress in the coating is very crucial. Thus the optimization of deposition condition for achieving maximum refractive index with optimized mechanical properties is a prerequisite for development of stable optical coatings. Especially, in the RF sputtering technique, the O₂/Ar gas flow ratio is one of the crucial deposition parameter which affects not only the film's stoichiometry but also its microstructure and related properties. A lot of studies have been reported regarding the effect of O₂/Ar gas flow ratio on the structural, optical and dielectric properties of HfO₂ thin films [78, 95, 119]. But till now there are no studies that investigate the effect of O₂/Ar gas flow ratio on the residual stress of the films, which is an important factor for the mechanical stability of the films. In the present study effect of O₂/Ar gas flow ratio on structure, morphology, optical properties, residual stress and LIDT of the RF sputtered HfO₂ thin films has been investigated. The study correlates the optical properties and residual stress with the microstructure of the films.

3.2.2 Experimental details

HfO₂ thin films on BK7 glass substrate have been prepared using RF magnetron sputtering in a fully automated vacuum system. A high purity (99.995%) HfO2 target having 75 mm diameter and 6 mm thickness was used as the sputtering source and was bonded to a watercooled target holder. The sputtering was carried out in argon ambience in the 'sputter up' configuration. The substrate-target distance was 60 mm for all the depositions. Prior to the deposition, a base pressure of 1×10^{-4} Pa was achieved in the chamber employing a turbo molecular pump backed by a rotary pump. Before starting the deposition, the target was sputter cleaned for 5-10 min to remove any contaminants and eliminate any differential sputtering effect. The RF power and the working pressure were fixed at 200 W and 0.4 Pa during the sputtering process, respectively. The Ar flow was kept constant at 20 SCCM while O₂ flow was changed from 0 to 6 SCCM for different samples. For each HfO₂ thin film, the O_2/Ar flow ratio was kept constant at the required ratio between 0 and 0.3. All the depositions were carried out without any external substrate heating. However, the substrate temperature rises during the deposition process due to the bombardment of neutral species and electrons [120]. The maximum temperature of the substrate during the deposition process was measured to be 100±10 °C at 200 W RF power. The film structure has been probed by grazing incidence x-ray diffraction (GIXRD) with 20 angle in the range of 25°-80° using Cu- K_{α} (λ =1.5406 Å) radiation in steps of 0.05°. The spectrum were recorded by keeping the incident angle fixed at a grazing angle of incidence of 2° in order to keep the probing region of the sample near its surface. AFM has been used to characterize the surface morphology of the films. The optical transmission spectra of the films were measured using spectrophotometer in the range 400-1100 nm for determination of refractive index and thickness. The residual stress has been evaluated from the substrate curvature measured by a laser Fizeau interferometer before and after film deposition.

3.2.3 Results and discussions

3.2.3.1 Film structure and morphology

The GIXRD pattern of the RF sputtered HfO_2 thin films are presented in Fig. 3.11. In all cases, the films are polycrystalline in nature and the peaks are attributed to diffraction from different planes of hafnia monoclinic phase. This figure shows that the predominant monoclinic phase is in the (-111) direction, which is consistent with the powder diffraction data of monoclinic hafnia [121]. The structure does not change much with increasing O₂/Ar flow ratio, which is consistent with the earlier investigation by William *et al.* [122] for the reactive DC magnetron sputtered HfO₂ films prepared at different oxygen partial pressure. The intensity of the (-111) peak does not show any significant change with the changing O₂/Ar flow ratio, whereas the peak position changes.



Fig. 3. 10: *GIXRD pattern of HfO*₂ *thin films prepared at different O*₂/*Ar flow ratios.*

The two dimensional AFM images of the HfO₂ films deposited at different O_2/Ar gas flow ratios are shown in Fig. 3.12(a)-(d). The root mean square surface roughness as well as the average grain size of the films have been computed from the AFM surface morphology of all the films and are listed in Table-3.2. From this figure, it is clearly seen that the film prepared without oxygen during sputtering shows higher surface roughness with bigger grain size as compared to the films prepared with oxygen. The film prepared at O_2/Ar gas flow ratio of 0.1 is observed to consist of compact spherical grains of uniform size resulting lower surface roughness. The surface morphology of the films prepared at O_2/Ar gas flow ratio of 0.2 and 0.3 are found almost identical. These films consist of very fine grains, which may be due to the formation of more grain boundaries as well as dynamic incorporation and segregation of oxygen during deposition [123].



Fig. 3. 11: AFM images of HfO_2 thin films prepared at different O_2/Ar flow ratio.

The morphological evolution of all the HfO_2 films can be explained through variation of deposition rate with the increasing O_2/Ar flow ratio. When there is no oxygen gas flow, a higher deposition rate resulting from a large sputtering yield with high energy sputtered particles favour the formation of larger grains [119]. With the introduction of oxygen into the sputtering process, the number of collision between the sputtered molecules and the plasma species increases, consequently decreasing the mean free path of the sputtered atoms. If this mean free path is less than the target-substrate distance, the displacement of the sputtered atoms will be reduced as well as randomized leading to dramatically decrease in deposition rate. This will decrease the sputtering yield and thus decrease grain size effectively.

3.2.3.2 Optical properties

The spectral transmittance of HfO_2 thin films prepared at different O_2/Ar flow ratio is shown in Fig. 3.13. The lower transmittance of films deposited without oxygen flow may be due to oxygen vacancies in HfO_2 film, which causes an increase in the absorption of the visible light. The film prepared at flow ratio of 0.1, 0.2 and 0.3 shows higher transmittance, which indicates that the film stoichiometry has been improved with oxygen pressure.



Fig. 3. 12: Transmission spectra of HfO_2 thin films prepared at different O_2/Ar flow ratio.

The refractive index and thickness of the films are evaluated using inverse synthesis method [85]. The dispersion of refractive index (n) is based on the single effective oscillator model according to Wemple and DiDomenico [96], while the dispersion of extinction co-efficient (k) is assumed to follow Cauchy's dispersion model and they are given by

$$n(\lambda) = \sqrt{1 + \left(\frac{E_0 E_d}{E_0^2 - (1240/\lambda)^2}\right)}$$
(3.8)

$$k(\lambda) = a + \frac{b}{\lambda^2} \tag{3.9}$$

Where λ (nm) is the wavelength of the light, E_0 (eV) is the single oscillator energy and E_d (eV) is the so-called dispersion energy. The constants *a* and *b* are Cauchy fitting parameters.



Fig. 3. 13: *Refractive index and Extinction co-efficient spectra of* HfO_2 *thin films prepared at different* O_2/Ar *flow ratio.*

A computational curve fitting is carried out to the measured transmission spectrum with the coefficients of the dispersion model and thickness of the film as fitting parameters [85]. The obtained fitting parameters and thickness values of the films are listed in Table-3.2. The

derived refractive index and extinction co-efficient spectra of the entire HfO₂ films are shown in Fig. 3.14 (a) and (b) respectively. The refractive index (at 550 nm wavelength) of the film varies from 1.87 to 2 with different O₂/Ar flow ratio. This range of refractive index is matching with the values reported earlier [95]. The obtained refractive index values are higher than that reported by Liu *et al.* [119] for RF sputtered HfO₂ thin films. This can be ascribed to difference in process parameters during deposition. The film packing density, which is an indirect indication of film densification, has been determined from the film refractive index by using Bragg and Pippard model [124]. Optical thin film of any dielectric material is simply a mixture of the pure dielectric material (with bulk refractive index n_b) and the pores (with refractive index n_0). The pores may or may not be filled with moisture. For an arbitrary mixture of dielectric material (with packing density p) and the pores (with packing density 1-p), the refractive index of the thin film (n_f) is given by

$$n_f = n_0 \sqrt{\frac{n_0^2 + [L(1-p) + p](n_0^2 - n_b^2)}{n_0^2 + [L(1-p)](n_0^2 - n_b^2)}}$$
(3.10)

Where *L* is the depolarizing factor related to the geometrical shape of the dispersed dielectric material. From the AFM morphology of HfO₂ thin films, it is clear that the grain shape of the material is spherical-like, corresponding to L=1/3 [124]. Assuming an empty pore ($n_0\approx1$), the packing density (*p*) of the film can be derived from Eq. (3.10) and is given by

$$p = \left(\frac{n_f^2 - 1}{n_f^2 + 2}\right) \left(\frac{n_b^2 + 2}{n_b^2 - 1}\right)$$
(3.11)

The estimated packing density using Eq. (3.11) for the HfO₂ films varies from 0.87 to 0.97.

The formulation of DiDomenico dispersion model is based on the two important physical parameters namely the dispersion energy (E_d) and the single oscillator energy (E_0) . The parameters E_d and E_0 are found decreasing with increasing compressive strain $(\Delta d/d)$ of the films, which gives a correlation between structure and optical properties as shown in Fig. 3.15. The dispersion energy parameter E_d is related to the formal valency of the anion (Z), the effective cation coordination number (Nc), and the total number of valence electrons per anion (cores excluded) (Ne) uniquely as $E_d = \beta N_c Z_a N_e$ [90], where β is an energy constant expressing the covalent or ionic character of the solid through the values 0.37±0.04 and 0.26±0.03 eV, respectively. This dependency of E_d on coordination number and chemical valency suggests further that nearest-neighbour atomic like quantities strongly influence the electronic as well as optical properties of materials. This indicates that the dispersion energy parameter E_d is strongly related to the crystal structure of the thin film, allowing it to be treated as a microstructural ordering parameter. Hence the dispersion energy E_d is affected by the lattice structure induced compressive strain as observed in Fig. 3.15.



Fig. 3. 14: Variation of dispersion energy (E_d) and oscillator energy (E_0) with lattice strain for HfO_2 thin films.

The parameter single oscillator energy E_0 is the "average" energy-gap parameter equivalent to the energy difference between the "centers of gravity" of the valence and conduction bands. This is very similar to the energy parameter ("Penn gap"), used by Penn' for the determination of the static refractive index in semiconductors [125]. The energy E_0 is proportional to the optical band gap (E_g) of the material. Hence a decreasing E_0 with increasing compressive strain as seen in Fig. 3.15 indicates band gap narrowing with increasing compressive strain. The reduction in band gap is explained by the shifting of conduction and valance band edges under strain [126]. Thus, the strain due to lattice structure can affect optical properties of the thin films such as optical band gap, refractive index, etc.

Table - 3. 2: Parameters derived from XRD, Transmission, and Substrate curvature measurement of the HfO_2 thin films.

O ₂ /Ar flow ratio	Thickness (nm)	d-111 (Å)	Strain (%)	E_d (eV)	E_0 (eV)	Refractive index (at 550 nm)	Packing density	Residual stress (GPa)
0	244	3.187	-1.33	15.10	6.80	1.87	0.87	-3.21 ± 0.11
-0.1	201	3.159	-0.47	22.87	8.23	2.00	0.97	$\textbf{-}1.50\pm0.04$
0.2	220	3.161	-0.51	18.69	7.27	1.96	0.94	$\textbf{-}1.59\pm0.03$
0.3	209	3.157	-0.41	24.05	8.82	1.98	0.95	$\textbf{-}1.17\pm0.04$

3.2.3.3 Residual stress

The surface shape profiles of the substrate before and after deposition of the films prepared at O_2/Ar flow ratio of 0.1, 0.2 and 0.3 respectively are shown in Fig. 3.18. The spherical shape component is extracted from the surface profile data by Zernike polynomial fitting analysis to estimate the substrate curvature [65]. The film residual stress (σ) has been evaluated from the substrate curvature using Stoney's equation [127]. The values of the parameters used in the calculation for BK7 glass substrate in our case are: $E_s=82$ GPa, $v_s=0.206$ and $t_s=1$ mm. The estimated residual stress is compressive in nature and the value ranges from -1.17 GPa to - 3.21 GPa for the films deposited at different O_2/Ar flow ratio. The total residual stress in a thin film is composed of intrinsic stress, thermal stress and extrinsic stress. Thermal stress is caused both by the thermal expansion co-efficient difference between the film α_f and the substrate α_s and by the temperature difference between the substrate temperature T_d during deposition and the ambient temperature T_0 . It can be calculated by [127]

$$\sigma_{th} = \left(\frac{E_f}{v_f}\right) \left(\alpha_f - \alpha_s\right) \left(T_d - T_0\right)$$
(3.12)

Where E_f (283 GPa) and v_f (0.298) are Young's modulus and Poisson ratio of the film respectively [128]. Since $\alpha_f = 3.8 \times 10^{-6} K^{-1}$ for HfO₂ is less than $\alpha_s = 7.1 \times 10^{-6} K^{-1}$ for BK7 glass substrate and the substrate temperature is 100 °C, the calculated thermal stress of 228 MPa is compressive in nature. But the measured stress is more than 1100 MPa, which indicates that the thermal stress does not play a dominant role in the overall stress. It may hence be deduced that the intrinsic stress, which originates from various defects, lattice mismatch between the film and substrate and grain growth [129] and/or extrinsic stress, which originates from microstructure changes because of adsorption of water or grain boundary oxidation [130] are the main contributors to the total residual stress.



Fig. 3. 15: 2D surface contour map of the substrate before and after deposition of HfO_2 films at O_2/Ar flow ratio of (a) 0.1, (b) 0.2, and (c) 0.3 respectively with 1 pixel ≈ 0.2 mm.

The variation of residual stress with varying O_2/Ar flow ratio is shown in Fig. 3.17(a). This figure shows that the compressive residual stress is decreasing with increasing flow ratio. The variation of compressive residual stress can be explained through the fact that the total residual stress in the sputtered film is a combination of tensile as well as compressive stress, where the ultimate residual stress is a result of dynamic competition between the tensile and compressive stress developed during growth of the film [131]. In a sputtered film, tensile stress is generated at the grain boundaries due to attraction between grains [132] and is inversely proportional to the square root of average grain size [106] as given by

$$\sigma_T = \sqrt{\frac{E_f}{(1-\upsilon_f)} \frac{2(2\gamma_s - \gamma_{gb})}{D}}$$
(3.13)

where is E_f Young's modulus, v_f is Poisson's ratio, D is the grain size, and γ_s and γ_f are the surface and grain boundary energies of the film, respectively. This Eq. (3.13) implies that the tensile stress increases with decreasing grain size and also with increasing surface to grain boundary energy difference.



Fig. 3. 16: Effect of O_2/Ar flow ration on (a) residual stress, (b) interplanar spacing, (c) film packing density, and (d) grain size of the films. The horizontal dashed lines in (b) represents the stress-free bulk interplanar spacing of (-111) planes for HfO₂.

Fig. 3.17(d) shows that with increasing O_2/Ar flow ratio, the grain size of the film decreases from 60 nm to 30 nm. This leads to an increasing tensile stress and could therefore explain the decrease of overall compressive stress with increasing O₂/Ar flow ratio. The origin of compressive stress in a sputtered film is either atomic peening [133] or adatom diffusion into grain boundaries leading to film densification [134]. The atomic peening causes the energetic atoms to enter into spaces of the growing film leading to lattice expansion parallel to the substrate surface. Since the film is not free to expand in the plane of the substrate, the entrapped atoms cause compressive stress [133]. The film packing density depends on the mass density of the grain boundary regions and the grain size. Grain boundary densification therefore leads to high density films. It is shown elsewhere that the stress generated due to grain boundary densification results in high packing density films having high compressive stress [135]. But in the present case as shown in Fig. 3.17(a) and (c), it is observed that the film with lower packing density shows higher compressive stress while film with higher packing density shows lower compressive stress. This clearly suggests that the observed compressive stress is largely due to lattice expansion because of atomic peening which is supported by the observed interplanar spacing shown in Fig. 3.17(b), rather than the grain boundary densification. The interplanar spacing (d) of the films gets closer to the stress-free interplanar spacing (d_0) with increasing O₂/Ar flow ratio as shown in Fig. 3.17(b), thereby results in decreasing compressive stress with increasing O₂/Ar flow ratio. It concludes that the decreasing compressive stress with increasing O_2/Ar flow ratio in the sputtered HfO₂ films is mainly due to the decreasing compressive stress component caused by lattice expansion as well as increasing tensile stress component caused by reduced grain size. Finally in order to get the optimized O₂/Ar flow ratio for stable optical coatings, the refractive index vs. surface roughness and refractive index vs. residual stress are plotted along with the straight line fit in Fig. 3.18 for different O₂/Ar flow ratio.



Fig. 3. 17: *Plot of (a) refractive index vs. residual stress, and (b) refractive index vs. surface roughness for the* HfO_2 *thin films*

Form this figure, it is seen that the film (prepared at without oxygen) having higher stress as well as higher roughness exhibits lower refractive index. This figure clearly suggests that, O_2/Ar flow ratio of 0.1 is the better deposition condition giving higher refractive index value of 2 and relatively lower residual stress of -1.5 GPa with better surface quality having minimum roughness of 4.25 nm. Hence the packing density or porosity controlled by O_2/Ar flow ratio during deposition plays a crucial role to obtain a useful balance between optical and mechanical properties of the film with better surface quality, which is similar to the results reported by Stenzel *et al.* [136].

3.2.3.4 Laser induced damage threshold

The LIDT value of the HfO₂ thin films has been determined from the damage probability plot. The measured LIDT value decreases from 14.5 J/cm² to 8.1 J/cm² for 1064 nm laser, and 4.2 J/cm² to 2.3 J/cm² for 532 nm laser, with increasing O_2/Ar flow ratio as shown in Fig. 3.19 This variation has been explained with the help of grain size of the films. From AFM image, it is clear that the film grain size is decreasing with increasing O_2/Ar flow ratio. Since the thermal conductivity is directly proportional to the grain size. With increasing grain size, grain boundaries which acts as thermal barriers reduce, therefore thermal conductivity increases. For dielectric thin films, laser induced damage is mainly dominated by absorbing

defect driven thermal damage process. Generally absorbing defects may exist in the film, the substrate, and the film-substrate interface. When high power laser is incident on it, it absorbs the light and produces enormous heat leading to catastrophic damage of the films. As per this process, the LIDT can be predicted as $F_{th} \approx \frac{16T_c}{\pi} (\rho_{film} C_{film} K_{film} \tau)^{1/2}$, where F_{th} is the damage threshold in J/cm², T_c is the melting temperature of the film, ρ_{film} is the film density, C_{film} is the specific heat at constant pressure of the film, K_{film} is the thermal conductivity of the film and τ is the laser pulse length. This clearly shows that LIDT decreases with decreasing thermal conductivity and vice versa.



Fig. 3. 18: *Variation of LIDT with O*₂/*Ar flow ratio for (a) 1064 nm and (b) 532 nm laser.* Laser induced thermal resistance factor (R_T), which is a key factor for mechanical damage of the films, is defined as $R_T = \sigma_{film} \frac{K_{film}(1 - v_{film})}{\alpha_{film} E_{film}}$, where σ_{film} , K_{film} , v_{film} , α_{film} , and E_{film} are the fracture stress, thermal conductivity , Poisson's ratio, co-efficient of thermal

expansion and thermal conductivity of the films respectively. The thermal resistance factor is also directly proportional o thermal conductivity. Therefore laser induced thermal as well as mechanical damage of thin films decreases with decreasing grain size. This corroborates the decreasing of LIDT with increasing O_2 /Ar flow ratio. The LIDT of HfO₂ thin films for 532 nm laser is lower than that of 1064 nm laser, which is mainly due to the multiphoton ionization process as described in the 1st part of this chapter for EB HfO₂ thin films.

3.2.4 Conclusion

A study investigating the microstructure, optical properties and residual stress of HfO_2 films deposited on glass substrate as a function of oxygen/argon (O₂/Ar) flow ratio during deposition has been carried out. The films are found to be polycrystalline in nature under compressive strain. Correlation established between the dispersion energy as well as the oscillator energy with the compressive strain of the films concludes that the strain due to lattice structure modification can strongly affect the optical properties such as optical band gap and refractive index of the thin films. The origin of compressive stress in the thin films is found to be atomic peening rather than grain boundary densification. The variation of total residual stress with O₂/Ar flow ratio is explained through intrinsic compressive stress because of lattice expansion as well as intrinsic tensile stress because of the grain growth. Finally, O₂/Ar flow ratio of 0.1 during the RF sputtered deposition process is found to be the optimal deposition condition for fabrication of stable HfO₂ thin films for optical coating applications.

 ZrO_2 is a high refractive index material and has similar crystal structure as HfO_2 . The refractive index as well as microstructure of ZrO_2 can be improved by adding small fraction (less than 20%) of foreign materials like MgO, SiO₂ etc. In the next chapter, ZrO_2 -MgO and ZrO_2 -SiO₂ mixed thin films are prepared at different oxygen partial pressure and their properties have been investigated.

Chapter 4: Study of Electron Beam Evaporated ZrO₂-MgO and ZrO₂-SiO₂ Thin Films

Design and development of optical thin films multilayer devices are constrained by the optical constants such as refractive index, absorption coefficient, band gap etc. of available coating materials. Hence it is necessary to find new materials as well as methodologies which can yield desired refractive index values for developing precision optical devices such as optical wave guides, rugate filters, narrow band filters etc [137]. In recent years, mixed composite oxide materials like SiO₂-Al₂O₃, ZrO₂-Ta₂O₅, ZrO₂-TiO₂, ZrO₂-Al₂O₃, TiO₂-Al₂O₃, ZrO₂-MgO, ZrO₂-SiO₂, HfO₂-SiO₂, Gd₂O₃-SiO₂ etc., which are mixture of two different materials having new optical and structural properties compared to its constituent material, have been used to fulfill the gap of desired refractive index values [8, 138, 139] by using different coating methods. In this context, different properties of EB evaporated ZrO₂ thin films by adding little amount of foreign materials like MgO and SiO₂ during deposition has been investigated. Since oxygen partial pressure during deposition is very much crucial for stable coatings, therefore following studies have been carried out. The effect of O₂ pressure on different properties of ZrO₂-MgO and ZrO₂-SiO₂ composite thin films are presented in 1st and 2nd part respectively as follows.

4.1 Electron beam evaporated ZrO₂-MgO thin films prepared at different oxygen partial pressure

4.1.1 Introduction

ZrO₂-MgO is a solid-solution based mixed composite oxide material. It has been evolved as a promising coating material to develop various types of optical devices because of its suitable optical properties like transparent spectral range from near-infrared to the ultraviolet, high refractive index and better laser induced damaged threshold [140]. The better optical performance with high stability of the films needs optimization of their mechanical properties along with microstructural characteristics and other functional properties for long-term environmental stability [141]. There are many factors which are responsible for mechanical stability of the optical thin films. One of the important factors is local indentation modulus, which strongly affects the residual stress generated in thin films. This elastic property of thin films differs significantly from those of the bulk materials due to the interfaces, microstructure, and the underlying substrates and is also affected by the process parameters and the deposition technique like structural and optical properties [142]. Therefore these properties should be investigated thoroughly.

Many techniques are being used for the determination of elastic modulus of thin films such as micro- and nano-indentation tests [143], laser induced surface acoustic wave [144], surface Brillouin light scattering measurements [145] and Atomic Force Acoustic Microscopy (AFAM) [57]. Out of all the techniques, AFAM technique is capable of giving both quantitative values of elastic modulus (indentation modulus for anisotropic films) like other techniques as well as qualitative picture of elastic modulus in terms of acoustic image simultaneously with surface topography of thin film sample; and also capable of giving quantitative mapping of surface elastic modulus by bidimensional reconstruction of the local elastic modulus of sample surface at nanoscale using AFAM two contact resonance frequency imaging technique [61]. This makes AFAM, a unique tool for the local investigation of the sample surface elastic properties. AFAM technique has been used to measure the elastic modulus of our ZrO₂-MgO mixed composite thin films. In the present work, the effect of oxygen partial pressure on optical properties; surface morphology, elastic modulus, and laser induced damage threshold of EB evaporated ZrO₂-MgO thin films has been investigated. The study has established a co-relation among the microstructural, optical and elastic properties of the films.

4.1.2 Experimental methods

A several set of such thin films on silicon (111) and quartz substrates were prepared by evaporating ZrO₂-MgO solid solution composite material using EB evaporation. The deposition rate of 5 Å/sec and the substrate temperature of 350°C were maintained during deposition of all the samples, while the oxygen pressure was varied from without oxygen pressure to 8×10^{-4} mbar. The details of the samples prepared along with their thickness as measured by in-situ thickness monitors are shown in Table-4.1. AFM has been used to investigate the surface morphology of the films. AFAM mode of the AFM is used for the quantitative analysis of elastic modulus/indentation modulus of the thin films. The transmission spectra of the films were measured using UV-VIS-NIR spectrophotometer in the range 190-1200 nm for determination of refractive index of the films. The relative uncertainty in the transmittance is 0.3%. In the measurement air was used as a reference. Densities of the films have been measured by grazing incidence x-ray reflectivity (GIXR) technique. The measurements have been carried out with Cu K_a (1.54 Å) source with grazing angle of incidence in the range of 0-0.6° and with an angular resolution of 0.001°. Laser induced damage threshold of the films has been measured using in-house developed LIDT set-up.

4.1.3 Results and discussion

4.1.3.1 Optical properties

The measured transmission spectra of the ZrO₂-MgO thin films prepared at different oxygen pressure are plotted in Fig. 4.1(a). The refractive index of the films has been determined by fitting the measured optical transmission spectra with theoretically generated spectra using suitable optical dispersion model. This is called inverse synthesis method, which is discussed in detail in the 2nd chapter of the thesis. The Optical properties of materials are best described by the complex frequency-dependent dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$, where the real part ε_1 and imaginary part ε_2 are related to the directly measurable parameters viz., the refractive index (*n*) and extinction coefficient (*k*) through the relations: $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$.



Fig. 4.1: *Transmission spectra of ZrO₂-MgO thin films prepared at different O₂ pressure.* There have been developed a number of models to describe the optical properties of amorphous materials for energies around the band gap. One of the most versatile is the Tauc-Lorentz (TL) model proposed by Jellison and Modine [146]. Although this model was derived for amorphous semiconductor, it can be applied to polycrystalline thin films as well. The TL model yields null value of ε_2 for energies less than the band gap which does not always agree with experimental evidence. Hence in the present analysis it has been assumed that the imaginary part of the refractive index, i.e., the extinction coefficient (k) of the ZrO₂-MgO binary films follow the Urbach model [91]. The experimental transmission spectrum is fitted using the co-efficient of the dispersion model and the thickness of the film as fitting parameters. Finally these fitting parameters are used to determine the refractive index and extinction coefficient spectra along with thickness of the films, which are listed in Table-4.1. The extinction co-efficient is negligible in the visible region; therefore the spectrum is not

plotted. The estimated error in refractive index is ± 0.01 only. The refractive index spectrum of all the ZrO₂-MgO films plotted in Fig. 4.2 is in agreement with previously reported refractive index values for such thin films [147].



Fig. 4. 2: Refractive index spectra of all the ZrO₂-MgO thin films.

Sample	O ₂ partial	Thickness	Density	Refractive	RMS	Grain
	pressure	(nm)	(g/cm^3)	index	roughness	size
	(mbar)			@ 550 nm	(nm)	(nm)
ZrM-1	0	529	4.6	1.93	4	98 ± 11
ZrM-2	0.6x10 ⁻⁴	435	4.6	1.96	3.18	77 ± 8
ZrM-3	1x10 ⁻⁴	521	4.4	1.95	1.5	82 ± 8
ZrM-4	$4x10^{-4}$	680	3.7	1.79	2.6	103 ± 13
ZrM-5	8x10 ⁻⁴	783	2.5	1.76	3	123 ± 12

4.1.3.2 Film density

The density of the films has been determined by measuring GIXR spectra of the samples. By fitting the X-ray reflectivity spectrum of the surface of a sample near its critical angle, estimation of film density ρ can be made quite accurately. The theoretical simulation and fitting of the GIXR spectra have been carried out using the "IMD" code under the "XOP" software package [86] and the best fits are achieved by minimizing the χ^2 value.



Fig. 4. 3: Experimental and fitted GIXR spectrum for a representative ZrO_2 -MgO thin film prepared at O_2 pressure of 1×10^{-4} mbar.



Fig. 4. 4: Variation of density and refractive index at $\lambda = 550$ nm of the ZrO₂-MgO thin films as a function of O₂ partial pressure.

Fig. 4.3 shows the measured and best fitted GIXR spectrum of a representative ZrO_2 -MgO thin film prepared at O_2 pressure of 1×10^{-4} mbar. The above exercise has been carried out to estimate densities of all the films, which are listed in Table-4.1. The error in density measurement is approximately ± 0.1 due to alignment of the sample position to the x-ray

beam and angular resolution of the instrument. The thicknesses of the films, derived from the optical transmission spectra, have been kept invariant during GIXR fitting. The density and refractive index value at wavelength of 550 nm of the films have been shown in Fig. 4.4 as a function of O_2 partial pressure. This confirms that the decreasing refractive index with oxygen pressure is mainly due to decreasing film density.

4.1.3.3 Surface morphology

The AFM measurements have been performed on the films with scan area 2.5 μ m x 2.5 μ m. The Fig. 4.5 show the AFM images of the films deposited at without O₂, 1x10⁻⁴ mbar, 4x10⁻⁴ mbar and 8x10⁻⁴mbar oxygen pressure respectively. The rms surface roughness and grain size of the films have been derived from the measured AFM surface morphology.



Fig. 4. 5: 2D AFM surface morphology of ZrO_2 -MgO film prepared at (a) 0 mbar, (b) $1x10^{-4}$ mbar, (c) $4x10^{-4}$ mbar, and (d) $8x10^{-4}$ mbar oxygen partial pressure.

The surface roughness of the films varies from 1.5 nm to 4 nm, while the grain size varies from 77 nm to 123 nm with O_2 pressure as listed in Table-4.1. The composite film deposited at without additional O_2 pressure shows higher roughness of 4 nm and the film deposited at $1x10^{-4}$ mbar O_2 pressure shows minimum roughness of 1.5 nm. With increasing O_2 pressure further above $1x10^{-4}$ mbar, the roughness increases with O_2 pressure. Table-4.1 shows that the grain size of the film increase with increasing O_2 pressure except for the film deposited at without O_2 pressure. With increasing oxygen partial pressure, the mean free path of the evaporated particles becomes shorter and the kinetic energy of the evaporated particles gets reduced because of collision with the gas molecules. The surface mobility of the evaporated particles resulting bigger grains and void rich structure. The void rich structure leads to lower packing density films [26]. Therefore the film density decreases with increasing O_2 pressure as shown in Fig. 4.4.

4.1.3.4 Elastic modulus

Elastic modulus or Indentation modulus of ZrO_2 -MgO binary thin films deposited at varying oxygen partial pressure has been estimated by performing AFAM measurements using DLC coated Si cantilever probes. DLC coated Si tips have been chosen for their better hardness and stability in tip geometry with indentation modulus of 590±20 GPa. Two DLC cantilevers have been employed because of inability of a single cantilever to perform the measurement over all the samples. The spring constants or force constants of the cantilevers are k_c =6 N/m (tip1) and 6.15 N/m (tip2). Indentation modulli of the samples ZrM-2, ZrM-3 & ZrM-4 prepared at different oxygen partial pressures ranging from 0.6x10⁻⁴ to 4x10⁻⁴ mbar have been determined from the contact resonant spectra using tip1, while tip2 has been employed for ZrM-1 and ZrM-5 thin films prepared at zero mbar and 8x10⁻⁴ mbar, respectively.



Fig. 4. 6: Measured 1^{st} and 2^{nd} contact resonance spectrum with a DLC tip cantilever at different static loads on (a) Si (111) reference sample, and (b) representative ZrO₂-MgO thin film prepared at $1x10^{-4}$ mbar oxygen partial pressure.

The contact-resonance spectra for Si (111) reference sample and the thin films have been measured for the 1st and 2nd flexural modes. For each thin film, the contact-resonance frequencies were measured for four different static normal loads $F_N = 450$, 500, 550 and 600 nN. Fig. 4.6 (a) and (b) show the measured 1st and 2nd contact-resonant spectra for Si (111) reference sample and a representative thin film (ZrM-3) prepared at O₂ pressure of 1x10⁻⁴ mbar. It shows that both the resonance frequencies and the amplitudes increase with increasing static normal load, as expected from the theory of flexural vibrations [148].

Table - 4. 2: *Resonance frequencies, contact stiffness and indentation modulus of* ZrO₂-MgO *thin films prepared at different oxygen partial pressure.*

Sample	1^{st}	2^{nd}	Contact	Indentation
	resonance	resonance	stiffness	modulus
	(kHz)	(kHz)	k (N/m)	M (GPa)
ZrM-1	745	2281	1702	161 ± 20
ZrM-2	678	2087	1874	130 ± 16
ZrM-3	662	2002	1633	106 ± 13
ZrM-4	678	1991	1437	89 ± 11
ZrM-5	750	2192	1188	94 ± 12

First, the solution of the Eq. (2.12) in Chapter-2 is found numerically for Si (111) reference samples by assuming a small range of values for L_{l} , and by plotting the contact stiffness k^{*} obtained from Eq. (2.9) as a function of L_l/L for the two modes as shown in Fig. 4.7(a). The ratio L_1/L for the point of intersection of the 1st resonance and 2nd resonance curves correspond to the solution of L_l/L and contact stiffness k^* for the Si (111) reference sample. The calculated relative error $\Delta k^*/k^*$ is approximately 3%, primarily due to the uncertainties in the cantilever geometry as well as contact resonance frequency. Subsequently, the contact radius "a" or the tip radius "R" has been determined from the contact stiffness using Eq. (2.13) for the reference Si (111) sample having indentation modulus of 175 GPa. The calculated contact radius "a" of tip-1 and tip-2 are 8 nm and 6 nm, respectively, while the calculated tip radii are 236 nm and 117 nm respectively. The measured thicknesses of all the films shown in Table-4.1 are more than 400nm. Since the measured film thickness of the thin films are greater than the "3a" (24 nm for tip-1 and 18 nm for tip-2) value, which is generally accepted as the minimum depth for neglecting stresses produced by the substrate-film interface, hence the effect of mechanical properties of the substrate during AFAM measurements can be safely neglected [149].



Fig. 4. 7: (a) Plot of k^* vs. L_1/L for Si (111) reference sample at 1^{st} and 2^{nd} contact resonance, and (b) Variation of indentation modulus of the ZrO_2 -MgO thin films as a function of oxygen partial pressure.

The contact resonant frequencies for the 1st and 2nd eigenmode for entire thin films have been measured and the contact stiffness k^* for the above samples have been calculated using Eq. (2.9) for a constant static load of 450nN with the L_1/L values obtained for the Si (111) reference. Since the exact tip geometry is unknown or due to wear or tip damage, the contact area between the tip and the sample may be somewhere between that of a flat punch and a spherical tip, therefore the indentation modulus M_S of the sample has been evaluated by averaging the values obtained in considering n=1 and n=3/2 in Eq. (2.15) [150]. The derived contact stiffness (k^*) values and indentation modulli of the thin films are shown in Table-4.2 with their contact resonance frequencies. The relative error in measurement of indentation modulus is about 12%, which is due to the error present in determination of contact stiffness, error in indentation modulus of the tip, error present in determination of spring constant of the cantilever due to uncertainty in cantilever geometry etc. The variation of indentation modulus with different deposition oxygen partial pressure has been shown in Fig. 4.7 (b) and is found to vary from 89 to 161 GPa. For comparison, Wen-Cheng et al. [151] have reported elastic modulus value in the range of 90 to 210 GPa for ZrO₂-MgO films, with 96.4% ZrO₂ and 3.6% MgO and measured by ultrasonic velocity method.

Fig. 4.7(b) shows that the indentation modulus or elastic modulus of the films decreases with increase of O₂ partial pressure. It is observed that the film density decreases with increasing O₂ pressure, which consequently increases the porosity in the films. The increase in porosity leads to the decrease in indentation modulus or elastic modulus of the films. This type of trend of decreasing elastic modulus with increasing porosity as well as decreasing density is reported earlier [152, 153]. The other possible mechanism for this effect might be due to the increased grain size of the films with increasing O₂ pressure. From Lennard-Jones potential, the elastic modulus (*E*) is derived as $E=C(E_n/h^3)$, where *C* is a constant depends on the material, E_n is the bond energy and *h* is the bond length; when the average bond length expands and the bond energy decreases with increasing grain size, the elastic modulus decreases [154]. It is also known that the elastic modulus within elastic limit of the elastic response curve is strongly correlated to the density of the material. Under the present studies it is observed that the density of the thin films decreases with increase of oxygen pressure consequently leading to the proportionate decrease in the elastic modulus or indentation modulus values. The above result is also corroborated in Fig. 4.4 in which correlation between the density and refractive index of these films with oxygen partial pressure are presented.

4.1.3.5 Laser induced damage threshold

The laser induced damage threshold (LIDT) of the films has been derived from the damage probability plot [69]. The obtained LIDT of the ZrO_2 -MgO thin films prepared at different O_2 pressures are shown in Fig. 4.8 with 10% error in the measured value. The LIDT increases from 5.5 J/cm² to 7.4 J/cm² by varying O_2 pressure from 0 mbar to $8x10^{-4}$ mbar. Similar trend of LIDT vs. O_2 pressure for ZrO₂ thin film has been reported earlier [155]. This variation has been explained by analyzing microstructure of the films.



Fig. 4. 8: Variation of LIDT of ZrO₂-MgO thin films with oxygen partial pressure.

Laser induced damage process of optical thin films is very complex. It strongly depends on laser parameters such laser wavelength, pulsed width, repetition rate etc. For nanosecond pulsed laser, the damage in dielectric thin films is mainly dominated by thermo-mechanical process, which strongly depends on thermal conductivity of material. It indicates the outward expansion of laser generated heat or temperature from the centre of laser irradiation [67]. The thermal conductivity depends on film density as well as grain size. From kinetic theory of phonons in solids, the thermal conductivity K of an insulating solid is expressed as:

$$K = \frac{1}{3}Cvl \tag{4.1}$$

where *C* is the heat capacity per unit volume, *v* is the average phonon velocity and *l* is the mean free path of a phonon between scatterings. With increasing film density, the porosity in film reduces; hence the mean free path of a phonon increases due to decrease in scattering of a phonon by the pore. This results increase in thermal conductivity with film density. Larger grain size means lower number of thermal barriers because of less grain boundaries in the film, therefore the thermal conductivity increases with increasing grain size. In the present case, the film density decreases, while grain size increases with increasing O_2 pressure. The laser damage threshold (E_{th}) is directly proportional to square root of thermal conductivity of the thin film as given by the following equation [108]:

$$E_{\rm th} = \frac{16T_{\rm c}}{\pi} (\rho C K \tau)^{1/2}$$
(4.2)

where T_c is the critical temperature (melting temperature of the material), K is the thermal conductivity, ρ is the density, C is the heat capacity of the film, and τ is the laser pulse length. The increasing behaviour of LIDT with O₂ pressure indicates that the thermal conductivity of the films increases with increasing O₂ pressure, which implies that, the grain size has dominant effect on thermal conductivity than that of film density. Similar increase of thermal conductivity of ZrO2 thin films with increasing O₂ pressure has been reported by Ling *et al.* [107]. They have also observed increasing crystallite size and decreasing film density with increasing oxygen pressure. Hence the LIDT of the films increases with increase of oxygen pressure, because of increasing thermal conductivity due to bigger grain size in the films.

4.1.4 Conclusion

A set of ZrO₂-MgO thin films has been grown on fused silica and Si (111) substrates using reactive EB evaporation technique at 350°C substrate temperature and at various predetermined oxygen partial pressures. The oxygen partial pressure was varied from 0 mbar to 8x10⁻⁴ mbar. The film refractive index is derived from transmission spectrum and the refractive index of the films varies from 1.96 to 1.76 at wavelength of 550 nm. The decreasing refractive index with increasing O₂ pressure is because of reduced film density. The grain size and roughness of the films have been derived from AFM surface morphology. The film grain size increases with increasing oxygen pressure, which supports the increasing porosity in the films with O₂ pressure. The elastic modulus of the films has been measured using AFAM technique. It is found that the ZrO₂-MgO thin films deposited under ambient deposition condition show highest indentation modulus of elasticity. The indentation modulus of the films observed to decrease monotonically for films deposited at higher oxygen partial pressures. The above observation corroborates with the variation of density of the films probed by GIXR measurement distinctly supplementing this trend. Such a trend may be easily attributed to the higher porosity and less packing density in the films resulted from decrease in the mean free path of the evaporated species under higher oxygen partial pressure. The LIDT of the films increases with increasing oxygen pressure of the film. This variation is attributed to increasing thermal conductivity of the film because of increasing grain size with O₂ pressure. This study has established a correlation among grain size, packing density, refractive index, elastic modulus and LIDT of the ZrO₂-MgO thin films.

4.2 Electron beam evaporated ZrO₂-SiO₂ thin films prepared at different oxygen pressure

4.2.1 Introduction

ZrO₂ is a highly useful thin film material having potential applications in protective and thermal barrier coatings, optical filters, storage capacitors etc. because of its outstanding thermal, chemical and mechanical stability and interesting optical and dielectric properties [156, 157]. It exhibits monoclinic phase, orthorhombic phase, tetragonal phase, cubic phase as well as amorphous structure [158]. In recent years, ZrO₂ is stabilized by adding a fair amount of different foreign oxide materials, leading to several distinct advantages such as tunability in the refractive index, optical band gap, decrease in intrinsic stress, smoother surface etc. [10]. For instance, the ZrO₂: X%SiO₂ (X=5-30) binary oxide films show higher refractive index as well as higher laser induced damage threshold with better surface morphology as compared to the pure ZrO_2 [7, 9]. But the performance of the coatings does not depend solely on its optical properties, but also on its mechanical properties such as residual stress and adhesion. Excessive residual stress can limit the reliability and function of thin film coating devices due to peeling, cracking and curling [127]. Lattice distortion, which contributes to lattice strain, is one of the important causes of film residual stress. Hence residual stress can be controlled by minimizing lattice distortion. It is well known that deposition oxygen partial pressure does not only change the lattice structure but also affect the film optical and microstructural characteristics. In this paper, the effect of oxygen pressure on the microstructural and optical properties of the ZrO₂:10% SiO₂ binary oxide films has been investigated. The optical parameters such as dispersive energy and optical band gap are also correlated with the film structure, crystallite size or grain size and surface morphology to explore the microstructure dependence of optical properties.

4.2.2 Experimental details

ZrO₂:10%SiO₂ composite thin films have been deposited on fused silica substrates at different oxygen partial pressure by EB co-evaporation. The film materials for SiO₂ and ZrO₂ were chosen from Cerac's batch number "S-1060" (purity 99.99%) and "Z-1056" (purity 99.995%) respectively. The deposition rate of 9Å/s for ZrO₂ and 1Å/s for SiO₂ were kept fixed during deposition to prepare ZrO₂:10%SiO₂ thin films. The oxygen pressure was varied from 0 mbar to 8x10⁻⁴ mbar with fixed substrate temperature of 300°C during deposition. The film composition was checked from its refractive index value by using effective medium models [159]. The film structure was carried out by grazing incidence x-ray diffraction (GIXRD) with 2θ angle in the range of 25°-80° using Cu-K_α (λ =1.5406 Å) radiation in steps of 0.05° with grazing angle of incidence of 2°. The phase identification was achieved by comparing the data from the ICDD international diffraction database. The optical transmission spectra of the films were measured using spectrophotometer in the range 190-1200 nm for determination of optical constants and thickness of the films. AFM was used to estimate grain size and surface roughness of the films. The grain size as well as grain distribution was analyzed using FESEM.

4.2.3 Results and discussion

4.2.3.1 Structure and lattice strain

GIXRD patterns of ZrO_2 :10%SiO₂ films prepared at different oxygen pressure are shown in Fig. 4.9(a). Without any oxygen pressure (0 mbar O₂), the peaks are all attributed to diffraction from different planes of zirconia tetragonal phase. With increasing oxygen pressure, the film shows more crystallization behaviour. The peaks at approximately 35^0 and 60^0 are attributed to the diffraction from tetragonal t(110) and tetragonal t(211) planes of tetragonal phase of ZrO₂. Diffraction peaks from the monoclinic phase is very weak, which indicates that fraction of monoclinic phase in the films is very low. The dominant phase in the film is the tetragonal. In all cases, the films show random orientation or polycrystalline nature. The intensity of the tetragonal t(110) peak increases with increasing oxygen pressure. At the same time, a new diffraction peak from monoclinic m(111) appears at an oxygen pressure of 2×10^{-4} mbar and the intensity of it increases with the increase of oxygen pressure. The evolution of monoclinic phase m(111) with oxygen pressure can be attributed to the oxygen vacancy concentration in the films. The oxygen vacancy concentration in thin film decreases with increasing oxygen pressure. Therefore the oxygen atoms required for the rearrangement of Zr-O bonds favouring monoclinic phase get fulfilled [27] and finally lead to form monoclinic m(111) phase. The most intense peak tetragonal t(110) of the XRD patterns has been used for the quantitative analysis of average crystallite size. The average crystallite size (*D*) of the thin films has been calculated using Scherrer's formula: $D = 0.94\lambda/\beta Cos\theta$, where λ is the x-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle of tetragonal t(110) phase and β is the full width half maxima (FWHM) of the tetragonal t(110) peak.



Fig. 4. 9: (a) XRD spectra of ZrO_2 -SiO₂ thin films prepared at different oxygen partial pressure and corresponding (b) measured tetragonal t(110) peak along with Gaussian fit.

The XRD peak of tetragonal t(110) phase of all the films along with its Gaussian fitting is shown in Fig. 4.9(b). The average crystallite size varies from 14 nm to18 nm with oxygen
pressure as listed in Table-4.3. The lattice distortion, which is a qualitative assessment for the residual stress in the films, has been estimated from the x-ray diffraction peaks [160]. The displacement of diffraction peaks from their corresponding strain-free data indicates lattice distortion. The lattice distortion of the films has been calculated from the most intense peak tetragonal t(110) using the following equation [160]

$$\frac{\Delta d}{d_0} = \frac{(d - d_0)}{d_0} \times 100\%$$
(4.3)

Where *d* is the inter planer spacing of the films corresponding to t(110) plane and d_{θ} is the standard plane spacing corresponding to the stress-free system (2.544 Å) of x-ray diffraction file PDF#881007. The values of *d* are calculated using the formula $2d \sin\theta = \lambda$, where θ is the Bragg angle corresponding to tetragonal t(110) peak and λ =1.5406 Å is the wavelength of x-ray. The derived value of *d* varies from 2.532 Å to 2.544 Å with varying oxygen partial pressure. The distortion responsible for lattice strain in the films is estimated using Eq. (4.3) and is given in Table-4.3. The film prepared at $4x10^{-4}$ mbar O₂ pressure shows least distortion which concludes that the residual stress can be minimized under certain deposition condition by minimizing the lattice strain.

Oxygen pressure (mbar)	Thickness (nm)	Crystallite size (nm)	$d_{110} (m \AA)$	Lattice distortion (%)	E_d (eV)	<i>E</i> ₀ (eV)	Eg (eV)	Roughness (nm)	Grain size (nm)
0	368	14.0±0.9	2.532	0.4756	20.3	8.32	5.18	3.51	7.5±1.0
0.6×10^{-4}	615	16.1±0.6	2.534	0.3970	21.68	8.38	5.06	2.38	9.0±1.0
2x10 ⁻⁴	573	15.0±0.6	2.532	0.4756	21.10	8.61	5.12	2.61	7.0±0.8
$4x10^{-4}$	356	17.7±0.6	2.544	0.0039	23.81	8.53	5.23	2.29	6.9±0.9
8x10 ⁻⁴	435	18.1±0.6	2.542	0.0825	23.97	8.67	5.28	2.25	6.5±0.6

 Table - 4. 3: Parameters derived from XRD, transmission, AFM and SEM measurement.

4.2.3.2 Surface morphology

The surface morphology of the films has been measured using AFM technique in non-contact mode using silicon-nitride cantilever. Fig. 4.10 shows the AFM images of the films prepared at different oxygen partial pressure. It is interesting to note that surface roughness of the films is lower at higher oxygen pressure as given in Table-4.3.



Fig. 4. 10: 3D AFM surface morphology of ZrO_2 -SiO₂ thin films prepared at (a) 0 mbar, (b) $0.6x10^4$ mbar, (c) $4x10^4$ mbar, and (d) $8x10^4$ mbar oxygen partial pressure.



Fig. 4. 11: *FESEM images of* ZrO_2 -Si O_2 *thin films prepared at (a) 0 mbar, (b)* $0.6x10^4$ *mbar, (c)* $4x10^4$ *mbar, and (d)* $8x10^{-4}$ *mbar oxygen partial pressure.*

By comparing AFM image of the films, it can be seen that the film prepared at 0 mbar oxygen pressure is more void rich structure showing rms surface roughness of 3.51 nm, while the film prepared at 8×10^{-4} mbar shows more dense structure with surface roughness of 2.25 nm, indicative for a very smooth film. The SEM image of the films is shown in Fig. 4.11. It is observed that the average grain size of all the films prepared at 0.6×10^{-4} mbar. The average grain size in the range 6.5-9.0 nm determined from the FESEM image is found almost same within the error bar, while the average crystallite size is in the range 14-18 nm determined from the x-ray diffraction peak and is found increasing with oxygen pressure above 2×10^{-4} mbar as seen in Fig. 4.9 (b). The grain size and crystallite size estimated for the same film is different, because they are deduced from two different techniques.

4.2.3.3 Optical properties

The transmission spectra of all the ZrO₂:10%SiO₂ films are shown in Fig. 4.12. The inset plot in this figure shows the transmittance spectra near the absorption edge. The relatively lower transmittance at low O₂ pressures may be due to nonstoichiometric ZrO₂:10%SiO₂ thin films. The improvement in the transmittance at higher oxygen pressure clearly indicates that the film stoichiometry gradually improved as the oxygen partial pressure increased. The optical constants such as refractive index and absorption co-efficient as well as thickness of the films are evaluated using inverse synthesis method. The dispersion of refractive index is based on the single oscillator model according to Wemple and DiDomenico [90] and is given by

$$n(\lambda) = \sqrt{1 + \left(\frac{E_0 E_d}{E_0^2 - (1240 / \lambda)^2}\right)}$$
(4.4)

Where λ is the wavelength of the light, E_0 is the single oscillator energy, and E_d is the dispersion energy. The imaginary part of refractive index *i.e.* extinction coefficient (*k*) of the films is assumed to follow the Urbach model [91].



Fig. 4. 12: Transmission spectra of ZrO_2 -SiO₂ thin films prepared at different O_2 partial pressure. The inset plot shows transmission near the absorption edge.



Fig. 4. 13: Measured transmission spectrum with best fit theoretical curve of the ZrO_2 -SiO₂ thin film prepared at $2x10^{-4}$ mbar oxygen pressure. The inset plot shows the refractive index spectra of all the thin films.

The experimental transmission spectrum has been fitted using the co-efficient of the dispersion model and thickness of the film as fitting parameters [12]. Finally these fitting parameters listed in Table-4.3 have been used to determine the thickness (*t*), the refractive index (*n*) and extinction coefficients (*k*) of the films. Fig.4.13 shows the representative experimental transmission spectrum of the film prepared at oxygen pressure of $2x10^{-4}$ mbar along with its best-fit theoretical spectrum. The refractive index spectrum for entire ZrO₂:10%SiO₂ thin films is shown in the inset of Fig.4.13.



Fig. 4. 14: (a) Plot of $(\alpha hv)^{1/2}$ vs. hv for all the ZrO_2 -SiO₂ thin films. Variation of (b) the refractive index and (c) the lattice distortion with oxygen partial pressure.

The absorption co-efficient (α) spectrums are derived from the transmission spectrum of the films. The absorption co-efficient of the films in the high absorption region is given according to Tauc's relation for the allowed indirect transition [51] by the following relation:

$$(\alpha E)^{1/2} = K \left(E - E_g \right) \tag{4.5}$$

Where K is constant depends on the transition probability and E_g is the optical band gap. Fig. 4.14(a) is a typical best fit of $(\alpha E)^{1/2}$ vs. photon energy E for all the films. The values of the optical band gap E_g were taken as the intercept of $(\alpha E)^{1/2}$ vs. E at $(\alpha E)^{1/2} = 0$. The optical band gap derived for each film is given in Table-4.3. It clearly shows that the band gap depends on the oxygen partial pressure and varies from 5.06 eV to 5.28 eV with the increase

in oxygen pressure. Fig. 4.14 (b) and (c) shows that the film with least lattice distortion has maximum refractive index and vice versa, which may be due to the variation in inter-planar distance in the films as observed in the XRD pattern. The film deposited at 0 mbar O_2 pressure shows poor crystalline structure as compared to the film prepared at 8×10^{-4} mbar. The interplanar distance strongly affects the film density. The film with larger interplanar distance and poor crystalinity shows poor packing density and hence poor refractive index. It suggests that the refractive index strongly depends on the film microstructure.



Fig. 4. 15: Variation of (a) crystallite size and (b) band gap with oxygen partial pressure.

In the present study, the band gap as well as the crystallite size increases with O_2 pressure, while there is no significant change in grain size as shown in Fig. 4.15. Therefore, no quantum confinement effect on the optical properties for the ZrO_2 :10% SiO₂ films has been observed as reported by C.V. Ramana *et al.* [161] for sputtered ZrO_2 films under varying growth temperature. The increase of band gap with oxygen pressure can be related to the enhanced monoclinic phase. Since the monoclinic- ZrO_2 phase has higher optical band gap as compared to that of tetragonal phase, the fundamental optical absorption edge would definitely shift towards shorter wavelength for the films that contain a monoclinic- ZrO_2 component compared to films that are purely tetragonal- ZrO_2 phase [162, 163]. Therefore the

film prepared at higher oxygen pressure (mixture of monoclinic and tetragonal phase) shows higher optical band gap as compared to the film prepared at lower oxygen pressure (only tetragonal phase). The intensity or crystalinity of monoclinic (111) phase increases with increasing oxygen pressure at higher oxygen pressure. This enhanced crystalinity of monoclinic phase leads to increase in optical band gap resulting blue shift of the spectrum.



Fig. 4. 16: (a) Plot of dispersion energy E_d as a function of XRD intensity of tetragonal t(110) phase and (b) Plot of surface roughness as a function of dispersion energy E_d for the films deposited at different oxygen partial pressures.

Through analysing more than 100 widely different solids and liquids, the dispersion energy parameter E_d is found dependent on the co-ordination number and atomic valency uniquely [164]. The dispersion energy E_d is an important parameter that measures the average strength of interband optical transitions and is associated with the changes in the structural order of the material the more ordered the materials the larger the dispersion energy E_d and that is the reason it is treated as a microstructural ordering parameter [96]. The values of E_d are presented in Fig. 4.16(a) as a function of x-ray diffraction intensity of tetragonal t(110) along with a parabola fitting curve. It shows that E_d at the largest intensity of tetragonal t(110) has the largest value i.e. the structural order of the films prepared at 8x10⁻⁴ mbar oxygen pressure is the highest, which corresponds to the structural change of the film seen from the XRD patterns. This type of correlation between the dispersion energy E_d and the intensity of XRD pattern has also been observed in the ZrO₂ films prepared by RF sputtering at different substrate bias [165]. From Fig. 4.16(b), it is clear that there exists a correlation between the dispersion energy E_d and the rms surface roughness. The film having higher E_d has the least rms surface roughness. Hence, the increase of the dispersion energy E_d is associated with structural ordering of grains or nanocrystallites to a more ordered phase and better grain morphology as confirmed by both the GIXRD and AFM measurements.

4.2.3.4 Elastic modulus

Elastic modulus or Indentation modulus of ZrO_2 -10%SiO₂ mixed oxide thin films deposited at different oxygen partial pressure has been determined using AFAM measurements as described in Chapter-2. The DLC coated Si tip used for the measurement has indentation modulus of 590 ± 50 GPa. The force constant of the DLC cantilever is k_c = 9.35 N/m. The 1st and 2nd contact-resonance spectrum for Si (111) reference sample and a representative ZrO₂-10%SiO₂ thin film prepared at oxygen pressure of 0.6x10⁻⁴ mbar are shown in Fig. 4.17.



Fig. 4. 17: 1^{st} and 2^{nd} contact resonance spectrum of (a) Si (111) reference sample and (b) representative ZrO_2 -SiO₂ thin film prepared at $0.6x10^{-4}$ mbar oxygen pressure.

Table - 4. 4: Resonance frequencies, contact stiffness, indentation modulus and LIDT of the ZrO_2 -SiO_2 thin films prepared at different oxygen partial pressure.

O_2 partial	1 st	2^{nd}	Contact	Indentation	LIDT
pressure	resonance	resonance	stiffness	modulus	(J/cm^2)
(mbar)	(kHz)	(kHz)	k* (N/m)	M (GPa)	
0	979	2885	1830	151 ± 12	3.48 ± 0.34
0.6x10 ⁻⁴	981	2919	1952	168 ± 13	4.12 ± 0.41
$2x10^{-4}$	982	2913	1916	163 ± 11	3.03 ± 0.30
$4x10^{-4}$	983	2912	1896	160 ± 12	2.47 ± 0.24
8x10 ⁻⁴	986	2927	1933	165 ± 13	2.71 ± 0.27



Fig. 4. 18: Plot of k^* vs. L_1/L for (a) Si (111) reference sample and (b) representative ZrO_2 -Si O_2 film prepared at 0.6×10^{-4} mbar O_2 pressure at 1^{st} and 2^{nd} contact resonance. The contact stiffness k^* has been determined by plotting k^* vs. L1/L for two contact resonance modes as shown in Fig. 4.18 for Si (111) reference and a representative zirconiasilica sample. The intersection point of the 1^{st} resonance and 2^{nd} resonance curves correspond to the solution of L_1/L and contact stiffness k^* for the respective samples. Same analysis procedure has been followed to determine contact stiffness of all the ZrO_2 -SiO₂ thin films under a constant static load. The calculated contact radius "a" of the tip is 8.4 nm. Since the

film thickness is very large as compared to "3a", hence the effect of mechanical properties of the substrate can be neglected. Since the exact tip geometry is unknown, therefore the indentation modulus Ms of the sample has been evaluated by averaging the values for a flat punch and a spherical tip.



Fig. 4. 19: Variation of indentation modulus and grain size of the ZrO_2 -SiO₂ thin films with deposition oxygen pressure.

The derived contact stiffness (k^*) values and indentation moduli of the thin films are shown in Table-4.4 with their corresponding contact resonance frequencies. The derived indentation modulus of the ZrO₂-SiO₂ thin films varies from 151 GPa to 165 GPa with different deposition oxygen partial pressure as shown in Fig. 4.19. This behaviour of indentation modulus is ascribed to grain size of the films. Numerous computer simulations and experimental studies have found that the elastic modulus varies proportional with grain size [166]. Form Fig. 4.19, it is clear that the indentation modulus varies in a similar manner like grain size with O₂ pressure. At higher and lower O₂ pressure, grain size is lower, hence the elastic modulus. For films prepared at O₂ pressure of 0.6x10⁻⁴ mbar, the grain size is maximum resulting maximum elastic modulus.

4.2.3.5 Laser induced damage threshold

The LIDT of the ZrO_2 -10%SiO_2 thin films prepared at different O_2 pressures is determined from the laser damage probability curve as shown Fig. 4.20. A straight line is fitted to the damage probability vs. laser fluence curve. The laser energy for which the straight line intersects the zero damage probability value is defined as LIDT. The estimated LIDT of all the films are listed in Table-4.4.



Fig. 4. 20: Damage probability plot for all the ZrO₂-SiO₂ thin films.

The LIDT varies from 2.71 J/cm² to 4.12 J/cm² having maximum LIDT value for the film prepared at 0.6×10^{-4} mbar as shown in Fig. 4.21 (a). The LIDT variation with O₂ pressure is explained by correlating it to the grain size of the films. From Fig. 4.21 (b), it is clear that the LIDT is almost proportional to the grain size of the film. It is well known that the thermal conductivity of the films increases with increasing grains size, because of lower thermal barrier in terms of grain boundaries. With increasing thermal conductivity, the laser induced heat energy dissipates more efficiently from the centre to outwards in the films leading to lower LIDT. Hence the film having bigger grains shows higher LIDT as observed for the ZrO₂-10% SiO₂ film.



Fig. 4. 21: (a) Variation of LIDT with deposition oxygen pressure. (b) Plot shows correlation between LIDT and grain size of the ZrO_2 -SiO₂ thin films.

4.2.4 Conclusion

The microstructure dependent optical properties of the ZrO_2 :10%SiO₂ thin films have been investigated. It is found that all the films exhibit strong tetragonal phase tetragonal t(110) while the films prepared at $2x10^{-4}$ mbar oxygen pressure or more also contain weak monoclinic phase m(111) and the crystalinity increases with increasing oxygen pressure. The film with least lattice distortion shows maximum value of refractive index. Optical band gap of the film is affected by crystalline phase. No quantum confinement effect on the optical properties has been observed. The dispersion of the refractive index is discussed in terms of single oscillator Wimple-DiDomenico model. The dispersion energy or order parameter E_d of the films has the largest value at the largest intensity of t(110) which corresponds to the structural order of the films. The film having higher E_d has the least rms surface roughness which corresponds to better grain morphology. It is observed that the optical properties of the films strongly depend on the microstructure influenced by the deposition oxygen pressure. The effect of grain size on the elastic modulus and LIDT of the films has been analyzed.

Chapter 5: Composition Dependent Properties of HfO₂-SiO₂ 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 ZrO₂, Al₂O₃, SiO₂ etc. to pure HfO₂, the optical properties, mechanical properties as well as laser damage resistance of such mixed films (HfO₂-ZrO₂, HfO₂-Al₂O₃, HfO₂-SiO₂ 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, HfO₂-SiO₂ mixed composite films with wide range of composition by continuous mixing of HfO₂ and SiO₂ have been deposited on fused silica substrates by electron beam coevaporation 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, 2nd harmonic) of such mixed films has been carried out and the dependency of the damage threshold as a function of SiO₂ 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 1×10^{-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 HfO_2 -SiO₂ mixed films have been achieved with $\pm 2\%$ 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.



Fig. 5. 1: *Transmission and reflection spectra of HfO*₂*-SiO*₂ *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]

$$\alpha_{film}(\lambda) = \frac{1}{d_{film}} \ln \left(\frac{1-R}{T/T_{sub}} \right)$$
(5.1)

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



Fig. 5. 2: Refractive index spectra of HfO₂-SiO₂ mixed thin films.



Fig. 5. 3: Absorption co-efficient spectra of HfO₂-SiO₂ mixed thin films near the band edge.

The optical band gap (Eg) of the films has been derived form the absorption co-efficient (α) 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 (α hv)^{1/2} = K (hv-Eg), where K is constant depends on the transition probability and Eg 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 (α hv)^{1/2} as a function of the photon energy hv 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 HfO₂-SiO₂ mixed composite films.



Fig. 5. 4: Plot of $(hv)^{1/2}$ vs. hv for all the HfO₂-SiO₂ 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 K α (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.



Fig. 5. 5: *Experimental X-ray reflectivity with best-fit theoretical spectrum of pure* HfO_2 *and* $HfO_2(90\%)$ -SiO₂(90%) mixed thin films.

HfO ₂ (%)-SiO ₂ (%)	Thickness Measured In Situ (nm)	Thickness Derived from Transmission Spectra (nm)	Bandgap (eV)	Film Density (g/cm ³)	Roughness (nm) GIXR	Roughness (nm) AFM	Grain Size (nm)	LIDT $F_{ m th}~({ m J/cm^2})$
100-0	521 ± 10	512 ± 0.3	5.57	8.42	3.35	5.62	196 ± 30	18.05 ± 2.88
90-10	517 ± 11	503 ± 0.3	5.62	8.90	1.53	1.12	59 ± 15	20.68 ± 3.30
80-20	419 ± 08	438 ± 0.4	5.67	7.62	0.50	1.01	49 ± 17	19.06 ± 3.00
70–30	479 ± 09	483 ± 0.8	5.68	7.13	1.36	1.27	49 ± 11	18.71 ± 3.00
60-40	582 ± 10	563 ± 0.4	5.71	6.54	0.85	1.35	49 ± 16	20.90 ± 3.34
50-50	571 ± 12	565 ± 0.8	5.72	6.20	1.93	2.16	88 ± 21	22.00 ± 3.52
40-60	626 ± 13	615 ± 1.2	5.76	5.43	0.52	1.44	69 ± 14	23.98 ± 3.83
30-70	694 ± 14	705 ± 0.8	5.83	5.34	0.32	1.52	69 ± 19	24.19 ± 3.87
20-80	642 ± 13	663 ± 0.8	_	3.62	1.48	1.59	59 ± 13	40.70 ± 6.51
10-90	590 ± 12	603 ± 0.4	_	2.64	1.50	1.67	94 ± 27	42.51 ± 6.80
0-100	621 ± 17	609 ± 0.8	_	2.60	1.41	1.51	81 ± 16	45.24 ± 7.21
Fused silica	_	_	$8.5^{\text{Ref.}}$	2.46	0.20	0.60	9 ± 3	57.60 ± 9.21

 Table - 5. 1: Parameters derived from transmission, GIXR, AFM, and LIDT measurements.



Fig. 5. 6: *AFM surface morphology of representative HfO*₂*-SiO*₂ *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 2nd 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.



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 HfO₂-SiO₂ 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 SiO₂ 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 HfO₂ 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:
$$f \frac{\varepsilon_1 - \varepsilon_{eff}}{\varepsilon_1 + 2\varepsilon_{eff}} + (1 - f) \frac{\varepsilon_2 - \varepsilon_{eff}}{\varepsilon_2 + 2\varepsilon_{eff}} = 0$$
 (5.2)

Maxwell Garnett model:
$$\frac{\varepsilon_{eff} - \varepsilon_2}{\varepsilon_{eff} + 2\varepsilon_2} = f \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}$$
 (5.3)

Lorentz-Lorentz model:
$$\frac{\varepsilon_{eff} - 1}{\varepsilon_{eff} + 2} = f \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} + (1 - f) \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2}$$
(5.4)

Drude model: $\varepsilon_{eff} = f\varepsilon_1 + (1 - f)\varepsilon_2$ (5.5)

where ε_1 and ε_2 are complex dielectric functions of the material SiO₂ and HfO₂, respectively and *f* is the volume fraction of SiO₂. ε_{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 HfO₂ and SiO₂ 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 HfO₂-SiO₂ mixed composite films with 10%, 20% and 30% SiO₂ content as compared to the pure HfO₂ 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 hafniasilica (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 -SiO₂ 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 SiO₂ (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 (~0.1 λ). 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 -SiO₂ mixed composite thin films with SiO₂ fraction. The inset plot is optical band gap vs. volume fraction of SiO₂.

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 (α) 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 ΔP in the film because of rapid heating at constant volume. The intrinsic stress generated due to this internal pressure ΔP 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 (ΔP) can be expressed as [186]:

$$\Delta P \approx A \frac{L\alpha}{C} \sqrt{\frac{E}{\rho}}$$
(5.6)

where $A = 4\beta^2 M (1/3(1-2\nu))$ 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 thinfilms, L is usually 1 μm or less), *α* 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*, *α* 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 (*α*) of the mixture decreases with increase of silica content (because a_{SiO2} =0.51x10⁻⁶ K⁻¹ < a_{HjO2} =3.8x10⁻⁶ K⁻¹) while the elastic modulus (E) decreases with increase of silica content (because E_{SiO2} =72 GPa < E_{HfO2} =380 GPa). But the specific heat (C) of the mixture increases with increase of silica content (because E_{SiO2} =746 JK⁻¹Kg⁻¹ > C_{HfO2} =16.7 JK⁻¹Kg⁻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 ΔP decreases with silica content.



Fig. 5. 10: Internal stress as a function of SiO₂ fraction in HfO₂-SiO₂ 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]

$$\frac{dN_e}{dt} = N\sigma^{(n)} \left(\frac{I}{h\nu} \right)^n \tag{5.9}$$

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 hv 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 (3x2.33 eV=6.99 eV) is more probable. The Intensity (I_c) necessary for 3-photon absorption (n=3), which may occur in the mixed films, can be estimated by solving Eq. (5.9):

$$I_{c} = \left(\sqrt[3]{\frac{N_{e}}{(N\sigma^{(3)}\tau)}}\right)E$$
(5.10)

Where $\sigma^{(3)}$ is the 3-photon absorption cross-section ($\approx 10^{-81}$ cm⁶ s²) [193] and τ 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 $0.01N_c$ 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 $N_c = (1000 \text{ nm}/\lambda)^2 \times 10^{21} \text{ cm}^{-3} = 1.88 \times 10^{21} \text{ cm}^{-3}$ [195]. Using Eq. (5.10) for 7 ns pulses, the lower and upper bounds of the LIDT are 294 J/cm² and 1400 J/cm², respectively. The observed LIDT ranges from 40 J/cm² to 45 J/cm² 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} cm⁶ s² 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} cm⁶ s² [113]. Using this modified cross section in Eq. (5.10) with the observed damage threshold of 40.7 J/cm², 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 SiO₂ [204] and HfO₂ [198] thin films and X. Fu *et al.* for Niobia-Silica and Zirconia-Silica mixtures [196].



Fig. 5. 11: Laser induced damage morphology of HfO₂-SiO₂ 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 defectdominated 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

HfO₂-SiO₂ 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.

Chapter 6: Deposition and Characterizations of HfO₂/SiO₂ and TiO₂/SiO₂ Multilayer Coatings

Dielectric thin film multilayers are used to fabricate different type of interference based optical devices such as high reflection (HR) mirrors, band pass filters, antireflection coatings etc. The multilayer devices are generally made by sequential deposition of quarter wave optical thickness of high and low index materials. There are different combinations of high and low index materials such as HfO₂/SiO₂, ZrO₂/SiO₂, TiO₂/SiO₂, Ta₂O₅/SiO₂, Nb₂O₅/SiO₂, Al₂O₃/SiO₂ and Sc₂O₃/SiO₂ [4], where SiO₂ is the low index material and the rest are high index materials. In the present thesis, we have chosen HfO₂/SiO₂ and TiO₂/SiO₂ to investigate their performance as multilayer HR mirrors. HfO₂ is the most widely used high refractive index material for UV-VIS region, while TiO₂ is considered for visible region of the electromagnetic spectrum. The HfO₂/SiO₂ multilayer HR mirrors are used for the development high power lasers. So it is better to have mirror having high laser induced damage threshold. Researchers have reported many ways to improve the LIDT of the postdeposited mirrors, out of which annealing is preferred the most. In the 1st part of this chapter the effect of annealing on optical properties, surface morphology and LIDT of EB evaporated HfO₂/SiO₂ multilayer HR mirrors has been presented. Band width of HR mirror is limited by the refractive index contrast between the two materials. As a result, omnidirectional reflection band for HfO₂/SiO₂ multilayer in the visible region is very narrow. TiO₂ exhibits higher refractive index than HfO₂ in the visible region. Moreover, sputtering gives better refractive index of a film than that of EB evaporation. For omnidirectional high reflection mirror, higher the refractive index; more will be the band width of the omnidirectional reflection region. Therefore, TiO₂/SiO₂ multilayer fabricated using magnetrons puttering technique as an omnidirectional mirror is presented in the 2nd part of this chapter

6.1 EB evaporated HfO₂/SiO₂ multilayer: Effect of annealing on its optical properties and laser induced damage threshold

6.1.1 Introduction

Laser induced damage in multilayer dielectric mirrors has been extensively studied for more than four decades [205]. There is various combination of high and low index coating materials for developing high reflection dielectric mirrors as discussed above. Among them, HfO₂/SiO₂ has been widely used as the best combination, due to its high LIDT [206]. But there is always a need to improve the LIDT of the multilayer mirrors for its stable performance in high power laser systems. Despite great improvements made in the multilayer optical coatings in recent years, enhancing laser damage resistance of optical coatings is still a challenge. Optical absorption, microstructural, thermal and mechanical properties of the films influence the damage process in dielectric optical coatings [207]. The laser induced damage of dielectric coatings in the nanosecond pulse regime is mainly due to absorption of laser energy as heat at nanometric absorbing defect sites [198]. The density of absorbing defects, surface morphology, structural and mechanical properties of thin films can be altered by thermal annealing process, which can influence the LIDT of the coatings [35]. So it is significant to study effect of annealing on the laser damage resistance of the multilayer mirrors. Most of the research work done so far related to LIDT of HfO₂/SiO₂ multilayer mirror is for pulsed laser of 1064 nm wavelength and the damage process is mainly associated with nodular defects [208]. Reports on LIDT of HfO₂/SiO₂ multilayer mirror under pulsed laser wavelength of 532 nm are scanty. To our knowledge, there is no report about the effect of annealing on LIDT of HfO₂/SiO₂ multilayer HR mirror. Here, spectral characteristics, microstructure and LIDT of EB evaporated HfO₂/SiO₂ multilayer HR mirror annealed at different temperatures have been investigated. The LIDT of the mirror gets improved after annealing. Effect of oxygen vacancy defect and thermal conductivity are

considered to explain the improved LIDT. The laser damage morphology of the mirror annealed at different temperatures is discussed in details.

6.1.2 Experimental details

HfO₂/SiO₂ multilayer mirrors were fabricated with 25 layers sequential deposition of HfO₂ and SiO₂ on BK7 glass substrate using a fully automated electron beam evaporation system. The multilayer design is (HL)¹²H, where H and L stand for quarter wavelength optical thickness of the HfO₂ layers and SiO₂ layers respectively. The electric field in the multilayer design is optimized for near normal incidence. Deposition rate and layer physical thickness were measured by quartz crystal monitor. Oxygen pressure was controlled by mass flow controller. A base pressure of 1×10^{-5} mbar was achieved in the coating chamber before deposition. Oxygen pressure of 1×10^{-4} mbar, substrate temperature of 300°C and deposition rate of 5 Å/sec were kept fixed during deposition of both HfO2 and SiO2 layers. The sequential depositions of quarter wave layers have been performed using a turning-point quarter-wave optical monitoring scheme. Post-deposition annealing of the mirrors were performed at 300°C, 400°C and 500°C respectively for 2 hours in ambient condition. The heating and cooling rates were 100°C/hr for the annealing process. The transmission spectra of the as-deposited and post-annealed multilayer mirrors have been measured using spectrophotometer in the range 400-800 nm to measure high reflection band. The structure of the multilayer mirrors has been investigated by XRD with 2θ angle in the range of 10° - 80° using Cu-K α (λ =1.5406 Å) radiation in steps of 0.02°. The surface grain morphology and grain size have been analyzed using a FESEM. The LIDT of the multilayer mirrors have been measured in the "1-on-1" mode according to ISO-11254-1 [83]. The second harmonic (532 nm) of a Q-switched Nd:YAG pulsed laser at a pulse width of 7 ns was used for the damage threshold measurement. The laser beam was focused on the test sample to generate high power density. The measured beam spot size was $30\pm5 \mu m$. Online damage was monitored by
optical microscope through any irreversible damage. The LIDT was determined from the measured damage probability plot [69]. The characteristics of damage morphology have been probed by optical microscope as well as FESEM.

6.1.3 Results and discussion

6.1.3.1 Optical properties



Fig. 6. 1: *Transmission spectra of as-deposited and annealed HfO*₂/*SiO*₂ *multilayer.*

The transmission spectra of the as-deposited and post-annealed HfO₂/SiO₂ multilayer mirrors are shown in Fig. 6.1. All the mirrors show reflectivity more than 99.9 % at wavelength of 532 nm. The high reflection band shifts towards shorter wavelength of the spectrum with increasing annealing temperature. The shift is mainly due to reduction in layer optical thickness (*nd*). The optical thickness of the HfO₂ and SiO₂ films is quarter wave, hence the centre of the reflection band is given by $\lambda_0 = 4n_Hd_H = 4n_Ld_L$. Here $n_H \& n_L$ are refractive indices at wavelength λ_0 and $d_H \& d_L$ are film thicknesses of HfO₂ and SiO₂ thin layer respectively. The decrease of optical thickness reduces the overall optical thickness. Therefore the spectrum shifts towards shorter wavelength. Leonard *et al.* [209] have reported that the decrease in SiO₂ layer thickness in HfO_2/SiO_2 multilayer mirror after annealing is the cause for shift of reflectivity peak towards shorter wavelength.

6.1.3.2 Structure and surface morphology

The XRD spectra of the as-deposited and post-annealed multilayers are shown in Fig. 6.2. They are polycrystalline in nature. All the multilayers contain only monoclinic phase of HfO₂. There are no preferred orientations in the as-deposited multilayer as well as in the multilayer annealed at 300°C. When the annealing temperature increases to 400°C and above, the intensityy of all the monoclinic peaks increases and m (111) becomes preferred orientation. The large increase in peak intensity indicates that crystallite size has increased significantly, which is confirmed by FESEM measurement.



Fig. 6. 2: *XRD* spectra of *HfO*₂/*SiO*₂ multilayer annealed at different temperatures.

The surface grain morphologies of the as-deposited and post-annealed multilayers are shown in Fig. 6.3(a)-(d). The as-deposited mirror surface consists of small fine grains. The grain size increases slightly after annealing at 300°C, but the grain boundaries becomes clearly visible. The grain size increases significantly with annealing temperature above 400 °C as shown in Fig. 6.3. When the annealing temperature is lower, the energy offered by annealing is mainly consumed to recover the film's initial microstructure and not enough to make the grain growth larger. But higher temperature annealing gathers more atoms together from available neighboring sites and results in grain growth [29, 210, 211]. The grain size has been calculated from the FESEM image and listed in Table-6.1.



Fig. 6. 3: FESEM morphology of as-deposited and annealed HfO₂/SiO₂ multilayer.

6.1.3.3 Surface roughness and scattering

The AFM images of the multilayers annealed at different temperature are shown in Fig. 6.4(a)-(d). The root mean square (RMS) roughness (σ) of the as-deposited multilayer is 3.8

nm. The roughness increases to 4.3 nm and 4.6 nm for the multilayer annealed up to 400°C. But on further annealing at 500°C, the roughness deceases to the value of 3.2 nm even lower than the as-deposited sample. This lower roughness value could be due to the reduction of surface energy through smoothening effects causing decrease in surface feature height for the sample annealed at 500°C. Surface roughness strongly affects the spectral characteristics of multilayer thin films. Therefore, total integrated scattering (TIS) loss has been estimated from the RMS roughness by the relation

$$TIS = 1 - \frac{R}{R_0} = 1 - \exp\left\{-\left(\frac{4\pi\sigma}{\lambda}\right)^2\right\} \cong \left(\frac{4\pi\sigma}{\lambda}\right)^2$$
(6.1)

where R_0 is the radiant reflectance of the surface in the absence of roughness, R is the specular reflectance of the surface, and λ is the wavelength. The calculated scattering loss of the multilayers annealed at different temperature is listed in Table-6.1. The scattering loss increases with annealing temperature up to 400°C but drops at 500°C exhibiting least scattering.



Fig. 6. 4: *AFM images of as-deposited and annealed HfO*₂/SiO₂ multilayer.

Annealing	RMS	Scattering	Grain	LIDT
Temperature	roughness σ	loss	size	(J/cm^2)
$(^{\circ}C)$	(nm)	(1×10^{-3})	(nm)	
as-deposited	3.8	8.1	17 ± 2	44.1 ± 3.8
300	4.3	10.3	18 ± 1	60.7 ± 6.4
400	4.6	11.7	24 ± 1	76.6 ± 3.2
500	3.2	5.6	32 ± 3	57.5 ± 3.2

Table - 6. 1: Parameters derived from AFM, FESEM and LIDT measurement.

6.1.3.4 Laser induced damage threshold

LIDT is obtained by damage probability analysis. The laser damage threshold F_{th} is defined as the mean value of the highest energy density with no damage F_{max} (ND) and the lowest energy density with damage F_{min} (D) [69] in the damage probability plot as shown in Fig. 6.5.

$$F_{th} = \frac{\left[F_{\min}(D) + F_{\max}(ND)\right]}{2}$$
(6.2)

The spread in damage threshold is given by



Fig. 6. 5: 50% damage probability plots of HfO₂/SiO₂ multilayer HR mirrors.

The laser induced damage threshold of all the multilayers has been calculated according to Eq. (6.2) and (6.3). The LIDT values of the as deposited and annealed multilayers are listed in Table-6.1. The LIDT increases with annealing temperature up to 400°C and then it drops at 500°C. The mirror annealed at temperature of 500°C shows cracks on its surface because of excess tensile stress, which are observed by optical microscopy. Therefore the LIDT of the mirror annealed at 500°C drops because of light intensification by surface cracks [212, 213]. The multilayer annealed at 400°C shows highest LIDT value of 77.6 J/cm² an increase of 74% more than that of the as-deposited multilayer mirror.

For nanosecond pulsed laser, the laser induced thermal damage is a combination of three processes: absorption of radiation, energy transport from the absorbing site and thermomechanical response of local heating. Since electric field is maximum at the top layer of the HfO₂/SiO₂ multilayer mirror, hence top HfO₂ layer is considered for explaining the damage process. The material parameters such as absorbing defect concentration in HfO₂, thermal conductivity of HfO₂ layer etc. could affect the damage process and are considered to explain the increasing LIDT with annealing as follows:

(1) Defects like oxygen vacanciess exist in HfO₂ film. Takeuchi *et al.* demonstrated the existence of shallow oxygen vacancy defects of 1.2 eV below the HfO₂ conduction band [214], while Ni *et al.* showed oxygen vacancy related defects of 2.3 eV and 2.0 eV in EB evaporated HfO₂ thin film [215]. The relationship between absorption coefficient and concentration of free electrons (or oxygen vacancies) can be derived using Drude model [216]. The relative permittivity (ε) due to N free electrons per unit volume is given by

$$\varepsilon = (n - ik)^2 = 1 - \frac{\omega_p^2}{\omega^2 - i\omega/\tau}$$
(6.4)

where
$$\omega = \frac{2\pi c}{\lambda}$$
 and $\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m}$ (6.5)

Solving Eq. (6.4), we get

$$2nk = \frac{\omega_p^2 \tau}{\omega(1+\omega^2 \tau^2)} \tag{6.6}$$

At high frequencies $\omega \tau >> 1$, now the Eq. (6.6) becomes

$$k = \frac{\omega_p^2}{2n\omega^3\tau} \tag{6.7}$$

Using Eq. (6.5) and (6.7), the absorption co-efficient is calculated as $\alpha = \frac{4\pi k}{r}$

$$\alpha = \frac{Ne^2 \lambda^2}{\varepsilon_0 m \pi^2 n c^3 \tau} \tag{6.8}$$

where *N*, *e*, *n*, *k*, *m*, τ , and λ are free electron concentrations, electron charge, refractive index, extinction co-efficient, mass of free electron, relaxation time and wavelength, respectively.



Fig. 6. 6: Transmission of as-deposited and annealed single-layer HfO_2 thin films and transmission spectra near the band edge (inset plot).

Fig. 6.6 shows measured transmission spectra of as deposited and annealed single layer HfO_2 thin films. The transmission value increases and the band edge shifts to lower wavelength with increasing annealing temperature. The transmission band edge is considered as a

qualitative indicator of the degree of absorption. Lower wavelength band edge corresponds to lower absorption. Inset plot in Fig. 6.6 shows that absorption loss decreases with increasing annealing temperature, which can be attributed to reduced oxygen vacancy defects in HfO₂ [217]. Annealing provides sufficient energy to the oxygen atoms to diffuse and reacts with the nonstoichiometric HfO_{2-x} inside the film, which ultimately reduces the oxygen vacancy [218, 219] and improves the film refractive index by crystallization [30, 219] in HfO₂ film. Similar type of decreasing oxygen vacancy defects and increasing refractive index by annealing process are also reported for Ta₂O₅ and TiO₂ films [36, 220]. The Eq. (6.8) says that the film absorption decreases with decreasing concentration of oxygen vacancy or electronic defect and increasing refractive index. Since LIDT is inversely proportional to the film absorption [221], hence the LIDT increases upon annealing.

(2) The increase in LIDT with annealing could also be due to grain size of the mirror surface. Thermal conductivity of thin film increases with increasing grain size [107, 222-225]. With increasing grain size, the mean free path of phonon scattering at grain boundaries increases and thermal boundary impedance reduces. This enhances the thermal conductivity, which effectively improves the LIDT. Laser induced thermo-mechanical response because of rapid heating leads to two failure stages: melting and mechanical failure. The effect of thermal conductivity on the two stages during laser damage has been analyzed.

(i) Melting: For nanosecond pulsed laser, damage in dielectric thin films occurs because of excess thermal energy caused by absorption of laser at absorbing nanodefect sites. When the temperature of the defects reaches to critical value such as melting point, damage occurs through melting and evaporation [67, 226]. There is always a size distribution of nanodefects in the host material. For a given pulse duration, there exists a critical size of nanodefects, which is most susceptible to damage. The thermal conductivity of the host material affects the temperature rise at the defect sites, subsequently the LIDT. Feit *et al.* [227] have proposed

equation of heat conduction for thin films with absorbing nanodefects. The temperature evolution with size of nanodefects under the laser fluence of 50 J/cm² (above threshold for our as-deposited mirror) is calculated [227]. Again, since the electric field is maximum at the top layer of the multilayer mirror hence top HfO₂ layer is considered for the present heat conduction calculation. Nonstoichiometric HfO₂ (extinction co-efficient k = 0.01) nanodefects are assumed to exist in the top HfO₂ layer [198]. Thermal diffusivity (D = $6.8 \times 10^{-7} \text{ m}^2/\text{s}$) and thermal conductivity (K = 1.67 W/mK) of the hafnia nanodefect is assumed same as the host HfO₂ film [198]. Damage occurs when the temperature of the defects reaches the melting point of the hafnia defects 2300 K [228]. The plot of dependence of temperature evolution on size of nanodefects at different thermal conductivities of host HfO₂ thin film is shown in Fig. 6.7. The critical size of the nanodefect is around 100 nm, which can be clearly seen from the Fig. 6.7. This figure shows that the temperature drops below the melting point of hafnia when the thermal conductivity increases from 1.67 W/mK to 1.90 W/mK; as a result the film surface remains undamaged even for laser energy of 50 J/cm². This supports the higher LIDT value (> 50 J/cm²) of the annealed multilayer mirrors.



Fig. 6. 7: *Temperature rise as a function of defect size in HfO*₂ *matrix.*

(ii) Mechanical failure: The intense laser light absorbed by the nanodefects creates intense plasma, which then generates considerable internal pressure resulting high tensile stress. This excess tensile stress causes cracking or delamination of the coating layers [229-231]. Thermal conductivity of host HfO_2 matrix is one of the deciding factors for the catastrophic mechanical failure. The expression of internal stress is given by [186]

$$\sigma = \alpha \frac{E}{3(1-2\nu)} \Delta T \tag{6.9}$$

where α (3.8 x 10⁻⁶ K⁻¹) is the thermal expansion, E (223 GPa) is the elastic modulus [232] and v (0.26) is the Poisson's ratio of HfO₂ films.



Fig. 6. 8: Thermal stress variation in radial direction from the surface of the defect in HfO_2 matrix with different thermal conductivities.

The laser induced rise in temperature (Δ T) around the absorbing nanodefects with critical size of 100 nm has been calculated using heat transfer model proposed by Duchateau *et al.* [233]. The optical and thermal parameters of the nonstoichiometric hafnia defects as well as host hafnia matrix used for the calculation are taken from elsewhere [198]. The thermal internal stress from surface of the defect for different thermal conductivities of host HfO₂ thin film is plotted in Fig. 6.8. The estimated thermal stress at the defect site is much more than the critical stress level of HfO_2 i.e. 850 MPa [234]. Away from the absorbing defect centre, stress decreases. The Fig. 6.8 shows that the stress at defect site reduces for increasing thermal conductivity of the host hafnia matrix which ultimately increases the LIDT. Hence, annealing increase the grain size, consequently the thermal conductivity leading to higher LIDT.

6.1.3.5 Laser damage morphology

The damage morphology of the multilayers just above threshold value is shown in Fig. 6.9. First column of the Fig. 6.9 is optical microscope image, second column is the corresponding FESEM image and third column is the magnified FESEM image. From the damage morphologies, it is clear that damage is due to both thermal as well as mechanical failure. From the microscopic image, the damage area appears as circular scalds having multiple elliptical craters at centre. The multiple craters at centre are clearly seen from the FESEM image. In these crater regions, the damage extends much deeper into the multilayer stack. The damage occurs at substrate multilayer interface and at the interface between film layers with melting and cracking, which can be seen from the magnified FESEM morphology. Laser induced damaged substrate surface is observed except for the multilayer annealed at 400°C, because of its higher laser damage resistance. No signature of nodular defects is observed. Hence it is clear that the origin of the damage must be nanoabsorbing defects whose size is small compared to thickness of a single layer. Plasma flash is observed during the laser damage experiment of the multilayers. The high temperature plasma expands and produces shock wave [235], which is responsible for the circular damage scalds as seen in Fig.6.9. The size of the circular scalds ranges from 65 μ m to 150 μ m in the energy range 50 J/cm² to 160 J/cm². The average size of the damage scald increases almost linearly with the laser fluence as shown in Fig. 6.10. Similar observations of plasma scalds are reported elsewhere [235, 236]. The peeling of multilayer stacks with terrace structure around the crater centre can be clearly seen from the third column of Fig. 6.9.



Fig. 6. 9: *Laser damage morphology of as-deposited and annealed HfO₂/SiO₂ multilayer.* By absorbing laser light, the thermal expansion of thin layer generates strong stress pulse in the perpendicular direction to layer plane and shearing stress along the layer plane. When this stress exceeds a critical value, the multilayer stack is lifted off the substrate and bulged and finally the whole stack pops off forming the crater walls with circular or elliptical shape. To explain the terrace structure, it is assumed that the evaporation starts at the topmost layer as the temperature is highest there. The temperature profile generally follows the laser intensity profile. Since the temperature decays with radial direction as well as with depth, therefore the corresponding stress follows the same profile. This lateral or radial temperature gradient leads to terrace like ablated structure [237]. Laser induced fracture and crack are observed for

the as-deposited and annealed (500°C) multilayer respectively, which is supported by the earlier reports on HfO_2/SiO_2 multilayer coatings [234, 238].



Fig. 6. 10: Damage size as a function of laser fluence.

6.1.4 Conclusion

Optical, microstructural and laser induced damage characteristics of as-deposited and annealed HfO₂/SiO₂ multilayer mirrors have been investigated. The high reflection band of the mirrors shifts toward a shorter wavelength with increasing annealing. As-deposited and annealed multilayer mirrors show polycrystalline structure. Crystalinity and grain size increase upon annealing. The LIDT value increases from 44.1 J/cm² to 77.6 J/cm² with annealing up to 400°C, which is explained through oxygen vacancy defects and thermal conductivity of HfO₂. Annealing reduces oxygen vacancy defects in HfO₂, as a result the optical absorption loss decreases, hence the LIDT increases. Annealing also improves grain growth, consequently improves the thermal conductivity of HfO₂. The increasing thermal conductivity reduces laser induced temperature rise as well as thermal stress, which in turn

increases the LIDT. The observed damage craters, circular scalds and terrace structure indicate that thermal effect dominates the damage process. The damage morphologies such as cracks or fractures are because of laser induced mechanical stress.

6.2 Magnetron sputtered TiO₂/SiO₂ thin film multilayer: Application as omnidirectional high reflection mirror

6.2.1 Introduction

Photonic crystals (PCs) analogues to electronic semiconductors conceptualized by Yablonovitch [239] and John [240] have been the subject of much attention over the past decade due to its potential applications in optoelectronics, laser technology, optical telecommunications and computing [241, 242]. They suggested that structures with periodic variations in dielectric constant (refractive index) having periodicity of the same order of magnitude as the wavelength of the electromagnetic radiation could create a range of forbidden frequencies called a photonic band gap (PBG) like electrons suffer in periodic potential of atomic lattice in a semiconductor [242]. The periodic refractive index variation in only one direction forms one dimensional photonic crystal (1DPC). The best example of 1DPC is an omnidirectional reflector (ODR) which can reflect all polarizations of incident light independent of the incidence angle over certain wavelength band [243]. ODR has potential applications, as for example hollow optical fiber for transmission of high power laser light [244], filters in solar cells [245], reflection calibration standards for all angles in experimental optics, all-dielectric coaxial cable for high frequency communications waveguiding or laser cavities for low threshold lasers [246] and so on. Till now, different deposition techniques, such as sol-gel method, electron beam evaporation and rf sputtering have been used to fabricate 1DPC as ODR by using tellurium/ polyethylene for infrared [247], TiO₂/SiO₂ [21] and GaAs/AlAs [22] for near infrared (NIR) and tin-sulphide/silica [246], Na₃AlF₆/ZnSe [20] and TiO₂/SiO₂ [38] for visible light.

For visible range, TiO₂ and SiO₂ are two well known high and low index dielectric oxide materials, respectively for 1DPC because of their no-absorbing and non-dispersive characteristics. Lin et al. [38] have reported omnidirectional PBG of 24 nm in the visible range in 12-pair TiO₂/SiO₂ 1DPC deposited using electron beam evaporation, while Chen et al. [21] have reported an omnidirectional PBG of about 70 nm in NIR range in 6-pair TiO₂/SiO₂ 1DPC deposited using sol-gel method. In recent years, a lot of attention has been towards achieving wider omnidirectional PBG [39-41]. An ultra wide normal PBG in visible range, which is almost triple the original width of the PBG was achieved by Lu *et al.* [41] in TiO₂/SiO₂ 1DPC by an approach, called defect-induced extension of PBGS. But spectral ripples were present within the PBG of that PC. These ripples allow light to pass within the PBG in the reflection spectra and make these devices less useful. Recently, TiO₂/SiO₂ based photonic crystal with random variation in layer thickness shows lower transmission in a broad spectral range with respect to the corresponding periodic photonic crystal, which can be used to realize broad band filters [248, 249]. Such disorder photonic crystal could give wider reflection band at the expense of reduced reflectivity due to presence of few spectral ripples in the photonic band, whereas periodic photonic crystal gives absolute reflectivity (R > 99%) with no ripples in the high reflection band. Therefore, the conventional periodic photonic crystal has been followed to achieve wide omnidirectional PBG in visible range. High packing density films are prepared using sputtering technique; hence refractive index is higher for sputter deposited films as compared to that of film prepared using electron beam evaporation or sol-gel method. In recent past, asymmetric bipolar pulsed dc (ABPDC) magnetron sputtering has been evolved as the most promising technique to deposit highquality, high refractive index and low defect dielectric oxide thin films as compared to other sputtering techniques [250, 251]. In the present work, ABPDC magnetron sputtering has been utilized to achieve maximum refractive index almost close to bulk value of TiO₂ and radio

frequency (RF) magnetron sputtering is used to deposit SiO_2 thin film with relatively lower refractive index by tuning process parameter during deposition. Following this procedure during deposition, one can create relatively higher refractive index contrasts, leading to wider reflection band or PBG.

In this part, wide high reflection photonic band gap in the visible NIR region and omnidirectional reflection band in the visible region with reflectivity R>99% have been demonstrated using TiO₂/SiO₂ multilayer by tailoring refractive index contrast of the materials. To the best of our knowledge, the demonstrated omnidirectional bandwidth of the fabricated device is found much wider than that reported in literature for periodic photonic crystal in the visible region, which is discussed later. Further, the microstructural and optical properties of the multilayer photonic crystal have been investigated to probe its layer structure, surface morphology and omnidirectional spectral characteristics. Eventually, the measured optical response of the photonic crystal is compared with the simulated results.

6.2.2 Experimental details

6.2.2.1 Multilayer design

Prior to fabrication of TiO₂/SiO₂ 1DPC, the deposition optimization of single layer TiO₂ and SiO₂ thin films has been performed for best refractive index contrast and the same condition has been used for fabrication of the photonic crystal. The single layer TiO₂ thin film is deposited using ABPDC magnetron sputtering, while single layer SiO₂ thin film is deposited using RF sputtering. The refractive index *n* and extinction co-efficient *k* of the optimized single layer TiO₂ and SiO₂ thin films are determined using spectroscopic ellipsometry (SOPRA model) and are plotted in Fig. 6.11. This figure clearly shows that, both the materials are transparent in the visible and NIR regions. The obtained refractive index of TiO₂ at wavelength of 550 nm is 2.627, which is higher than that already reported in literature [252-254] using reactive pulsed DC magnetron sputtering technique.



Fig. 6. 11: *Measured refractive index and extinction co-efficient spectra of (a)* TiO_2 *and (b)* SiO_2 *thin films.*



Fig. 6. 12: Calculated reflection (R) contour as a function number of periods or bilayers (N) and wavelength.

TiO₂ and SiO₂ has refractive index ratio of 2.55:1.44 at wavelength of 700 nm, which is sufficient for achieving omnidirectional band in the visible region. The number of layers required for the 1DPC has been decided by simulating reflectivity spectrum with number of periods of the multilayer [255] as shown in Fig. 6.12. Here, one period thickness of TiO₂/SiO₂ is $d = d_{H+} d_L$, where d_H and d_L are the thickness of high index TiO₂ (n_H) and low index SiO₂ (n_L) thin film respectively. This figure clearly shows that the reflectivity at the centre wavelength (here λ =700 nm) increases with increasing number of periods and the calculated reflectivity is around 99.999% for 10 periods in the TiO₂/SiO₂ 1DPC. Therefore 10 periods have been chosen to fabricate high reflectivity omnidirectional PBG. The top layer is made of TiO₂ to make it environmentally stable. The multilayer structure of the 1DPC is (*HL*)¹⁰*H*. Here, *H* stands for high index TiO₂ layer and *L* stands for low index SiO₂ layer with each having quarter wave optical thickness *i.e.* $n_H d_H = n_L d_L = \lambda/4$, where λ = 700 nm is the centre wavelength of the high reflection band.

6.2.2.2 Fabrication

The TiO₂/SiO₂ 1DPC was fabricated with sequential deposition of TiO₂ and SiO₂ on BK7 glass substrate using multi-target magnetron sputtering system. This system consists of three numbers of magnetrons (75 mm diameter) fully compatible with dc, ABPDC, and RF power supplies. The sputtering targets used were of 99.9 % pure TiO₂ and SiO₂ target (Cerac SS-324) of 3 inch diameter and 5 mm thickness. The advantage of oxide target sputtering over reactive sputtering from the metallic target gives superior stoichiometric films that are essential for fabrication of high-quality stable optical coatings with much reduced supply of oxygen gas during deposition. The targets were sputter cleaned for 15 min to remove possible surface contaminations prior to actual film depositions. Target to substrate distance was kept at 59 mm. The Ar and O₂ flow rates were independently controlled by using mass flow controllers. A base pressure of 1×10^{-6} mbar was achieved in the chamber employing a turbo

molecular pump backed by a rotary pump. The optimized deposition condition for TiO₂ and SiO₂ thin films has been maintained during multilayer growth. TiO₂ was optimized using ABPDC power supply with pulse power of 230 Watt with 816 ns pulse width and 127 kHz pulse frequency and the optimum deposition condition, as obtained, was 4 sccm oxygen flow and 20 sccm argon flow yielding the deposition pressure of 5.6×10^{-3} mbar. SiO₂ was optimized with RF power supply with RF power of 200 Watt and the optimum deposition condition was 2 sccm O₂ flow and 20 sccm Ar flow yielding the deposition pressure of 3×10^{-3} mbar. The thicknesses of the individual layers were monitored using two multichannel quartz crystal monitors. All the depositions are carried out without any external substrate heating.

6.2.2.3 Characterization

The TiO₂/SiO₂ 1DPC has been characterized using field enhanced scanning electron microscopy (FESEM) to verify the number of layers and thickness of each layer. Since both the substrate as well as thin film layers of the 1DPC are electrically insulator, therefore a very thin layer of gold was coated on the 1DPC to make it conductive. Atomic force microscopy (AFM) has been used to characterize the surface morphology of the 1DPC at 0° angle of incidence has been measured using UV-VIS-NIR spectrophotometer in the range 300-1000 nm to observe the photonic band gaps in this spectral range. For determination of omnidirectional photonic band gap in the visible regime, the transmission spectra of the 1DPC have been measured for both transverse electric (TE) and transverse magnetic (TM) polarizations by means of a polarizer over the incident angle range 0° -70°. The reflection (R) spectra have been derived from the transmission (T) spectra in the transparent region according to R=1-T formula.

6.2.3 Results and discussion

6.2.3.1 Cross-sectional and surface morphology

The cross-sectional FESEM image of the fabricated TiO₂/SiO₂ 1DPC is shown in Fig. 6.13. The image is taken in split scanning mode. The left and right part of the figure show secondary electron (SE) image and back scattered electron (BSE) image respectively, taken from the same area simultaneously. While SE image clearly shows 21 individual layers of alternating SiO₂ and TiO₂; the same creates dark and light contrast in BSE image respectively, Ti being higher atomic number than that of Si. The top dark zone in BSE image corresponds to vacuum. The measured thickness of SiO₂ layers are almost matching with the desired thickness as shown in Fig. 6.14. The same is observed for high index TiO₂ layers except for 5th and 7th layers. Significant deviation in thickness of 5th and 7th layer from the designed value may be due to the fluctuations in process parameters during their depositions. But the variation in thickness of these two layers has negligible effect on the photonic band gap of the 1DPC, which is discussed latter.



Fig. 6. 13: Cross-sectional FESEM image of 21 layers TiO₂/SiO₂ 1DPC.



Fig. 6. 14: Thickness of SiO₂ and TiO₂ thin layers measured using FESEM.



Fig. 6. 15: 2D AFM surface morphology of TiO₂/SiO₂ 1DPC.

The surface quality of the 1DPC can be seen from the AFM surface morphology as shown in Fig. 6.15. The surface is smooth and consists of fine grains with rms surface roughness (σ) of

2.7 nm. The effect of roughness on the reflectivity is given by [256] $R = R_0 \exp\left(-\left[\frac{4\pi\sigma}{\lambda}\right]^2\right)$,

where *R* is the measured reflectance and R_0 is the designed reflectance. Using σ =2.7 nm, the estimated value of R/R₀=0.9954, 0.9968 and 0.9977 for the wavelength of 500 nm, 600 nm and 700 nm respectively. This implies that the surface roughness of the 1DPC has negligible effect on the reflectivity in the visible spectrum.

6.2.3.2 Photonic band gap in TiO₂/SiO₂ multilayer photonic crystal

The most important optical characteristics i.e. reflection spectrum of the 1DPC is shown in Fig. 6.16. The theoretical reflection of the 1DPC is simulated taking actual thickness of each layers using transfer-matrix method developed by Abeles [257]. The experimentally measured reflection of the 1DPC shows a very good agreement with the theoretical reflection spectra as shown in Fig. 6.16. This demonstrates that the adopted multilayer model using transfer matrix method is adequate, supporting the assumption of plane homogeneous layers with sharp interfaces. The measured high reflection bands are exactly matching with the simulated high reflection bands. The interferences fringes outside the high reflection band almost match with the theoretically generated fringes. The simulated reflection spectra of the 1DPC using actual thickness of each layer measured using FESEM clearly shows that the thickness variation in these two layers has negligible effect on the high reflection band or PBG. The achieved high reflection band (592-837 nm, $\Delta\lambda$ =245 nm) at normal incidence as shown in Fig. 6.16 is much wider than the value (560-730 nm, $\Delta\lambda$ =170 nm) reported by Chiasera et al. [258] and Scotognella et al. [259] in the visible NIR region for TiO₂/SiO₂ periodic photonic crystal. The obtained results were then compared with theoretical photonic band structure.



Fig. 6. 16: *Measured* (O) *and calculated* (—) *reflection spectra of the TiO*₂/*SiO*₂ *1DPC*.

The 1D photonic band dispersion along axis of the multilayer has been calculated solving Maxwell equations together with the use of Bloch theorem [260]. The secular equation describing the angular frequency-wave vector i.e. ω (k) dispersion is given by

$$\cos(kd) = \cos(k_1d_1)\cos(k_2d_2) - \frac{1}{2} \left(\frac{n_1(\omega)}{n_2(\omega)} + \frac{n_2(\omega)}{n_1(\omega)} \right) \times \sin(k_1d_1)\sin(k_2d_2)$$
(6.10)

Where k is the Bloch wave vector along the multilayer axis, $d=d_1+d_2$ is the period, and d_i , $n_i(\omega)$, $k_i=n_i(\omega/c)$ are thickness, refractive index and wave vector in the layer *i*, respectively, with *i*=1, 2 referring to the TiO₂ and SiO₂ layers, respectively. The ω (k) dispersion derived from above equation represents the 1D photonic dispersion for an infinite multilayer. The frequency ω (k) dispersion is converted to wavelength λ (k) dispersion using $\lambda = (2\pi c/\omega)$. The calculated photonic band structure of TiO₂/SiO₂ 1D PC is shown in Fig. 6.17 (a). The photonic band gap that lies at Brillouin zone edge is larger, while the band gap that lies at the centre of the Brillouin zone is smaller. It can be clearly noticed that the calculated photonic band gaps and their band width in Fig 7 (a) match very well with the high reflection bands and their band width in the experimental reflection spectrum shown in Fig. 6.17 (b). The PBG of $\Delta\lambda_{1g}=245$ nm and $\Delta\lambda_{2g}=18$ nm are observed at band centre of $\lambda_{1g}=700$ nm and $\lambda_{2g}=376$ nm respectively.



Fig. 6. 17: Calculated photonic band dispersion compared to the experimental reflection spectra of the TiO_2/SiO_2 1DPC.

6.2.3.3 Omnidirectional high reflection photonic band

Now the omnidirectional photonic band characteristic of the TiO₂/SiO₂ 1DPC has been explored. It is well known that omnidirectional reflection requires the photonic band gap for both S- and P-polarized light should persist from normal incidence to glancing incidence. But in 1DPC, there are two main factors which limit to achieve absolute photonic band gap. The first is that the widths of P-polarization stop band decreases with increasing angle of incidence, usually leading to closing of the overall PBGs. The second is that at Brewster's

angle, the P-polarization light cannot be reflected. However the absence of absolute PBGs does not mean that there is no omnidirectional reflection [39]. The condition for the existence of omnidirectional PBG is that there should not be any propagating mode for either polarization of light which can couple with the incident wave at any incident angle i.e. the maximum value of refracted angle θ_{max} should be less than internal Brewster's angle θ_B [261]. Using Snell's law at air-high index interface for the present 1DPC $n_H \sin \theta_H = n_0 \sin \theta$, where n_0 is the refractive index of the air and θ is the angle of incidence on the multilayer structure. Hence the maximum refraction angle is defined as $\theta_{max} = \sin^{-1}(n_0/n_H)$ and the Brewster's angle is $\theta_B = \tan^{-1}(n_L/n_H)$. Since $\theta_{max} < \theta_B$ for the TiO₂/SiO₂ 1DPC, the effect of Brewster's angle can be completely ignored. Hence the incident wave cannot couple to the Brewster window, leading to the existence of omnidirectional PBG [262].



Fig. 6. 18: Calculated contour plot of the reflectivity spectra of the TiO_2/SiO_2 1DPC as a function of the incident angle and wavelength for both polarizations of light.

The dependency of photonic band edges on the angle of incidence in 1DPC is given by the following analytical equation suggested by John Lekner [19]

$$\lambda^{\pm} = \frac{\pi \left(D_H + D_L\right)}{\frac{\pi}{2} \pm \phi^{\pm}} \tag{6.11}$$

where the superscript \pm above λ and ϕ represent the upper (+) or lower (-) edge of the stop band and

$$D_H = d_H \left(n_H^2 - n_0^2 \sin^2 \theta \right)^{1/2}, \quad D_L = d_L \left(n_L^2 - n_0^2 \sin^2 \theta \right)^{1/2}$$
(6.12)

where n_0 is the refractive index of the incident medium and θ is the angle of incidence. ϕ^{\pm} is defined by

$$\phi^{\pm} = \sin^{-1} \left(\frac{x-1}{x+1} \right) - \frac{x-1}{4\sqrt{x}} \left(\frac{D_H - D_L}{D_H + D_L} \right)^2 \left[\frac{\pi}{2} \pm \sin^{-1} \left(\frac{x-1}{x+1} \right) \right]^2 + O \left(\frac{D_H - D_L}{D_H + D_L} \right)^4$$
(6.13)

where
$$x = \left(\frac{n_{H}^{2} - n_{0}^{2} \sin^{2} \theta}{n_{L}^{2} - n_{0}^{2} \sin^{2} \theta}\right)^{1/2}$$
 for P-polarization (6.14)

and
$$x = \left(\frac{n_H}{n_L}\right)^2 \left(\frac{n_H^2 - n_0^2 \sin^2 \theta}{n_L^2 - n_0^2 \sin^2 \theta}\right)^{-1/2}$$
 for S-polarization (6.15)

Now the omnidirectional photonic band structure of the TiO₂/SiO₂ 1DPC is calculated using Eq. (6.11) - (6.15) and the results are shown in Fig 6.18. The omnidirectional photonic band gap is determined by the lower wavelength band edge of *P*- (or *S*-) polarized light at normal incidence 0° and its upper wavelength band edge of the *P*-polarized light at glancing angle incidence 90° , which is marked by shaded area in Fig. 6.18. From this figure, it is clear that absolute omnidirectional PBG exists in the spectral range of 590-640 nm for the TiO₂/SiO₂ 1DPC (the green shaded area in Fig. 6.18) with gap to mid-gap ratio about $\approx 8\%$.



Fig. 6. 19: Measured reflection spectra of 21-layer TiO_2/SiO_2 1DPC for S-polarized (dotted line) and P-polarized (solid line) light at different angle of incidence ranging from $0^{\circ} - 70^{\circ}$. The green color shaded area is the omnidirectional photonic band gap. The multilayer HR mirror reflects omnidirectional for this photonic band.

The measured reflection spectra of the 1DPC for both polarizations of light at different angle of incidence are shown in Fig. 6.19. For the S- and P-polarizations, the high reflectance band shifts to shorter wavelengths with increasing incident angle. The S-polarization bandwidth increases while the P-polarization bandwidth decreases with increasing incident angle. Fig. 6.19 shows that there is an overlapping reflectance band common to all spectra taken between the incident angles of 0° -70°; this is the omnidirectional photonic band gap for reflectivity R>99%. For S-polarization, there is a 159 nm omnidirectional reflection band in the wavelength range 592-751 nm. For P-polarization there is a 76 nm band in the wavelength range 592-668 nm. The superposition of S- and P- polarizations results in an omnidirectional photonic band gap $\Delta\lambda$ =76 nm in the spectral range 592-668 nm with band to mid-band ratio $\Delta\lambda\lambda$ =12% with reflectivity more than 99% (the green shaded area in Fig. 6.19). These results are in good agreement with the predicted omnidirectional PBG for this TiO₂/SiO₂ 1DPC, which is approximately 80 nm. The observed omnidirectional PBG is found almost three times than reported by Lin et al. [38] and much wider than other reported values [263, 264] in the visible region for TiO₂/SiO₂ periodic photonic crystal. The TiO₂/SiO₂ 1DPC mirror exhibits golden appearance in white light at normal incidence as well as oblique incidence, observed with the naked eye. This wide band reflector can be potentially used as laser mirrors which can cover the whole gain band width of several types of lasers in the red and near infrared part of the spectrum as well as filters for solar cells. The fabricated 1DPC device are made of refractory oxides, hence it can exhibit higher laser induced damage threshold and can be well-sustained in extreme environments like elevated temperatures, corrosion and radiation. This study will help to fabricate optical quality and stable wide band omnidirectional filters, which can be used in the field of optical communications and laser technology.

6.2.4 Conclusion

TiO₂/SiO₂ multilayer 1DPC has been prepared by sequential deposition of ABPDC magnetron sputtering of TiO₂ and RF magnetrons sputtering of SiO₂ to achieve wide omnidirectional high reflection photonic band in the visible region. It is characterized for its potential application as omnidirectional reflector in the visible spectrum. The microstructure and optical response of the TiO_2/SiO_2 multilayer photonic crystal have been investigated by AFM, SEM and spectrophotometer respectively. The surface of the multilayer is very smooth. The characterization of the fabricated 1DPC concludes that the magnetron sputtering deposition process has achieved 1DPCs necessary parameters; including layer thicknesses, refractive index, surface roughness etc. The use of ABPDC sputtering process helps to deposit TiO₂ thin layer having refractive index almost close to bulk value, which ultimately leads to obtain wider photonic band gap ($\Delta\lambda = 245$ nm) in the visible and near infrared region (592-837 nm) at normal incidence. The experimental optical characteristic of the 1DPC is found in good agreement with the simulation results. Finally wider omnidirectional photonic band gap of 592-668 nm ($\Delta\lambda$ =76 nm) with band to mid-band ratio $\Delta\lambda/\lambda$ =12% over the incident angle range of 0° -70° for R>99% has been achieved in the visible region. In addition, the width of omnidirectional PBG can be further enhanced by making silica (SiO₂) layers more porous by using glancing angle deposition in the magnetron sputtering system.

Chapter 7: Summary and Future Prospects

7.1 Summary

The thesis presents the study of deposition and characterization of different properties of some important refractory oxide thin films and multilayers used for optical coating applications. Deposition of single layer and multilayer thin films has been carried out using EB evaporation and sputtering. The deposited single layer thin films are HfO₂, ZrO₂-MgO, ZrO₂-SiO₂ and HfO₂-SiO₂ mixed oxide composites, while the multilayer coatings are HfO₂/SiO₂ and TiO₂/SiO₂. We have used different characterization tools viz. UV-VIS-NIR spectrophotometer, XRD, XRR, AFM, SEM, AFAM, Substrate curvature method and Laser induced damage threshold (LIDT) measurement set-up to probe optical properties, microstructure, mechanical properties and LIDT value of the thin films and multilayer optical coatings. Porosity in a thin film mainly controls the refractive index of the film, consequently the spectral characteristics. The porosity can be controlled by tuning oxygen partial pressure during deposition. The present thesis has given more importance on the study of effect of deposition oxygen partial pressure on different properties of several widely used optical thin films. Improvement in optical properties and LIDT can be achieved by mixing two materials or by post deposition annealing as described in Chapter-1. In that context, the thesis also specifically targeted to study the influence of composition and annealing on different properties of mixed oxide composite thin films and multilayer high reflection mirror respectively. Finally the thesis has able to details of fabrication and characterization of a wide band omnidirectional mirror in the visible region has been presented in the thesis. The major highlights of the thesis are briefly summarized below.

HfO₂ thin films were deposited by EB evaporation at different oxygen (O_2) partial pressures. The effect of O_2 pressure on microstructure, optical properties, residual stress and LIDT of the films has been investigated. All the films are amorphous in nature. The film density decreases, while the grain size and surface roughness of the films increase with increasing oxygen partial pressure. The film refractive index decreases and optical band gap increases with increasing O_2 pressure. The variation of residual stress with O_2 pressure is correlated with film microstructure. The decrease of LIDT with increasing O_2 pressure has been observed for both harmonics of Nd: YAG laser.

Other set of HfO₂ thin films have been deposited on BK7 glass substrate by RF sputtering technique at different oxygen/argon (O₂/Ar) gas flow ratios. The effect of O2/Ar flow ratio on different film properties has been reported. The films are polycrystalline in nature. The dispersion energy as well as the oscillator energy derived from the single-oscillator Wemple–DiDomenico model is correlated with the compressive strain. The variation of the residual stress with O_2/Ar flow ratio is explained through lattice expansion induced intrinsic compressive stress due to atomic peening and grain size dependent intrinsic tensile stress in the films. With respect to quality optical coating applications of reactively sputtered HfO₂ thin films, an optimum O_2/Ar flow mixing ratio (0.1 in the present work) is needed in order to achieve a useful balance between the refractive index and the residual stress of the film.

Effects of oxygen partial pressure on optical properties, surface morphology, elastic modulus and LIDT of EB evaporated ZrO2-MgO binary composite thin films have been investigated. The refractive index of the films decreases from 1.96 to 1.76 at wavelength of 550 nm with increasing O_2 pressure because of reduced film density. The grain size of the films increases with increasing O_2 pressure. The indentation modulus or elastic modulus of the films decreases monotonically for films deposited at higher oxygen partial pressures. The

increase in LIDT with increasing O_2 pressure has been explained through film grain size. This study has established a correlation among grain size, packing density, refractive index, elastic modulus and LIDT of the ZrO₂-MgO thin films.

A set of ZrO_2 :10%SiO₂ thin films have been deposited on fused silica substrate by coevaporation of ZrO_2 and SiO₂ using EB evaporation technique at different oxygen partial pressure. The influence of O₂ pressure on different properties of the films has been studied. All the films exhibit strong tetragonal phase and the crystalinity increases with increasing O₂ pressure. No crystallite size effect on the optical properties of the films has been observed. The optical band gap is affected by crystalinity rather than crystallite size or grain size of the film. A correlation among surface morphology, dispersion energy and crystalinity has been established. The effect of grain size on the elastic modulus and LIDT of the films has been described.

The HfO₂-SiO₂ mixed oxide composite thin films of various compositions in the (x)HfO₂:(100-x)SiO₂ (x = 0% to 100%) systems have been deposited on fused silica substrates by co-evaporation of HfO₂ and SiO₂ through reactive EB evaporation. Then different properties of the films are probed. The refractive index decreases and the optical band gap increases with increasing silica fraction in the mixed oxide composite thin films. The surface morphology has been modified by varying silica fraction. The compositional dependent refractive index as well as absorption co-efficient has been analyzed using different effective medium approximation (EMA) models in order to evaluate the suitability of these models for such mixed oxide films. The increase of LIDT with increasing silica fraction has been analyzed. The transition in LIDT value for films having more than 80% silica content has been explained through defect assisted multiphoton ionization process. The laser damage morphology of the films has been probed by optical microscopy and the characteristics of the damage morphology are discussed.

HfO₂/SiO₂ periodic multilayer high reflection mirrors have been prepared with 25 layers of sequential deposition of HfO₂ and SiO₂ on BK7 glass substrate using reactive EB evaporation technique. The mirrors are then annealed in the temperature range from 300°C to 500°C. The effects of annealing on structure, optical properties, surface morphology, and LIDT of the mirrors have been investigated. A shifting in high reflection band of the mirror towards shorter wavelength has been observed with increasing annealing. Crystalinity and grain size increase upon annealing. The LIDT value increases with annealing, which is explained through oxygen vacancy defects as well as grain size dependent thermal conductivity. The damage area increases with increasing laser fluence. Craters, circular scalds and terrace like ablated structures are observed in the laser damage morphology of the multilayer mirrors.

TiO₂/SiO₂ multilayer one dimensional photonic crystal has been fabricated by sequential asymmetric bipolar pulsed DC magnetron sputtering of TiO₂ and RF magnetron sputtering of SiO₂ to achieve wide band omnidirectional mirror. The optical properties, cross-sectional and surface morphology of the omnidirectional mirror have been investigated. The surface of the mirror is found very much smooth. The deposited thickness of the multilayer almost matches with the designed thickness except for 5th and 7th layer, which has negligible effect on photonic band gap or of high reflection band. Wide high reflection photonic band gap of 245 nm in the visible and near infrared regions has been achieved. The experimentally observed omnidirectional high reflection photonic band 592-668 nm ($\Delta\lambda$ =76 nm) with reflectivity R>99% over the incident angle range of 0°-70° is found almost matching with the calculated omnidirectional PBG. The omnidirectional PBG is found much wider as compared to the values reported in literature so far in the visible region for TiO₂/SiO₂ periodic multilayer. The experimental spectral characteristic of the mirror is found in good agreement with the simulated results.

7.2 Future prospects

The author has planned to carry out several studies using these thin film optical coating materials. Followings are the list of some of the future planned research works.

- Residual stress and elastic modulus of mixed oxide composite thin films will be investigated. Post-annealing process of the composite films will be performed to improve their mechanical properties.
- 2. Different multilayer devices (ZrO₂-MgO/SiO₂ and ZrO₂-SiO₂/SiO₂) made of ZrO₂-MgO or ZrO₂-SiO₂ mixed composite as high refractive index and SiO₂ as low refractive index shall be prepared and their characteristics performance will be compared with that of HfO₂/SiO₂ multilayer.
- **3.** Effect of thermal annealing on TiO₂/SiO₂ multilayer device deposited using both EB evaporation and sputtering will be investigated. Then both the results will be compared to qualify the performance of the two multilayer devices.
- **4.** Heterogeneous multilayer structure will be designed and prepared to achieve wide omnidirectional photonic band.
- **5.** In this thesis, the optical properties of the films and multilayers have been investigated using spectrophotometer. However, ellipsometry is another method which is more accurate than the spectrophotometer, will be tried on the basis of several optical dispersion models.
- **6.** Present thesis only uses normal angle deposition (ND) techniques to prepare the thin films and multilayer coatings. The mixed oxide composite thin films and multilayers will be prepared using oblique angle deposition (OAD) technique to explore their different properties. The films or multilayers prepared by both ND and OAD will be compared for their useful applications in the field of optical coatings.

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