Nano-mechanics of Optical Structures for High Laser-Damage Threshold Applications

by

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Dedicated to the memory of Professor Stephen D. Jacobs
Biographical Sketch

The author was born in Lucknow, India. He attended U.P. Technical University from 2005 to 2009, and graduated with a Bachelor of Technology degree in Mechanical Engineering. He began his graduate studies at the University of Rochester in the Department of Mechanical Engineering in September 2009 under the direction of Professor John C. Lambropoulos. His Master’s research centered on the understanding of slow crack growth in fused silica. As a Master’s student, the author interned at Corning Incorporated, Painted Post, NY from June to December 2010. The author received the Master of Science degree in 2011 and began doctoral studies in the Department of Mechanical Engineering in the same year.

His Ph.D. research, which was carried out in part at the University of Rochester’s Laboratory for Laser Energetics, was supervised by Professor John C. Lambropoulos. Contributions of his doctoral research included the development of a novel methodology to correlate nano-scale mechanical damage (coupled with electron microscopy and numerical simulations) to the laser-damage resistance of pulse-compression gratings used in OMEGA EP.
In conjunction with his Ph.D. research, the author also obtained a Master of Science in Technical Entrepreneurship and Management (TEAM) in May 2014. He also interned at Corning Incorporated, Painted Post, NY from June to August 2014. The author was awarded the Frank J. Horton Graduate Research Fellowship to support his graduate work.

The following publications were a result of work conducted during graduate study at the University of Rochester.

**Referred journal articles**


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Ductility and Fracture at the 50 to 100-nm Scale,” in Optical Fabrication and Testing, OSA Technical Digest (online) (Optical Society of America, 2012), paper OTu4D.1.


**Non-referred articles**


**Presentations**


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I express many thanks to Late Professor Stephen D. Jacobs who provided
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Abstract

This dissertation focuses on the use of scanning electron microscopy (SEM), nano-indentation and finite-element analysis (FEA) to observe, measure and validate the nano-mechanical properties (elastic modulus, hardness, yield stress, deformation, fracture) of nm-level features in important optical micro- and nano-structures. The optical micro- and nano-structures include single layer oxide films, multilayers comprised of oxide layers, and optical diffraction gratings. In addition to the nano-mechanical properties, we also study deformation in brittle silica walls that comprise the grating by suppressing fracture as well as on the nano-mechanics of defects in optical structures. We use this understanding of nano-mechanics in diffraction gratings to show that it naturally complements optical testing (laser-induced damage threshold tests), and mechanical fields (for example, deformation fracture strain) expose the same regions of the grating structure in a manner analogous to optical fields (for example, electric fields). A major conclusion is that deformation can be entirely separated from fracture in patterned surfaces. This result is in distinct contrast to bulk surfaces where fracture is always preceded
by deformation.

In Chapter 2 we use nano-indentation to perform mechanical characterization of optical oxide single-layer and multi-layer thin films, and the results are interpreted based on the deposition conditions used. These oxide films are generally deposited to have a porous microstructure that is optimized to maximize the laser induced damage thresholds, but changes in deposition conditions lead to varying degrees of porosity, density, and possibly the microstructure of the thin film. Of the four single-layer thin films tested, alumina was observed to demonstrate the highest values of nano-indentation hardness and elastic modulus. We also demonstrate how single-layer thin film data may be used in the analysis of multilayer thin films and present an experimental study of indentation size effects (ISE) on multilayer thin films (silica-hafnia system). These multilayer coatings show a decrease in hardness for an increase in indentation loads when using a Cube-corner tip. The data are interpreted using the Nix & Gao model of gradient plasticity, and predicts an excellent correlation between the depth dependence of hardness in our silica-hafnia multilayer thin films.

In Chapter 3 we characterize “blisters”, defects observed in multilayer dielectric (MLD) coatings after exposure to acid cleaning procedures. Nano-indentation is used to make site-specific indentations across blisters to measure the mechanical response, especially their elastic compliance under different conditions of loading. Two regions of statistically different mechanical response are identified within a blister defect and compared to the undisturbed
regions of the MLD coating. We conclude that different blisters follow the
genral trend that maximum compliance is always seen in the “extended re-
gion” of the blister, furthest from the blister’s initiating nodule/scratch and
the coating age might have an effect on the indentation response for larger
depths of penetration into the thin film. Additionally, our numerical model
is used to estimate the extent of “blistering” in a coating, a result verified
through cross-sectional SEM images of the “blister” defect.

In Chapter 4 we measure the mechanical response of optical multilayer
dielectric (MLD) diffraction gratings, geometries which are constrained in
only one transverse direction but free in the other, using nano-indentation.
Primarily, 2 types of indentation response were observed: indents almost per-
fectly centered on a particular grating “wall”, without extending to a sidewall
or the edge and without disturbing any adjacent walls; and indents made off-
center on a “wall” which were catastrophic even at the same low load. The
indentation record of load versus displacement uniquely distinguishes these
two regimes, and is also correlated to the properties of bulk surfaces. The
centered indents allow us to invoke a state of entirely ductile deformation
and measure the yield stress of silica at the nm-scale (∼4.1 - 4.6 GPa). The
direct measurement of yield stress if silica at the nm-level is an exciting re-
sult. Off-centered indents at the same loads fracture the grating walls and
this is used to hypothesize a fracture mechanism and measure an estimate
of fracture stress (∼1.1 - 3.3 GPa). Non-linear, 3-D FEA using ABAQUS®
validates our experimental results as well as the deformation mechanism.
Finally, in Chapter 5 we use the “slightly” off-centered indents on the gratings walls to study a combined response of ductility and fracture. Load-displacement curves in conjunction with observations from SEM images provide estimates of fracture strain. Mechanical field thresholds, represented by fracture strain, are used to correlate nano-mechanical damage in gratings to their optical performance (measured through laser-induced damage thresholds). FEA reveals that nano-indentation tests expose the same regions on the grating structure as an optical test. Here we draw attention to the important effects of inhomogeneities and non-uniformities (geometrical and material) in concentrating mechanical fields. Therefore, nano-mechanical testing complements and could even precede optical testing to gauge the performance of diffraction gratings.

In summary, our work reveals that elasticity, ductility and fracture at the nm-level can each be studied separately, in contrast to micromechanical deformation; that SEM plays an important role in identifying relevant features; that in addition to characterization, nano-indentation may be useful as a diagnostic tool to study response to intense light fields; and that numerical simulations naturally complement the experimental nano-mechanics to model the complex nm-level response of optical nanostructures.
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This work was supervised by Professor John C. Lambropoulos of the Mechanical Engineering Department and in part by late Professor Stephen D. Jacobs (until May 2014) of the Program of Materials Science. The author also held extensive discussions with Dr. James B. Oliver for insight related to this work. The author was supported through a Horton Fellowship at the Laboratory for Laser Energetics (LLE) [University of Rochester]. This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0001944, the University of Rochester, and the New York State Energy Research and Development Authority.

Chapter 2 is based on a conference proceedings publication for Optical Society of America (OSA), Optical Fabrication Testing (2010) – co-authored with Professor John C. Lambropoulos, and an article published in Applied Optics (2015) – co-authored with Dr. James B. Oliver and Professor John C. Lambropoulos. The single-layer and multi-layer thin films used in this chapter were deposited at LLE by the Optical Manufacturing (OMAN) of
which Dr. Oliver is a member of. The viewgraph in Figure 2-6 was obtained with assistance from Mr. Christopher Smith (LLE) using a scanning electron microscope (SEM) located at LLE.

Chapter 3 is based on a paper from the conference proceedings of Material Research Society (MRS) in 2012 with co-authors Dr. Heather P.H. Liddell, late Professor Stephen D. Jacobs and Professor John C. Lambropoulos. The defect density map in Figure 3-2 was created by Dr. Liddell. Also, both the coating used in this study were cleaned by Dr. Liddell to prepare for the indentation experiments. The focused ion beam (FIB) cross-section image of a blister shown in Figure 3-12 was created with assistance from Mr. Brian McIntyre (University of Rochester).

The multilayer dielectric (MLD) gratings used to study ductility and fracture of silica at the nm-scale in Chapters 4 and 5 were made by depositing MLD coating on a glass substrate at LLE by the OMAN group and then patterned using lithography at an outside location by a vendor. The in-situ SEM nano-indentation experiments discussed in Section 4.3.1 of the chapter were performed by Dr. Jeffrey Wheeler of EMPA, Switzerland (now at ETH Zurich, Switzerland). The results in Figures 4-8 (b) and 4-9 were obtained by experiments conducted by Dr. Wheeler. The ductility observations in silica gratings discussed in Chapter 4 are based on an article published in AIP Advances (2011) with co-authors Dr. Liddell, late Professor Stephen D. Jacobs and Professor John C. Lambropoulos.

In Chapter 5, the MLD grating samples studied were cleaned using proto-
The contributions of collaborators are also identified specifically in the text wherever possible and applicable. All other work conducted for the dissertation was completed independently by the author.
Table of Contents

Biographical Sketch iii
Acknowledgments vii
Abstract x
Contributors and Funding Sources xiv
List of Tables xxii
List of Figures xxxvi
List of Symbols xxxvii
1 Introduction 1
References 9

2 Nano-mechanical properties of single- and multi-layer optical
oxide thin films grown by electron-beam deposition 11

2.1 Introduction .......................................................... 11
Table of Contents

2.2 Materials and Methods ........................................ 14
  2.2.1 Electron beam deposition of single- and multi-layer thin films ........................................ 14
  2.2.2 Nano-indentation ........................................ 17

2.3 Results ..................................................... 19
  2.3.1 Single-layer thin films .................................. 19
  2.3.2 Silica-hafnia multilayer thin films ...................... 24

2.4 Discussion .................................................. 28
  2.4.1 Single-layer thin films .................................. 28
  2.4.2 Silica-hafnia multilayer thin films ...................... 36

2.5 Conclusions ................................................ 43

References ..................................................... 45

3 Surface forensics of multi-layer dielectric coatings - mechanical characterization of “blister” defects ................. 51
  3.1 Introduction ................................................ 51
  3.2 Materials and Methods ..................................... 54
  3.3 Results .................................................... 58
  3.4 Discussion ................................................ 66
    3.4.1 “Blisters” on sample 44T ......................... 66
    3.4.2 “Blisters” on sample 20T ......................... 67
    3.4.3 Analytical modeling of the “blister” defect ........ 69
  3.5 Conclusions ................................................ 75
# Table of Contents

3.A Appendix ................................................. 76

References ..................................................... 78

4 Nano-scale separation of ductile and brittle deformation in patterned high-aspect ratio silica using nano-indentation 81
  4.1 Introduction ............................................. 81
  4.2 Materials and Methods ................................. 85
    4.2.1 Fabrication of MLD gratings ....................... 85
    4.2.2 Nano-indentation of patterned silica ............... 85
  4.3 Results ................................................ 89
    4.3.1 Experiments ......................................... 89
    4.3.2 Numerical simulations .............................. 94
  4.4 Discussion ............................................... 106
    4.4.1 "Centered" indents: Extraction of nano-scale yield strength of silica .......................... 106
    4.4.2 "Off-centered" indents: Extraction of nano-scale fracture strength of silica .................. 111
  4.5 Conclusions ............................................. 116

References ..................................................... 119

5 Nano-mechanics of laser-induced damage in optical MLD gratings 122
  5.1 Introduction ............................................. 122
5.2 Materials and Methods

5.2.1 Fabrication of MLD gratings

5.2.2 Optimized procedure for cleaning MLD gratings to maximize laser damage thresholds

5.2.3 Laser damage testing – set-up, process and parameters

5.2.4 Nano-indentation of MLD gratings

5.3 Experimental results

5.3.1 LIDT results for gratings as a function of the cleaning processes

5.3.2 Nano-indentation data - concept of minimum deflection to fracture

5.3.3 Relation of nano-indentation-induced fracture and laser-induced damage threshold

5.3.4 Relation of yield stress and laser-induced damage threshold

5.3.5 Thickness discontinuity observed in grating walls from cleaning and their measured LIDT (J/cm²)

5.3.6 Pores/surface heterogeneities observed on the grating floor

5.4 Numerical Simulations

5.4.1 3-D FEA of a 50% off-centered indent

5.4.2 Radiation pressure
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4.3</td>
<td>2-D FEA of gratings (penetration depth = 50 nm, 100% off-centered) - geometric discontinuities</td>
<td>150</td>
</tr>
<tr>
<td>5.5</td>
<td>Discussion</td>
<td>156</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Effect of cleaning procedures on LIDT</td>
<td>156</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Thickness undulation and concentration of mechanical fields</td>
<td>157</td>
</tr>
<tr>
<td>5.5.3</td>
<td>Surface heterogeneities on the grating “floor”</td>
<td>160</td>
</tr>
<tr>
<td>5.5.4</td>
<td>Radiation pressure</td>
<td>161</td>
</tr>
<tr>
<td>5.5.5</td>
<td>Correlation of optical and mechanical tests (LIDT and $\Delta_{\text{minimum}}$)</td>
<td>162</td>
</tr>
<tr>
<td>5.6</td>
<td>Conclusions</td>
<td>169</td>
</tr>
</tbody>
</table>

**References**  

**6 Summary and Recommendations for future work**  

6.1 Summary of main results                178

6.2 Recommendations for future work        180

6.2.1 Multi-layer thin films under different environmental conditions  180

6.2.2 Application of indentation on patterned optical surfaces: strength and robustness of very thin finished glass edges  185

**References**  

188
List of Tables

2.1 Process parameters for electron-beam deposition (including plasma-assist deposition) of single-layer coatings. ....... 17
2.2 Extracted near-surface mechanical properties corresponding to penetration depths of ∼10% to 15% of the total film thickness. 24
2.3 Extracted near-surface mechanical properties corresponding to penetration depths of ∼10% to 15% of the total film thickness. 26
2.4 Comparison with bulk and film properties reported in the literature. ......................................................... 31

3.1 Greatest compliance is in the “extended” region or the area closest to the top layer of the MLD. This region saw the lowest value of elastic modulus, 41.90 ±1.07 GPa. .................... 60

5.1 Cleaning process for the MLD gratings used in this work. ... 129
5.2 Summary of LIDT results for gratings and specific cleaning methods used. .............................................. 132
List of Figures

1.1 Diffraction gratings in the OMEGA EP are a bottleneck for reaching ultra-high intensities on the laser target (4, 5, 6, 7). 3

2.1 The 54-in. vacuum chamber used to deposit the reported single- and multi-layer thin films. 15

2.2 Multilayer thin film design used for this study. 16

2.3 SEM images of the single-layer thin film coating used in this study. 20

2.4a Load-displacement curves for single-layer hafnia thin film. 21

2.4b Load-displacement curves for single-layer silica thin film. 21

2.4c Load-displacement curves for single-layer alumina thin film. It should be noted that the abscissae for Figs. 2-4(a) and 2-4(b) are identical to that for Fig. 2-4(c). 22

2.4d Load-displacement curves for single-layer niobia thin film. 22
2.5 Measured near-surface values of elastic modulus and hardness for the four single-layer coatings. The blue band indicates the region of interest and encompasses the values measured for 10% to 15% of the total film thickness for each single layer, respectively. It should be noted that the abscissae for Figs. 2-5(a) and 2-5(b) are identical to those of Figs. 2-5(c) and 2-5(d).

2.6 Cross-section of a multilayer thin film coating used in this study. It is made up of alternating layers of silica and hafnia.

2.7 Load-displacement curves using a Berkovich tip show penetration depths $\sim 500-2500$ nm ($\approx 19$ individual layers in the multilayer stack for loads ranging from 10 - 400 mN).

2.8 Load-displacement curves using a Cube-corner tips how penetration depths $\sim 600-3500$ nm ($\approx 23$ individual layers in the multilayer stack) for loads ranging from 10 - 400 mN.

2.9 SEM image of an indent made using a Berkovich tip typical for loads 10 - 20 mN.
2.10 Elastic modulus corresponding to penetration depths approximately equal to 10% to 15% of the total film thickness. The data labels on the plots represent the mean of the measured values. (b) Hardness corresponding to penetration depths of approximately equal to 10% to 15% of the total film thickness. The data labels on the plots represent the mean of the measured values. 

2.11 Modulus for the different materials reported in this study in bulk and thin-film forms. No bulk value of niobia is reported. 

2.12 Results using the Berkovich tip – no dependence on hardness is observed. 

2.13 Results using the Cube-corner tip – hardness increases with decreasing load/depth. 

2.14 Square of hardness plotted against the reciprocal of the penetration depth, gives a good linear fit with a correlation coefficient of 0.9 or $R = 0.9487$. 

2.15 Depth dependence of the hardness of the MLD film plotted according to equation 2.9. 

2.16 Concept of material pile-up to explain ISE in metallic thin films. Figure adapted from McElhaney et al. (30). 

2.17 SEM image showing material pile-up as evidence of ISE in our MLD thin films.
3.1 “Blister” defects on MLDs caused by exposure to acid piranha. The final crack in the MLD, furthest from the nodule, is the top MLD layer. Reprinted from Mehrotra et al. (10) with permission from Cambridge University Press. . . . . . . . . . . 53

3.2 (a) Blister distribution on 44T after piranha cleaning (total blister count: 56); (b) Blister distribution on 20T after piranha cleaning (total blister count: 515) [10]. . . . . . . . . . . . . . . . . . . . . . 55

3.3 Nanoindenter XP: utilizes a magnetic coil assembly to apply the force and capacitance gage to measure the displacement. . 56

3.4 CSM testing: The application of an oscillating force which is superimposed on the load forcing the indenter tip allows for measurement of contact stiffness at all depths. Adapted from Fischer-Cripps (12). . . . . . . . . . . . . . . . . . . . . . . . . . . . . 57

3.5 Indentation response of the blister in sample 44T at a load of 10 mN. Reprinted from Mehrotra et al. (10) with permission from Cambridge University Press. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 59

3.6 Indentation response of blister on sample 44T at 1 mN. Note the indentation response of blister 2(a), (b) and (c) - they correspond to the same blister. Notice the baseline data obtained on the undisturbed region of the coating. Reprinted from Mehrotra et al. (10) with permission from Cambridge University Press. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 61
3.7a Comparison of the indentation response of a blister site and the undisturbed ("good") region of the MLD coating, 44T, for a CSM test set to a penetration depth of 5000 nm. Reprinted from Mehrotra et al. (10) with permission from Cambridge University Press.

3.7b 3 blisters on coating 44T show "plateau" effect when indented using a CSM test for penetration of 5000 nm. This shows that different blisters on the same coating respond to a CSM indentation test in an identical manner. Reprinted from Mehrotra et al. (10) with permission from Cambridge University Press.

3.8 Indentation response of blisters on sample 20T using a load of 1 mN. Reprinted from Mehrotra et al. (10) with permission from Cambridge University Press.

3.9 CSM testing on sample 20T by penetrating 5000/5500 nm into the defect site. Reprinted from Mehrotra et al. (10) with permission from Cambridge University Press.

3.10 SEM image of a blister. The fracture in the MLD only at the top surface is visible.

3.11 Atomic force microscope (AFM) image of a "blister" defect.

3.12 The "blister" defect is modeled as a parabolic beam of width b(x).
3.13 FIB image of a cross-sectioned “blister” defect on a MLD
(∼ 5µm thick) reveals the extent of cracking ∼ 4µm, thus
verifying our numerical results of t ∼ 4 – 4.8µm. . . . . . . . . 73
3.14 w (a) is seen to have a (small) dependence on the parabolic
profile of b(x). . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 74
3.15 Coating design for run 44T0954. . . . . . . . . . . . . . . . . . 76
3.16 Coating design for run 20T1056. . . . . . . . . . . . . . . . . . 77

4.1 Schematic (adapted from Smith et al. [12] and Ashe et al.
[13]) showing grating manufacture process used at PGL. The
grating is patterned using SBIL, undergoes two reactive ion
beam etching (RIBE) processes to etch away ARC and shape
the pillar geometry, and finally it is chemically cleaned to strip
photoresist, ARC and debris. . . . . . . . . . . . . . . . . . . . . . 86
4.2 SEM micrograph showing a close-up of the grating pillar ge-
ometry (oblique view obtained from a cleaved grating). . . . . 87
4.3 Controlled nano-indentation can invoke 3 different responses
in MLD gratings. These are ductile, ductile-brittle mixed and
fracture (pure brittle); also discernable by looking at their
respective load-displacement curves. . . . . . . . . . . . . . . . 88
4.4 Indents were generated in an array to invoke ductile and brittle response in the silica walls at loads of 0.4 mN and 0.5 mN. “Centered” indents were confined to a single wall whereas the “off-centered” indents caused fracture in adjacent walls too. Reprinted from Mehrotra et al. (14) with permission from Cambridge University Press. 90

4.5 “Centered” indents made at 0.4 and 0.5 mN show deformation on a single silica wall. Reprinted from Mehrotra et al. in MRS Proceedings (14) with permission from Cambridge University Press. 91

4.6 “Off-centered” indents at 0.4 and 0.5 mN loads show catastrophic damage to the silica walls. The damage extends to three grating walls. Reprinted from Mehrotra et al. in MRS Proceedings (14) with permission from Cambridge University Press. 91

4.7 Load-displacement curves for indentation on “pillars” at 0.4 and 0.5 mN loads. Comparison to bulk fused silica is also shown. Reprinted from Mehrotra et al. in MRS Proceedings (14) with permission from Cambridge University Press. 92

4.8a Load-displacement curves from in-situ SEM indentation performed at EMPA show the changes in nano-mechanical response of the sample as offset is changed from 0 nm (centered indent) to 200 nm (fully off-centered indent). 93
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8b</td>
<td>Maximum load corresponding to each offset distance for indents in Figure 4-8(a).</td>
<td>94</td>
</tr>
<tr>
<td>4.9</td>
<td>SEM images of in-situ nano-indentation shows the transition from a “centered” indent in (a) to completely “off-centered” in (f). Damage evolves as the offset goes from 0 to 200 nm.</td>
<td>95</td>
</tr>
<tr>
<td>4.10</td>
<td>2-D finite-element analysis (FEA) of a “centered” nano-indentation experiment corresponding to conditions generated at a load of 0.5 mN.</td>
<td>96</td>
</tr>
<tr>
<td>4.11</td>
<td>Meshing and set-up of a 2-D plane-strain simulation for a “centered” indent.</td>
<td>97</td>
</tr>
<tr>
<td>4.12</td>
<td>“Centered” indent at a penetration depth of 170 nm shows a von-Mises stress of $\sim 4.7$ GPa in the region of contact (top of the wall).</td>
<td>98</td>
</tr>
<tr>
<td>4.13</td>
<td>“Off-Centered” indent at a penetration depth of 170 nm shows a maximum principal stress of $\sim 3.1 - 3.6$ GPa along the walls of the grating and at the base.</td>
<td>99</td>
</tr>
<tr>
<td>4.14</td>
<td>Von-Mises stresses corresponding to a nano-indentation experiment performed at a load of 0.5 mN. The maximum stresses are observed at the top of the grating wall.</td>
<td>100</td>
</tr>
</tbody>
</table>
4.15a 25% off-centered indent at a penetration depth of 100 nm. It is evident that this amount of offset is not enough to affect the adjacent silica wall. The maximum principal stresses generated are concentrated on the wall that made contact with the indenter tip. As a result there is mainly plastic deformation (represented by the “stretching”) and possibly some fracture at the base of the wall.

4.15b This figure shows the maximum principal stresses plotted on the grating’s surface after nano-indentation was performed at an offset distance of \( \sim 120 \) nm from the central axis of the grating wall and is referred to 50% off-centered indent. Clearly, at a modest penetration depth of 100 nm, the damage has extended to the adjacent silica wall as well. The wall on the left, where contact is first made, also experiences some initial plastic deformation (“stretching”) but soon high levels of stress (\( \sim 4.5 \) GPa) become concentrated at the base of the wall.

4.15c Completely or, 100% off-centered indent at a depth of \( \sim 100 \) nm produces similar damage on the adjoining wall.

4.16a 100% off-centered indent at a 50 nm penetration depth.

4.16b 100% off-centered indent at a 100 nm penetration depth.

4.16c 100% off-centered indent at a 170 nm penetration depth.

4.16d 100% off-centered indent at a 250 nm penetration depth.
4.17 Illustration showing the indentation response of the grating pillar as explained by our stress-strain model. ................................................................. 107

4.18 Correlation of $(\sigma_Y / H_v)$ with measured hardness and Young’s modulus for $\nu = 0.1, 0.2$ and $0.3$. Notice that the hardness $H_v$ is measured using a Vickers indent. ................................................. 110

4.19 Hypothesis on the fracture mechanism of the grating walls. ................................................................. 112

4.20 SEM images of broken grating walls help in calculation of fracture stress at the base of the wall. The dimensions ‘aa’ and ‘bb’ are $\sim 2000$ nm and $\sim 800$ nm respectively. ................................................................. 113

4.21 The 3 unique responses to nano-indentation performed on a MLD grating helps in analyzing ductility and fracture separately; this is otherwise not possible in bulk materials. At the nano-scale, glass (silica) shows uncharacteristically high strengths (1- 4 GPa) because in the form of a patterned surface it can accommodate stresses by “stretching” like metals. ................................................................. 118

5.1 SEM image of N-on-1 laser-induced damage site on the MLD grating structure. ................................................................. 130

5.2 Three distinct nano-indentation responses are seen in MLD gratings. ................................................................. 133

5.3 Load-displacement curves of nano-indentation on gratings. ................................................................. 135
5.4 Location of initiation of fracture is measured using the load-displacement curves for off-centered indents made on the MLD gratings. ................................. 136
5.5 Relationship of LIDT and minimum depth of penetration into the MLD grating needed to initiate fracture. ................................. 137
5.6 Relationship of LIDT and minimum depth of penetration into the MLD grating needed to initiate fracture. ................................. 138
5.7 Relationship of LIDT and minimum depth of penetration into the MLD grating needed to initiate fracture. ................................. 139
5.8 Pores on the “floor” of the grating structure can lead to reduced LIDT of the grating. ................................. 140
5.9 Finer meshing is used in the region of contact of the indenter tip on the grating structure. ................................. 143
5.10 Grating was modeled as an elastic-plastic material with silica “walls” and one hafnia layer of the MLD coating. The height of the grating is 440 nm, and the spacing is 500 nm. ................................. 144
5.11 The ABAQUS® simulations were run using these 4 set-ups to represent “centered” and “off-centered” indents. ................................. 145
5.12a Damage is restricted to a single wall for penetration depth of 50 nm. The height of the grating is 440 nm, and the spacing is 500 nm. ................................. 146
5.12b As penetration depth is increased to 100 nm, damage extends to the adjacent wall. ................................. 147
5.12c At penetration depth of 170 nm there is significant damage on the adjacent wall. 147

5.12d At full penetration depths of 250 nm, both walls will fracture indicated by the build-up of tensile maximum principal stress along the walls. 148

5.13 Simulation shows that the mechanical contribution of radiation pressure exerted on the gratings is concentrated at the base of the walls. The height of the grating is 440 nm, and the spacing is 500 nm. 150

5.14a Ideal grating (no defects) - no significant accumulation of stresses at 50 nm penetration depth. 152

5.14b Disfigured grating shows accumulation of stresses at 50 nm penetration depth. 153

5.15a Plastic strain depicted as a shear band is not prominent except in the area of contact with the indenter tip. 154

5.15b Shear band due to the plastic strain is prominent due to the disfigured shape of the grating modeled and extends across the top width of the grating wall. 154

5.16 Concentration of high levels of tensile stress at the pore on the grating “floor” from nano-indentation testing. 155

5.17a Stresses concentrated at the base of the grating walls during an optical test cause “uprooting” as seen here. Thermal stresses cause “melting” of the material. 163
5.17b “Chipping” mechanism of failure in gratings after a laser damage test. ....................... 164

5.18 Geometry of grating in contact with nano-indenter tip used to calculate fracture strain. ....................... 166

5.19 Normalized plot showing the dependence of damage thresholds on fracture strain developed in gratings during nano-indentation testing. ....................... 168

5.20 Nano-indentation exposes the same areas of the grating structure as an optical test by concentrating mechanical fields (stress, strain) in the regions normally associated with amplified electric fields. ....................... 170

6.1 Comparison of nanoindentation data obtained at various RH% from Ashcroft lab. Clearly the higher humidity levels have a marked difference on the mechanical properties of the multilayer. Data from England is also compared to data from our lab. ....................... 182

6.2 Load-displacement curves generated (Ashcroft lab) at different loads for the multilayer held at RH ~80%. The plots show a “step” type behavior that can be correlated to the number of layers in the multilayer tested. ....................... 183
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>Load-displacement curves generated (Ashcroft lab) at different loads for the multilayer held at RH $\sim 80%$. The plots show a “step” type behavior that can be correlated to the number of layers in the multilayer tested.</td>
<td>186</td>
</tr>
<tr>
<td>6.4</td>
<td>Load-displacement curves generated (Ashcroft lab) at different loads for the multilayer held at RH $\sim 80%$. The plots show a “step” type behavior that can be correlated to the number of layers in the multilayer tested.</td>
<td>187</td>
</tr>
</tbody>
</table>
## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$\Delta$</td>
<td>Initiation of fracture</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Strain</td>
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<tr>
<td>$\lambda$</td>
<td>Proportionality constant</td>
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<td>$\gamma$</td>
<td>Absorptivity</td>
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<td>Shear Modulus</td>
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<td>Poisson ratio</td>
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<td>$\sigma_Y$</td>
<td>Yield stress</td>
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<td>Contact area</td>
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<td>$b$</td>
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<td>$b$</td>
<td>Grating base, p.110</td>
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<tr>
<td>$B$</td>
<td>Bulk Modulus</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light</td>
</tr>
<tr>
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<td>Thermal diffusivity</td>
</tr>
<tr>
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</tr>
<tr>
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<td>Indentation force</td>
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<td>$h^*$</td>
<td>Indentation length parameter</td>
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<td>$H_0$</td>
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<td>$L$</td>
<td>Blister length, p. 69</td>
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<tr>
<td>$p_{rad}$</td>
<td>Radiation pressure</td>
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<td>Load</td>
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<td>$S$</td>
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<td>--------</td>
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</tr>
<tr>
<td>$T_{cr}$</td>
<td>Critical temperature</td>
</tr>
<tr>
<td>V</td>
<td>Volume fraction</td>
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<tr>
<td>w</td>
<td>Blister deflection</td>
</tr>
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<td></td>
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Chapter 1

Introduction

As work in inertial confinement fusion (ICF) and the fast ignition concept have expanded and evolved over the past few decades, so too have the laser systems that support ICF research. Ultra-short pulse, high power laser systems place stringent requirements on optical components in terms of both optical performance and resistance to laser damage. At the Laboratory for Laser Energetics (LLE) [University of Rochester], the peak power capability – and thus the overall performance – of the petawatt-class OMEGA EP (Extended Performance) laser system is limited by the laser damage resistance of diffraction gratings (Figure 1-1) in the chirped-pulse amplification (CPA) [1, 2, 3] pulse compressors for each beam line. Improving the damage thresholds of these components is therefore an important objective at LLE.

The multilayer dielectric (MLD) gratings used in OMEGA EP’s pulse compressors are surface relief gratings, composed of an MLD mirror with a periodically grooved top diffraction layer. The MLD high reflector is a modified quarter-wave stack of alternating low and high refractive index layers
on a glass substrate, typically hafnia ($HfO_2$) and silica ($SiO_2$) coated onto BK7 or fused silica glass. The grating is patterned by small-beam interference lithography (SBIL) and etched into the top silica MLD layer. During the final step, aggressive chemical cleaners such as acid piranha (mixture of $H_2O_2$ and $H_2SO_4$) are used to strip away residual photoresist, antireflective coating (ARC), and other debris from the grating surface. There is some concern that this cleaning step mechanically weakens the fragile grating pillars, possibly affecting the grating's optical performance as well as its resistance to laser damage. The development of a methodology for monitoring a grating's mechanical properties could enable a better understanding of the fabrication and cleaning process, and point to appropriate modifications that will preserve the grating's integrity.

This thesis, therefore, is aimed towards measuring the mechanical response of optical multilayer dielectric (MLD) coatings and MLD diffraction gratings using nano-indentation and related tools. The advantage of using nano-indentation is that it has sub-nm resolution in measured deflections, and as such can sense surface-specific properties of the material at defined locations as well as the response of nano/micro sized structures that might be manufactured on it.

Our research methodology uses nano-indentation (experimental tool), electron microscopy (analytical tool), and finite-element simulations (computational tool) to analyze nano- and micro-structures, 100 nm - 5 μm, (MLD coatings) and patterned nano-structures, 20 nm - 500 nm, (MLD gratings).
Chapter 1. Introduction

We have answered the following broad questions:

1. How does glass (comprised mainly of brittle amorphous silica) behave at the nano-meter scale? What is the strength of glass (or, silica) at the nm-scale? Can we study controlled deformation in patterned silica surfaces to understand the nano-level phenomenon affecting the behavior of amorphous silica?

2. Can we use the understanding of nano-mechanics of deformation in silica meta-surfaces, from above, to seek correlations with optical testing in MLD gratings (for example, laser-induced damage tests)? How do defects in these nano-structures affect the concentration of mechanical (stress, strain)
and optical (electric, magnetic) fields?

However, it must be pointed out that there are a number of challenges that need to be addressed before a correlation between optical (laser) damage and nano-mechanical features/response can be established. These challenges are four-fold.

Firstly, we are working with an optical device with materials in non-bulk form – single layer thin films, multilayer dielectric coatings and high-aspect ratio silica walls in the form of diffraction gratings built on top of bulk glass. Specifically, MLD diffraction gratings are composed of amorphous silica deposited by evaporation of quartz and patterned using lithography techniques. Bulk glass is brittle and therefore measurement of uniaxial yield stress is not possible since fracture precedes yield. Geometries like multilayer diffraction grating “walls”, constrained in one transverse direction but free in the other, produce indentation response which is significantly different from both bulk materials (fully constrained) and free-standing pillars (completely unconstrained) when tested at the nanoscale. Therefore, we have to address the relative contributions of glass deformation (governed by hardness or uniaxial yield stress) and glass fracture (governed by fracture toughness) in determining the overall deformation of surfaces. Whereas nano-indentation of flat surfaces couples fracture and deformation, we show that nano-indentation of patterned optical surfaces allows the separate estimates of deformation and fracture of optical materials. In other words, a patterned surface may separately exhibit ductile or brittle behavior at the same imposed load or depth.
of penetration.

Secondly, our materials of interest are either completely amorphous (silica) or very slightly crystalline, but mostly amorphous (hafnia). This makes deformation more challenging to understand than in crystalline micro- and nano-structures where slip lines and dislocations accompany deformation and are extensively understood and researched. The challenge in our work is that deformation mechanisms, elasticity and plasticity are not well understood for amorphous materials at the nano-scale from the experimental point of view.

Thirdly, the overall scope of this work encompasses features as small as 10’s of nanometers (silica grating walls and surface defects such as pores) to 10’s of micrometers (individual layer thin films and associated “blister” defects). This requires our research methodology to be robust enough to address the entire range of features in our optical devices.

Lastly, from the computational aspect it is important to identify features on the MLD gratings that can be modeled efficiently to produce meaningful results that can be compared to experimental data on the nano-level. For example, we need to simulate defects on these optical nano-structures, but will it be computationally efficient to do so in 3-D space? Choosing between 2-D and 3-D simulations for modeling defect-induced and defect-free deformation that truly represents nano-indentation experiments is essential to achieve optimal results and insights into nano-mechanical behavior of our materials.

Therefore, we have used a combination of experimental, analytical and
computational tools to address the grand challenge of correlating the laser damage response to the nano-mechanical response in important optical structures (MLD diffraction gratings). We approach this by first measuring the thin film properties – both individual and multilayers, carrying out surface forensics, that is, defect characterization in MLDs, and then addressing ductility and brittleness at the sub-100 nm scale of brittle silica walls in optical gratings and, finally making our way to correlate mechanical and optical fields. Each aspect of this approach is briefed below and detailed in the following chapters.

In Chapter 2 we have measured the nano-mechanical properties of single-layer thin films (silica, hafnia, alumina and niobia) corresponding to their respective thicknesses used in multi-layer formation. The thin films are deposited using electron-beam deposition methods (accompanied by plasma-energy source for niobia) and are optimized for maximizing laser-damage thresholds for use in the OMEGA EP laser system. We emphasize that these measurements are specific to our thin films only because deposition tools and conditions have a profound impact on the microstructure of the film and hence, its mechanical properties. Also, performing experiments on single-layer films of thicknesses corresponding to those used to manufacture entire 5 - 8 μm thick MLDs allows us some basis to extrapolate properties of MLD based on properties of their single-layer components.

We have established nano-mechanical properties (elastic modulus, E and hardness, H) of our MLD coatings we use our understanding of these nano-
indentation experiments to investigate “blister” defects in MLDs in Chapter 3. Aggressive cleaning chemistries that incorporate acid piranha are used on MLDs in order to increase their laser-damage thresholds and are meant to remove any form of organic contaminants and other residues from the surface of the coating. Under certain circumstances, the cleaning procedures can sometimes lead to the formation of “blisters” on our MLD coatings. In this chapter we investigate the influence of these defects on the near-surface mechanical properties of the MLDs. We also use analytical methods to understand the geometry and the formation mechanism of these “blister” defects.

In Chapter 4, we turn our focus to the entire optical device - MLD diffraction gratings, or the (silica) grooves/walls built on the top silica layer of the high laser-damage threshold coatings analyzed in Chapters 2 and 3. The patterned nature of the top surface of these devices – parallel nano-walls, allows us to use carefully controlled nano-indentation to separate ductile deformation from brittle fracture. This phenomenon is otherwise not possible in bulk, brittle surfaces as fracture precedes pure ductile deformation or in other words, there is no yield preceding cracking in bulk materials. This result, in our opinion, is novel and unique. We have shown in this chapter that it is possible to obtain ductile deformation in glass (silica) at the 50 - 100 nm-scale and therefore, calculate its yield stress. Accompanying numerical simulations show an excellent correlation with our experimental results. Estimates of fracture strength at the nano-scale for silica are also derived.
Chapter 1. Introduction

The experimental methods used in Chapter 4 are expanded upon in Chapter 5 to include the combined effects of ductility and fracture in MLD gratings for correlating nano-mechanical damage and laser-induced damage. In this chapter, we explore the use of fracture strain (used to measure the mechanical performance of MLD gratings) to relate mechanical deformation via fracture to laser-induced damage thresholds (measure of optical performance of MLD gratings). Additionally, we model defects and undulations (material and geometrical inhomogeneities) associated with the gratings to investigate where nano-indentation mechanical fields (stress, strain) and laser-damage optical fields (electric, magnetic) are concentrated on the surface of the grating structure.

In the last section of the dissertation - Chapter 6, we summarize the main conclusions of our study and present considerations for future work.
References


Chapter 2

Nano-mechanical properties of single- and multi-layer optical oxide thin films grown by electron-beam deposition

2.1 Introduction

Oxide coatings for optical applications such as high-intensity laser systems must meet stringent specifications of long-lasting optical stability and high laser-damage resistance. Therefore, it is necessary to accurately estimate intrinsic and thermally induced stresses and mechanical properties of these coatings. Silica ($\text{SiO}_2$), hafnia ($\text{HfO}_2$), and alumina ($\text{Al}_2\text{O}_3$) are among the most-important oxide thin-film materials for the manufacture of coatings that have high laser-damage thresholds. Examples include high-reflectivity mirrors and polarizers [1] manufactured from multilayer dielectric (MLD) coatings consisting of ~200-nm-thick, alternating low- and high-refractive-index layers ($\text{SiO}_2$ and $\text{HfO}_2$, respectively) coated on glass (fused silica, BK7, etc.) substrates, for a total physical thickness of ~5 to 8 μm [2]. The
mechanical properties of the single layers of these oxide thin films with thicknesses equivalent to those used in multilayers as well as the entire multilayer are of interest to us.

One of the important applications of the measured nano-mechanical properties is in studying the failure of thin films in a multilayer system composed of alternating layers of silica and hafnia; this was used in an earlier published work [3] that focused on understanding the fracture mechanics of a defect in optical multilayer thin-film systems when exposed to cleaning procedures. Another application of measuring properties of single-layer thin films is in the design of mechanical properties (modulus and hardness) of thin-film multilayers. This makes it critical to know the accurate properties for individual films that comprise these multilayers.

It is known [4, 5, 6] that changing the parameters of the deposition process—namely, oxygen backfill pressure, temperature, and rate of deposition—causes a change in the structural integrity of the thin film including its porosity and microstructure. This might lead to differences in measured mechanical properties even under the same test conditions for the same material deposited on an identical substrate. Therefore, when reporting measured mechanical properties of thin films, they should ideally be accompanied by information on deposition parameters, and the reported values should be used only as a reference under those stated deposition conditions.

In our work, we use nano-indentation on thin, single- and multi-layer films, to extract simultaneously from the measured load-displacement curves
the elastic modulus and hardness of these films.

Additionally, indentation size effects (ISE) have been investigated in the multilayer thin films (\textit{SiO}_2 – \textit{HfO}_2 systems). These effects are generally known to be dominant in metallic thin films [7]. Although our multilayers are mostly amorphous, the presence of hafnia in the stack might lead to this effect. Studies have confirmed that micro hardness is a function of the applied test load, where the experimentally measured hardness increases as test loads decrease [8]. This effect is termed as ISE and has been attributed to a variety of reasons [9] including result of glass viscous flow at rapid strain-rate near the surface (Brau), combined elastic and plastic deformation, friction between indenter material [8, 10], strain-gradient plasticity [7, 11, 12, 13] and as an artifact induced by indentation pile-up [14, 15]. No one reason completely or universally describes the ISE but each appears applicable for specific cases. In the region of scale between the atomistic and gradient microstructure regimes, there are possibly one or more phenomena that may contribute to an indentation size effect. Investigators have shown that the hardness of single crystalline and polycrystalline metals generally exhibit indentation size dependence in the nano and micro-scale regimes. It predicts an ISE because micro-plastic deformation in metals depends both on the local strain and the strain gradient caused largely due to geometrically necessary dislocations. The role of these geometrically necessary dislocations have been modeled using both mechanism-based [7] and phenomenological [12] strain gradient plasticity models.
2.2 Materials and Methods

2.2.1 Electron beam deposition of single- and multi-layer thin films

Three single-layer thin films - $SiO_2$, $HfO_2$, and $Al_2O_3$ - were grown using electron-beam deposition (EBD), while niobia ($Nb_2O_5$) was grown using plasma-ion–assisted electron-beam deposition (PIAD). The $SiO_2 - HfO_2$ multilayer system was manufactured using EBD simply by alternating both materials in the same coating until the desired design is achieved. All depositions were performed in vacuum using the 54 in. coating system shown in Figure 2-1. Hafnium metal was evaporated from a six-pocket electron-beam gun and oxidized as it condensed at the substrate surface by back-filling the vacuum chamber with oxygen gas to a pressure of $8.0 \times 10^{-5}$ Torr. Alumina was also deposited from the six-pocket electron-beam source, while silica was deposited from a continuously rotating pan-type electron-beam gun. Niobia was grown by evaporating niobium metal (99.99% pure) as the source material using a single plasma source to energetically assist the electron-beam deposition process. Using a plasma source ensures the complete oxidation of the film, which is otherwise not possible with regular EBD and also allows for a more-energetic process, leading to increased densification of the thin film [16]. Substrate (glass) temperature was maintained at 140°C for depositing all films except niobia for which the substrate temperature was 130°C (we had earlier established that these were the optimized growth pa-
rameters for our films). Deposition was performed on five 25.4-mm-diam x 0.25-mm-thick fused-silica substrates placed in the planetary rotation system for each material deposition. The thicknesses of the deposited single layers along with the process parameters are summarized in Table 2-1. Four samples of silica-hafnia multilayers were prepared on Pyrex substrates measuring 25.4-mm-diam x 1-mm-thickness using the same process parameters as for single-layer films. Design of one such multilayer system is shown in Figure 2-2. Thicknesses of the films being deposited were monitored and controlled inside the coating chamber using a three-quartz-crystal monitoring setup.

Figure 2.1: The 54-in. vacuum chamber used to deposit the reported single-and multi-layer thin films.
### Chapter 2. Nano-mechanical properties of thin films

#### Figure 2.2: Multilayer thin film design used for this study.

<table>
<thead>
<tr>
<th>Layer#</th>
<th>Material</th>
<th>Thickness (nm)</th>
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<tbody>
<tr>
<td>1</td>
<td>Hafnia</td>
<td>135.6</td>
</tr>
<tr>
<td>2</td>
<td>Silica</td>
<td>180.0</td>
</tr>
<tr>
<td>3</td>
<td>Hafnia</td>
<td>135.6</td>
</tr>
<tr>
<td>4</td>
<td>Silica</td>
<td>180.0</td>
</tr>
<tr>
<td>5</td>
<td>Hafnia</td>
<td>135.6</td>
</tr>
<tr>
<td>6</td>
<td>Silica</td>
<td>180.0</td>
</tr>
<tr>
<td>7</td>
<td>Hafnia</td>
<td>135.6</td>
</tr>
<tr>
<td>8</td>
<td>Silica</td>
<td>180.0</td>
</tr>
<tr>
<td>9</td>
<td>Hafnia</td>
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<td>10</td>
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<td>11</td>
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<td>28</td>
<td>Silica</td>
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| AIR    |            |                |

Total Thickness (in um): 46
Table 2.1: Process parameters for electron-beam deposition (including plasma-assist deposition) of single-layer coatings.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Deposition rate (nm/s); Temp (°C)</th>
<th>Oxygen back-fill pressure (Torr)</th>
<th>Electron-beam voltage (keV)</th>
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<tr>
<td>Hafnia</td>
<td>160</td>
<td>0.15; 140</td>
<td>8.0 x 10^-5</td>
<td>7.5</td>
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<tr>
<td>Silica</td>
<td>180</td>
<td>0.46; 140</td>
<td>not used</td>
<td>6</td>
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<tr>
<td>Alumina</td>
<td>160</td>
<td>0.20; 140</td>
<td>8.0 x 10^-5</td>
<td>7.5</td>
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<tr>
<td>Niobia*</td>
<td>500</td>
<td>0.12; 130</td>
<td>not used</td>
<td>6</td>
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</table>

*55.0 standard cubic centimeters (sccm) of O$_2$ were used as a process gas for reactive deposition above the plasma chamber to increase both the reactivity of the plasma and the oxidation of the film.

2.2.2 Nano-indentation

All indentation experiments on the single- and multi-layer thin films were performed on the MTS Nano Instruments Nanoindenter XP. The system was fitted with a Berkovitch tip, which is a three-sided, pyramidal diamond tip (face angle $\sim 65.03^\circ$), and the tip area’s function was calibrated by performing nano-indentation on fused silica. In addition to the Berkovitch tip, a Cube-corner tip (face angle $\sim 35.26^\circ$), was also used to perform indentation testing on multilayers. Our study focused on measuring the hardness and elastic modulus of the single-layer coatings via the Oliver–Pharr method [17]. The empirical observation [18], which states that for the reliable measurement of mechanical properties it is necessary that the obtained nano-indentation data have minimal or, if possible, no “substrate effect,” was followed to report near-surface values of elastic modulus and hardness. This implies that the
maximum depth of penetration of the indenter tip into the thin film, when making such measurements, should not be more than 10% to 15% of the total film thickness, especially when calculating the hardness value for the thin films.

a. Single-layer thin film samples

Typical loads varied from 0.15 to 1.5 mN, and data were obtained for penetration depths amounting up to $\sim$50% of individual film thicknesses. Eight to twelve indents were performed on one sample of each of the single-layer thin films. Given the significantly small thicknesses (<200 nm) of $SiO_2$, $HfO_2$, and $Al_2O_3$, various loads ranging from 0.15 to 15 mN were used to generate results for penetration depths varying from 10% to 50% of the total single-layer thickness. On the other hand, $Nb_2O_5$ was a slightly thicker film (500 nm) and loads of 0.2 to 15 mN were required to probe 5% to 70% of the total film thickness. Indents were approximately spaced 100 to 150 $\mu$m apart to prevent any overlap.

b. Multilayer thin film samples

Loads in the range of 10 mN to 400 mN were used to perform indents on four samples of identical silica-hafnia multilayer coatings using both Berkovich and Cube-corner tips. 25 indents were made for lower loads (10 - 50 mN) whereas 12 indents were made at higher loads (100 - 400 mN). Load-displacement curves were recorded for each indent. The parameters chosen were kept con-
stant for both the tips. The surface approach velocity was kept constant at 5 nm/s. Drift correction was performed and the allowable drift rate was 0.05 nm/s. While applying the load, the time to load and also the time to hold were set to 10 s. The percent unloading was set to 90%. The hold periods are used to allow time dependent plastic effects to diminish.

2.3 Results

2.3.1 Single-layer thin films

The cross sections of the films used for testing are shown using SEM in Figure 2-3. It is noteworthy that the interface of the silica film on the silica substrate cannot be seen because of the chemical homogeneity of the film and substrate. Figure 2-4 shows the load-displacement curves for all measurements, which indicate that there were no anomalies such as “pop-in” events observed in the measurement of the above-reported values and that the tests were, therefore, reliable for reporting the near-surface mechanical properties. Once these data are generated, the elastic modulus and hardness can be reported as a range over the 10% to 15% of the film thickness tested (shown in Figure 2-5). Based on the above results, elastic modulus and hardness corresponding to nano-indentation penetration depths of ~10% to 15% are reported in Table 2-2. It should be noted that these measured values are specifically for the deposition conditions mentioned earlier in the study.
Chapter 2. Nano-mechanical properties of thin films

Figure 2.3: SEM images of the single-layer thin film coating used in this study.
Figure 2.4a: Load-displacement curves for single-layer hafnia thin film.

Figure 2.4b: Load-displacement curves for single-layer silica thin film.
Figure 2.4c: Load-displacement curves for single-layer alumina thin film. It should be noted that the abscissae for Figs. 2-4(a) and 2-4(b) are identical to that for Fig. 2-4(c).

Figure 2.4d: Load-displacement curves for single-layer niobia thin film.
Chapter 2. Nano-mechanical properties of thin films

Figure 2.5: Measured near-surface values of elastic modulus and hardness for the four single-layer coatings. The blue band indicates the region of interest and encompasses the values measured for 10% to 15% of the total film thickness for each single layer, respectively. It should be noted that the abscissae for Figs. 2-5(a) and 2-5(b) are identical to those of Figs. 2-5(c) and 2-5(d).
Chapter 2. Nano-mechanical properties of thin films

Table 2.2: Extracted near-surface mechanical properties corresponding to penetration depths of \(\sim 10\%\) to 15\% of the total film thickness.

<table>
<thead>
<tr>
<th>Single-layer thin film</th>
<th>Elastic Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hafnia</td>
<td>128 ±12</td>
<td>8.7 ±0.4</td>
</tr>
<tr>
<td>Silica</td>
<td>93 ±5</td>
<td>12.3 ±0.3</td>
</tr>
<tr>
<td>Alumina</td>
<td>148 ±17</td>
<td>12.1 ±0.6</td>
</tr>
<tr>
<td>Niobia</td>
<td>130 ±4</td>
<td>8.1 ±0.5</td>
</tr>
</tbody>
</table>

2.3.2 Silica-hafnia multilayer thin films

The cross-section of a silica-hafnia multilayer system using the EBD is shown in Figure 2-6. The coating is composed of alternating low-refractive index (silica \(\sim 180\) nm thick) and high-refractive index (hafnia \(\sim 130\) nm) layers. While silica is completely amorphous, it is seen that hafnia deposits as a columnar structure made up of small crystallites which lends it a slight-crystalline nature.

The measured indentation response is reported in the form of load-displacement curves for both Berkovich (Figure 2-7) and Cube-corner tips (Figure 2-8). The fact that the thickness of our multilayer coating is several microns relaxes the empirical law [18] followed strictly for the single-layer films in order to eliminate the substrate effect. Instead, we made sure that depth of penetration did not exceed the thickness of the thin film.

Using the data from indents (an example is shown in Figure 2-9) performed using a Berkovich tip the following values of hardness and elastic modulus are reported in Table 2-3.
Chapter 2. Nano-mechanical properties of thin films

Figure 2.6: Cross-section of a multilayer thin film coating used in this study. It is made up of alternating layers of silica and hafnia.

Figure 2.7: Load-displacement curves using a Berkovich tip show penetration depths $\sim 500$–$2500$ nm ($\approx 19$ individual layers in the multilayer stack for loads ranging from 10 - 400 mN.
Chapter 2. Nano-mechanical properties of thin films

Figure 2.8: Load-displacement curves using a Cube-corner tips how penetration depths $\sim 600-3500$ nm ($\approx 23$ individual layers in the multilayer stack) for loads ranging from 10 - 400 mN.

Table 2.3: Extracted near-surface mechanical properties corresponding to penetration depths of $\sim 10\%$ to $15\%$ of the total film thickness.

<table>
<thead>
<tr>
<th>$P$ (mN)</th>
<th>Displacement (nm)</th>
<th>$E$ (GPa)</th>
<th>$H$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>337</td>
<td>2.5</td>
<td>36.6</td>
</tr>
<tr>
<td>10</td>
<td>477</td>
<td>2.6</td>
<td>38</td>
</tr>
<tr>
<td>50</td>
<td>1072</td>
<td>2.65</td>
<td>44.7</td>
</tr>
<tr>
<td>100</td>
<td>1498</td>
<td>2.7</td>
<td>48.8</td>
</tr>
<tr>
<td>200</td>
<td>2068</td>
<td>2.9</td>
<td>52.4</td>
</tr>
<tr>
<td>400</td>
<td>2797</td>
<td>3.2</td>
<td>56.3</td>
</tr>
</tbody>
</table>
Figure 2.9: SEM image of an indent made using a Berkovich tip typical for loads 10 - 20 mN.
2.4 Discussion

2.4.1 Single-layer thin films

To put the values shown in Figure 2-5 in perspective and see how they compare against each other, the extracted mechanical properties of each of the tested films were plotted as the elastic modulus [Figure 2-10(a)] and hardness [Figure 2-10 (b)]. Alumina has the highest modulus and hardness, which can probably be attributed to the relatively dense film structure without the presence of micro-columnar pores indicated by the fact that these films exhibit tensile stresses while allowing for very slow water-diffusion rates [19, 20]. Silica, which is also amorphous, has a high hardness (highest along with alumina) but the lowest modulus among the tested films. Hafnia, deposited using electron-beam technology, is slightly crystalline and has a porous, columnar microstructure [4, 21] (shown in the SEM images in Figure 2-3). It is seen that the measured nano-indentation modulus and hardness of hafnia is very similar to that of niobia. To determine the microstructure of niobia x-ray diffraction (XRD) phase scans, glancing angle scans and texture measurements were conducted on the single-layer thin film. Tests revealed that the film was mostly amorphous, but no conclusions were made about the porosity of the niobia single-layer coating.

Table 2-4 compares the measured values and properties of thin films used in the present study to those of films (manufactured with the same materials)
that are reported in literature, deposited by similar techniques, and used for similar applications such as in optical interference coatings. The measured Young’s modulus of the four films used in this study, reported in Figure 2-11 as “Thin film (present study),” is compared to Young’s modulus of the same four films from literature [22, 23] and is shown as “Thin film (literature)” in Figure 2-11. The film values are also compared to bulk values (where data were available). The bulk value was significantly higher than that of any film of the same material (no bulk value of niobia is reported).

For films deposited using conventional electron-beam deposition (hafnia, silica, and alumina), the values of modulus reported in the present study were different from the films reported in literature, even though the same growth technique was used, indicating the importance of particulars of the deposition conditions. For hafnia, this difference in modulus can be attributed to differences in the temperature to which the substrate is heated. Higher substrate temperatures used for hafnia, as reported in the literature [22], are seen to be associated with films of higher stiffness and lower levels of porosity. Therefore these films are expected to be much denser than films used in the present study, which have a more-porous microstructure from both the low kinetic energy of the atoms condensing on the substrate and the lower substrate temperatures. It is important to note here that this study was not carried out to deposit films whose mechanical properties match with films reported in literature.

The films used in the present study are designed and deposited in a highly
Chapter 2. Nano-mechanical properties of thin films

Figure 2.10: Elastic modulus corresponding to penetration depths approximately equal to 10% to 15% of the total film thickness. The data labels on the plots represent the mean of the measured values. (b) Hardness corresponding to penetration depths of approximately equal to 10% to 15% of the total film thickness. The data labels on the plots represent the mean of the measured values.
Table 2.4: Comparison with bulk and film properties reported in the literature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Thickness (nm)</th>
<th>Young's Modulus (GPa)</th>
<th>Measurement Method</th>
<th>Important deposition condition(s); known film properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hafnia [22]</td>
<td>Bulk</td>
<td>-</td>
<td>~300*</td>
<td>EMA/EFA slope (dσ/dT)</td>
<td>-</td>
</tr>
<tr>
<td>Hafnia [22]</td>
<td>Thin film (e-beam)</td>
<td>86</td>
<td>~200*</td>
<td>EMA/EFA slope (dσ/dT)</td>
<td>Substrate temperature 300°C; monoclinic; packing density 0.86 (porosity 0.14)</td>
</tr>
<tr>
<td>Hafnia</td>
<td>Thin film (e-beam)</td>
<td>160</td>
<td>128</td>
<td>Present study– nano-indentation</td>
<td>Substrate temperature 140°C; slightly monoclinic with crystallite size ~10 nm; suspected high porosity suggested from SEM images</td>
</tr>
<tr>
<td>Silica [22]</td>
<td>Bulk</td>
<td>-</td>
<td>72</td>
<td>EMA/EFA slope (dσ/dT)</td>
<td>-</td>
</tr>
<tr>
<td>Silica [22]</td>
<td>Thin film (e-beam)</td>
<td>60</td>
<td>72</td>
<td>EMA/EFA slope (dσ/dT)</td>
<td>Substrate temperature 300°C; amorphous</td>
</tr>
<tr>
<td>Silica</td>
<td>Thin film (e-beam)</td>
<td>180</td>
<td>93</td>
<td>Present study– nano-indentation</td>
<td>Substrate temperature 140°C; amorphous; porous</td>
</tr>
<tr>
<td>Alumina [22]</td>
<td>Bulk</td>
<td>-</td>
<td>~400*</td>
<td>EMA/EFA slope (dσ/dT)</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>Alumina [22]</td>
<td>Thin film (e-beam)</td>
<td>55</td>
<td>~70*</td>
<td>EMA/EFA slope (dσ/dT)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Alumina</td>
<td>Thin film (e-beam)</td>
<td>160</td>
<td>148</td>
<td>Present study– nano-indentation</td>
<td>Not determined</td>
</tr>
<tr>
<td>Niobia</td>
<td>Bulk</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Niobia [23]</td>
<td>Thin (PECVD) film</td>
<td>550</td>
<td>130</td>
<td>Szymanowski et al.– nano-indentation</td>
<td>100 to 200 sccm of O₂; amorphous; H ~ 10GPa</td>
</tr>
<tr>
<td>Niobia</td>
<td>Thin (PECVD) film</td>
<td>550</td>
<td>130</td>
<td>Present study– nano-indentation</td>
<td>55 sccm of O₂; amorphous; H ~ 8GPa; substrate temperature 130°C</td>
</tr>
</tbody>
</table>

*Indicates that for these materials, biaxial modulus was converted to Young’s modulus (using Poisson ratio values [16]) for purposes of comparison for this study.

PEVCD: plasma enhanced chemical vapor deposition; PIAD: plasma-ion–assisted deposition; EMA/EFA: effective medium approximation/effective field approximation.
Chapter 2. Nano-mechanical properties of thin films

Figure 2.11: Modulus for the different materials reported in this study in bulk and thin-film forms. No bulk value of niobia is reported.

controlled way to maximize their laser-damage resistance [1]. The modulus reported in literature for thin film silica is $\sim 25\%$ lower than what was measured in this study. This result is in contradiction to what one would expect based on the higher substrate temperatures alone that were used in the study reported in the literature [22]. This clearly indicates that other factors such as deposition rates (shown in Table 1 for the present study), geometry and size of the coating chamber (54 in. chamber for the present study) [24], and the angle of incidence of coating vapors on the substrate [24] (unknown cur-
Chapter 2. *Nano-mechanical properties of thin films* 33

rently) are also extremely important. It has been shown in literature [25, 26] that the thin-film density has a linearly decreasing relationship with the tangent of the incident angle of the evaporant flux, thereby indicating that porosity or void content of the film is increasing. Therefore, the combined effect of these parameters and the way they are controlled will govern the film structure (density and porosity) and consequently, its mechanical properties.

It is interesting to observe that, even for similar film thickness, our data via nano-indentation (present study) yield significantly different elastic modulus values compared to the approach via effective medium approximation. These differences are shown in Figure 2-11. This leads us to believe that the various coating parameters, such as size of the vacuum chamber, deposition rates used, substrate temperature, as well as deposition angle might be responsible for this difference. Interestingly, plasma-assist–deposited niobia films (literature and present study) have identical values of modulus (and similar hardness values), even though different amounts of process gas ($O_2$) were used to deposit the respective films. In this case, we surmise that the deposition technique was the dominating factor and changing one of the process parameters had no significant impact on the measured mechanical properties of this thin film.

As an example of this approach, we demonstrate how single-layer thin film properties may be used to analyze multilayer dielectric (MLD) thin films used for high-laser damage threshold applications. We will select a hafnia-silica multilayer thin film system, merely as an example, to show how
individual thin-film properties (elastic modulus, $E$) can be used to predict the shear modulus, $\mu$ and bulk modulus, $B$ for the multilayer thin-film using the relations:

\[
\mu = E/2(1 + \nu) \quad (2.1)
\]

and,

\[
B = E/3(1 - 2\nu) \quad (2.2)
\]

In this case the volume fractions of hafnia and silica in the multilayer thin film system are 0.39 and 0.61, respectively. The upper and lower limits on shear modulus and bulk modulus were calculated by the rule of mixtures,

\[
(\mu_{MLD})_{upper} = \mu_{\text{hafnia}}V_{\text{hafnia}} + \mu_{\text{silica}}V_{\text{silica}} \quad (2.3)
\]

\[
(B_{MLD})_{upper} = B_{\text{hafnia}}V_{\text{hafnia}} + B_{\text{silica}}V_{\text{silica}} \quad (2.4)
\]

and,

\[
1/(\mu_{MLD})_{lower} = (V_{\text{hafnia}}/\mu_{\text{hafnia}}) + (V_{\text{silica}}/\mu_{\text{silica}}) \quad (2.5)
\]
\[
1/(B_{\text{MLD}})_{\text{lower}} = (V_{\text{hafnia}}/B_{\text{hafnia}}) + (V_{\text{silica}}/B_{\text{silica}})
\] (2.6)

where, \(V_{\text{hafnia}}\) and \(V_{\text{silica}}\) are the volume fractions of hafnia and silica. The lower and upper limits on bulk modulus were calculated to be 58.4 GPa and 63.5 GPa, respectively, whereas the limits on shear modulus were found to be 44.5 GPa and 45.2 GPa, respectively. These bounds can now be averaged to estimate the bulk and shear moduli for the multilayer. Furthermore, Poisson ratio (\(\nu\)) and Young’s modulus (\(E\)) for the multilayer can also be calculated using the relations,

\[
\nu = (3B - 2\mu)/(6B + 2\mu)
\] (2.7)

and,

\[
E = 2\mu(1 + \nu)
\] (2.8)

In this example, these values work out to be \(\nu_{\text{MLD}} = 0.20\) and \(E_{\text{MLD}} = 108\) GPa. Such material properties can then be used to interpret the underlying fracture mechanics of these multilayer thin film systems [3].
2.4.2 Silica-hafnia multilayer thin films

Presence of slightly-crystalline hafnia (39% by volume in the silica-hafnia multilayer stack) led to investigations of load dependence on nano-indentation hardness using both Berkovich and Cube-corner tips. This is illustrated in Figures 2-12 and 2-13.

Figure 2.12: Results using the Berkovich tip – no dependence on hardness is observed.

It is clearly seen that hardness increase with increasing penetration depths for experiments using a Berkovich tip but an opposite effect is observed for experiments conducted using a sharper Cube-corner tip. This observation, also seen as a decrease in hardness with increasing penetration depths in Figure 2-13, suggests the presence of indentation size effects (ISE) in these
multilayer thin film coatings. ISE is defined as the experimental observation of increase in hardness as the indenting load is decreased or as the decrease in hardness as the depth of indentation into the surface increases.

This observed load and depth of penetration dependence (Figure 2-13) using Cube-corner tip can be rationalized using the mechanism-based strain gradient theory by Nix and Gao [7]. The Nix & Gao model verifies describes the ISE as observed in these multi-layer thin film coatings. The conditions for plastic flow may depend not only on the strain, but also on the magnitude of any strain gradient that may be present in the material. The effect of using a much sharper cube corner tip is easily observed as one sees the high depths of penetration for loads as compared to “blunted” tip of Berkovich. The true advantage of using a cube corner is not exactly evident from this work, but use of sharper tips is encouraged while determining plastic properties for more reliable and reproducible results. Also, the problem of tip rounding
correction which arises when using more rounded tips like Berkovich are more or less eliminated [27].

Since conventional plasticity theories do not include any material length scales, they cannot be used to predict and fit indentation size effects for indents at the micron and sub-micron scale, where the size effect is evident. Strain gradient plasticity theories [12, 28, 29] are, therefore, needed to explain the size effects. Nix and Gao [7, 11, 13, 28] developed a mechanism based strain gradient (MSG) model that can be used to rationalize the indentation size effects in crystalline materials. Our work here explores if this theory can be extended to ceramic thin films. The MSG model is used to model geometrically necessary dislocations (GND’s) arising out of size-dependent plasticity. This was an effort to develop a strain gradient theory plasticity theory with an intrinsic material length scale. Furthermore ISE is frequently observed in metallic materials when the characteristic length scale of non-uniform plastic deformation is close to a micron: The smaller the size, the harder the material. Conventional plasticity lacks an intrinsic length scale and hence cannot predict the size effects observed in experiments. Also, the presence of dislocations serves to increase the effective yield strength of the material and this in turn means an increase in hardness. In fact in a crystalline material the number density of GND’s created within the plastic zone due to the indent has been calculated by Nix and Gao. Their MSG theory is described by the following characteristic expression for the depth dependence of hardness:
where, $H$ is the hardness for a given indent depth, $h$; $H_0$ the size independent hardness or the hardness in the limit of infinite depth, and $h^*$ is a characteristic length parameter that characterizes the depth dependence of the hardness and depends on the shape of the indenter. This model predicts that the square of the hardness should be linearly related to the reciprocal of the indentation depth. Using the data from Figure 2-13, we plot $H^2$ versus $(1/h)$. The intercept of this straight line is the $H_0$ and slope is $h^*$. This is shown in Figure 2-14. Now, we can plot $(H/H_0)^2$ versus $(1/h)$ (Figure 2-15) to validate our data against the Nix & Gao model. An excellent value of correlation coefficient strongly suggests that these multi-layer thin films exhibit ISE which can be rationalized using the Nix & Gao MSG theory.

When contact of the tip with the film involves plastic deformation, the material may either sink in or pile up and a secondary explanation justifying the evidence of ISE is material pile-up around the indentation area. In some materials, the volume deformed under the indenter pushes out into the sides of the indenter forming a pile-up, as shown in Figure 2-16 [30]. Due to this pile-up shape, the actual contact depth is larger than the measured contact depth. Hence, the calculated projected area based on the recorded contact depth will underestimate the pile-up contact area. In our case of hafnia-silica...
Figure 2.14: Square of hardness plotted against the reciprocal of the penetration depth, gives a good linear fit with a correlation coefficient of 0.9 or \( R = 0.9487 \).

In a multi-layer thin film, material pile is observed all around the indent especially around the sides. Figure 2-17 is a SEM picture taken of an indent made using the cube corner tip at a load of 30 mN. It is one of the 25 indents that were made on the surface of the thin film using this load. Higher magnifications are used to specifically show how layers of the indented material is piled-up around the indentation zone providing a concrete pictorial evidence of ISE in this silica-hafnia multilayer stack.
Figure 2.15: Depth dependence of the hardness of the MLD film plotted according to equation 2.9.

Figure 2.16: Concept of material pile-up to explain ISE in metallic thin films. Figure adapted from McElhaney et al. [30].
Figure 2.17: SEM image showing material pile-up as evidence of ISE in our MLD thin films.
2.5 Conclusions

A nano-indentation study was performed on four single-layer thin films and one multilayer (silica-hafnia) thin film system used in high-power laser systems to understand their mechanical properties, specifically hardness and Young’s modulus. The following main conclusions are reported:

1. Alumina and silica demonstrate the highest values of hardness approximately equal to 12 GPa. The highest value of elastic modulus was also shown by alumina approximately equal to 148 GPa.

2. The properties of the film are directly related to not only the deposition techniques but also deposition factors, such as substrate temperature, deposition rates, and amount of oxygen used for back-fill and even the geometry and size of the coating chamber. These factors can be controlled to produce thin films for very specific applications such as coatings with high laser-damage thresholds, but changing these parameters can significantly change the film’s density and porosity (or the microstructure of the film) and therefore directly affect the hardness and modulus measurements.

3. Accurate and reliable measurements of single-layer films are important to understanding the fracture mechanics and failure mechanisms of multilayer thin-film systems manufactured from the same materials.

4. For multilayers manufactured using silica and hafnia (Figure 2-2), we have measured hardness and elastic modulus, 2.5 - 3.2 GPa and 40 - 56 GPa respectively, using a Berkovich tip.
5. Indentation size effect (ISE) was observed in hafnia-silica multilayer thin films when indented using a Cube-corner tip, which is put on a firm footing using the Nix Gao model. This model, normally reserved for crystalline structures and/or metallic thin films, works out well here as evidenced by a good correlation between \((H/H_0)^2\) and \((1/h)\) in Figure 2-15. The reason for this is suspected to be the slight crystalline nature imparted to hafnia during electron beam deposition.

6. SEM images showing material pile-up around indents made using Cube-corner tip also shows conclusive proof of ISE in these silica-hafnia multilayer thin film coatings.
References


[17] W.C. Oliver and G.M. Pharr. An improved technique for determining hardness and elastic modulus using load and displacement sensing in-


Chapter 3

Surface forensics of multi-layer dielectric coatings - mechanical characterization of “blister” defects

3.1 Introduction

High reflectivity mirrors manufactured from multilayer dielectric coatings (or, optical oxide multilayers) are essential to the successful performance of high-peak-power laser systems. With rapid progress in inertial confinement fusion (ICF) research over the last few decades, the MLD-coated optics used in high-intensity laser systems such as OMEGA and OMEGA EP (Extended Performance) at the Laboratory for Laser Energetics (LLE) [University of Rochester] must exhibit high optical quality and resistance to laser-induced damage. In order to meet these objectives the MLD coatings should be free of any surface defects that could act as potential damage nucleation sites during laser operation. The materials of choice for LLE MLDs consist of ~ 200 nm- thick alternating low and high refractive index layers ($SiO_2$ and
Chapter 3. Surface forensics of MLD coatings

$HfO_2$, respectively) coated on glass (fused silica, BK7, etc.) substrates, for a total physical thickness of $\sim 5\mu m$.

MLD gratings are critical optical components used for pulse compression in OMEGA EP. They are manufactured by patterning photoresist, deposited on top of the MLD, with small-beam interference lithography (SBIL) [1]. The pattern is etched into the top silica layer of the MLD to form the grating [2, 3, 4]. Removal of residual organics and oxide residues from the photoresist/etch process is essential for establishing adequate laser damage resistance of the MLD grating, and it is accomplished with an aggressive acid piranha (mixture of $H_2O_2$ and $H_2SO_4$) treatment at elevated temperatures. Under certain conditions, this cleaning step has been shown to create “blister” defects in the MLD below the surface grating [5]. Blisters are $\sim 25 - 60\mu m$ in size, asymmetrical and represent localized fracture and delamination within the MLD (see Figure 3-1). The protrusion of a blister above the surface is on the order of 500 nm. They are thought to be formed when trapped liquid which entered the MLD through a nodule, scratch or other surface defect escapes [6, 7, 8, 9]. Blisters may be buried within the multilayer, or they may extend to the surface of the grating. The goal of this work is to characterize the mechanical compliance of blisters in MLDs, and nano-indentation is an ideal technique.
Figure 3.1: “Blister” defects on MLDs caused by exposure to acid piranha. The final crack in the MLD, furthest from the nodule, is the top MLD layer. Reprinted from Mehrotra et al. [10] with permission from Cambridge University Press.
3.2 Materials and Methods

Experiments were performed on samples from coating runs 44T-09-54 and 20T-10-56 (designs appended at end of the chapter). Both samples were LLE-coated, standard e-beam deposited hafnia/silica high reflectors. The sample from run 44T-09-54 was a quarter of a 50x1 mm part with a fused silica substrate (double-side polished at Sydor). The sample from run 20T-10-56 was an eighth section of a 100x3 mm part with a BK7 substrate (also double-side polished at Sydor). Many samples were produced in each OMAN coating run, and the work in this chapter was performed on only a single sample from each run. For brevity, the samples will be identified in this memo simply as “44T” and “20T”, referring to samples 44T-09-54 #1 and 20T-10-56 #450-3A respectively. The samples were piranha cleaned using the following protocols:

**44T-09-54 #1 (“44T”)** Coated 9/3/09 [LLE OMAN]; cleaned 10/28/09 using Piranha 2:1, 40 minute ramp to 70° C, no soak, 45 minute ramp to room temperature.

**20T-10-56 #450-3A (“20T”)** Coated 8/13/10 [LLE OMAN]; cleaned 9/22/10 using Piranha 2:1, submerged at 90° C, 25 minute ramp to room temperature.

After piranha cleaning, the samples were mapped using the Leica Nomarski microscope. A total of 56 blisters were counted on 44T, and a total of 515 blisters were counted on 20T, corresponding to approximate blister
densities of 11.4 and 52.5 blisters/cm$^2$ for 44T and 20T respectively [11]. The distributions of blisters across the two parts are shown in Figure 3-2. [Note that a dot may represent a single blister or a cluster of many blisters.]

![Figure 3.2: (a) Blister distribution on 44T after piranha cleaning (total blister count: 56); (b) Blister distribution on 20T after piranha cleaning (total blister count: 515) [10].](image)

All indentation experiments were performed on the MTS - Nanoinstruments nano-indenter XP (Figure 3-3). The system was used with a Berkovich tip which is a three sided, pyramidal diamond tip (face angle $\sim 65.03^\circ$) and the tip area function was calibrated by performing nano-indentation on fused silica. The calibration method is based on the assumption that the Young’s modulus is relatively independent of the indentation depth. Thus, fused silica which has a relatively constant Young’s modulus is used as a standard sample for tip calibration.

This instrument applies a load by magnetic coil; the displacement is continuously measured with a capacitance gauge. The displacement can be
measured to a sub-nm resolution. A part of the test set-up requires that the instrument settle to a user-specied critical drift rate. The indenter is kept in an insulated cabinet and on a vibration-isolation table. If the room containing the instrument has significant vibrations or temperature gradients it may take some time for the drift rate to settle to the user-selected value. Our tests utilize the default critical drift rate of 0.05 nm/s. The surface approach velocity used was 5 nm/s. The percent unloading was set to 90% and a hold period of 10 s specified.

![Nanoindenter XP](image)

Figure 3.3: Nanoindenter XP: utilizes a magnetic coil assembly to apply the force and capacitance gage to measure the displacement.

Experiments were performed using two modes of indentation; (a) Load specific indentation, which is testing by controlling the load that the tip exerts on the surface of the film and subsequently monitoring the displacement produced because of that load and, (b) Continuous Stiffness Measurements
(CSM), illustrated in Figure 3-4 [12]. In this mode of testing, the nano-indenter applies a load to the indenter tip to force the tip into the surface while simultaneously superimposing an oscillating force with force amplitude generally several orders of magnitude smaller than the nominal load. It provides accurate measurements of contact stiffness at all depths. For our testing, we utilized the “CSM Easy Mode” available as a standard option on the instrument. This requires only the targeted depth as the input parameter. The instrument can then apply the corresponding force until the input depth of penetration is achieved. Large displacements require large loads, and for loads greater than 700 mN one has to switch to a “high load head”. From initial testing and previous experience we know that for our targeted depths (> 5 μm), the load required will be more than 700 mN. So we used this mode using the “high load head”.

Figure 3.4: CSM testing: The application of an oscillating force which is superimposed on the load forcing the indenter tip allows for measurement of contact stiffness at all depths. Adapted from Fischer-Cripps [12].
3.3 Results

Both the samples were characterized using specified load indentation and continuous stiffness measurement (CSM) on the nanoindenter (MTS XP). Utilizing the above mentioned modes of experimentation, we analyzed both our samples. The samples were probed for extracting data not only at the “blister” sites but also on the nearby undisturbed part of the coating, free of any defects in order to establish a baseline comparison basis for the results from the defects.

Defect-free areas of the coating (same samples) were also tested to establish any difference in the indentation response from the blister defects and determine a baseline metric for the unaffected MLD. After identifying and locating the blister on the sample, we establish the blisters’ mechanical properties, especially compliance, to determine differences from the undisturbed coating.

For probing the blister on sample 44T (lower temperature cleaning, lower blister areal density) we selected a relatively low load (10 mN) in order to exclude any substrate effects. 10 indents spaced 10 μm apart were made at this load with a Berkovich tip (Figure 3-5). Displacement, hardness and elastic modulus were measured for each of these 10 indents made on the blister (shown in Table 3.1). Differences between the blister and bulk MLD were dramatic, with Young’s modulus dropping 25% and hardness dropping 40% at the blister location.
Chapter 3. Surface forensics of MLD coatings

Figure 3.5: Indentation response of the blister in sample 44T at a load of 10 mN. Reprinted from Mehrotra et al. [10] with permission from Cambridge University Press.
Table 3.1: Greatest compliance is in the “extended” region or the area closest to the top layer of the MLD. This region saw the lowest value of elastic modulus, 41.90 ±1.07 GPa.

<table>
<thead>
<tr>
<th>Location</th>
<th>Modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Displacement (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Good” coating</td>
<td>54.9 ±2</td>
<td>4.2 ±0.1</td>
<td>379.7 ±3.8</td>
</tr>
<tr>
<td>“Blister” (nodule)</td>
<td>48.3 ±1.2</td>
<td>3.3 ±0.4</td>
<td>421.4 ±22.3</td>
</tr>
<tr>
<td>“Blister” (extended)</td>
<td>41.9 ±1.1</td>
<td>2.5 ±0.1</td>
<td>475.5 ±3.8</td>
</tr>
</tbody>
</table>

More experiments were performed on different blister sites using an even lower load of 1 mN (Figure 3-6). It should be noted that in this figure, trails represented by 2a, 2b and 2c represent line of indents made in 3 different regions across the same blister. The similarity in the indentation response is evident and shows very good consistency for a single blister. Continuous Stiffness Measurement (CSM) testing was also employed to gauge the mechanical response of these blisters. In this test, the tip was programmed to penetrate the blister site to a depth of 5 μm. Also, the response of the “good” coating is significantly different from the indentation response of the “blister” defect itself. The results obtained are shown in Figure 3-7(a) and 3-7(b). For comparison, blisters on sample 20T (higher temperature cleaning, higher blister density), were also tested. The appearance of a typical blister on this sample was smaller from those seen on 44T. The sample, 20T, was first tested at small loads (1 mN) and then at large penetration depths (CSM testing). For measuring the indentation response at 1 mN, five blisters were
located on this sample and tested. The undisturbed part of the coating was also tested so as to obtain baseline data. The results for the 1 mN tests and CSM tests are shown in Figures 3-8 and 3-9, respectively [11, 10].

Figure 3.6: Indentation response of blister on sample 44T at 1 mN. Note the indentation response of blister 2(a), (b) and (c) - they correspond to the same blister. Notice the baseline data obtained on the undisturbed region of the coating. Reprinted from Mehrotra et al. [10] with permission from Cambridge University Press.
Chapter 3. Surface forensics of MLD coatings

Figure 3.7a: Comparison of the indentation response of a blister site and the undisturbed (“good”) region of the MLD coating, 44T, for a CSM test set to a penetration depth of 5000 nm. Reprinted from Mehrotra et al. [10] with permission from Cambridge University Press.
Figure 3.7b: 3 blisters on coating 44T show “plateau” effect when indented using a CSM test for penetration of 5000 nm. This shows that different blisters on the same coating respond to a CSM indentation test in an identical manner. Reprinted from Mehrotra et al. [10] with permission from Cambridge University Press.
Figure 3.8: Indentation response of blisters on sample 20T, using a load of 1 mN. Reprinted from Mehrotra et al. [10] with permission from Cambridge University Press.
Figure 3.9: CSM testing on sample 20T by penetrating 5000/5500 nm into the defect site. Reprinted from Mehrotra et al. [10] with permission from Cambridge University Press.
3.4 Discussion

3.4.1 “Blisters” on sample 44T

Figure 3-5 clearly shows that there is no substrate effect and the mechanical properties of the blistered and un-blistered regions in the MLD coating, 44T, can be resolved. Data analysis (ANOVA) shows that the indented area can be differentiated into three regions of statistically significant differences in mechanical properties. The results for these 3 regions identified as “Good” or, the undisturbed coating (regions without blisters), “Blister” (Nodule region) and “Blister” (Extended region - not the center or the location where the initiating nodule was) are shown in Table 1. The data shows that the “blister” is more compliant than the surrounding MLD which is relatively undisturbed.

After having established that the blister was more compliant than the nearly undisturbed region of the coating, it was necessary to be able to reproduce these results for repeatability, accuracy and confidence in the measuring technique. For these purposes we repeated the experiment on a different blister site with an even lower load of 1 mN. The lower load data (at 1mN) allowed us to make a large number of indents (hence more data points) over the defect site without concern about overlapping indentations. Notice the behavior of the “good” coating under the same conditions of loading, shown in Figure 3-6. The mechanical response of the undisturbed “good” region shows consistency and is significantly different from the response of the blis-
Chapter 3. Surface forensics of MLD coatings

Three regions. In these plots, Figure 3-6, it is observed that different blisters on the same sample behave differently but all follow the same general trend: greatest compliance is always associated with the “extended region” of the blister. The maximum compliance depends on the blister. One explanation is the varying geometries along the trail of indentation on the blister. We also observe that the blisters as a whole are much more compliant than the defect free regions of the coating.

The curves in Figure 3-7 (b) for the CSM tests on different blisters show distinctive “plateau” regions, where the indenter penetration has increased from two to several microns without any increase in loading. The total penetration on these blisters has far exceeded the depth they were programmed to go to, indicating either breakage of the coating layers weakened during the cleaning process or the presence of air gap(s). Comparison in Figure 3-7 (a) with the undisturbed regions of the coating under the same conditions reveals that the “good” coating areas do not depict the “plateau” behavior that was associated with the blisters.

3.4.2 “Blisters” on sample 20T

The general trend of indentation response for blisters in sample 20T is the same as seen for blisters in sample 44T - the blister is most compliant in the “extended region” but there are noticeable differences in the nature of the load-displacement curves. For indents made at 1mN, the drop in the displacement values from the region of maximum compliance to the nodu-
lar region is very abrupt in blisters on sample 20T (Figure 3-8). Compare this to blisters on sample 44T (Figure 3-6) in which there is a much gradual fall in displacement values as we move from the extended region (most compliant part of the blister defect) to the nodular region. The magnitude of the displacement in both the samples (44T versus 20T) is different and is observed to be more for sample 20T. The data for the “good” part of the coating also suggests higher (and more variable) values of displacement than the “good” coating in sample 44T (Figure 3-6 versus Figure 3-8). CSM tests on several blisters were conducted (programmed to penetrate to a depth of 5 - 5.5 μm) and the results are depicted graphically in Figure 3-9. Interestingly, the “plateau” effect observed in the previous sample (44T) is almost completely absent. Blister 3 in this plot (Figure 3-9) shows some signs of the effect, but does not resemble the huge “flats” that were seen to be associated with blisters on 44T (in Figure 3-7 (b)) from similar testing. In fact, the indentation response of the blisters for the CSM tests is almost identical to the indentation response of the “good” coating.

The difference in behavior of the blisters from different samples (44T vs. 20T) under similar conditions of testing (CSM tests) is not fully understood but these discrepancies may be attributed to: (a) age of the coating (time between the coating /cleaning and nano-indentation testing) or also possibly the age of the blisters (time between when the blisters were formed and when they were indented), (b) specific cleaning process used, and (c) there could be an effect of the substrate used (here fused silica versus BK7) or even
potentially the difference in coating design. For example, different substrates might lead to different thermal stresses during the cleaning process.

3.4.3 Analytical modeling of the “blister” defect

Guided by SEM (Figure 3-10) and atomic force microscope (AFM) (Figure 3-11) images we have modeled the “blister” as a cantilevered parabolic plate (Figure 3-12).

Figure 3.10: SEM image of a blister. The fracture in the MLD only at the top surface is visible.
Assume that force, $P$ indents this beam (length, $L$) at a distance, ‘$a$’ from the origin. The parabolic dependence of width across the beam of thickness, $t$, is shown in Figure 3-12 and can be expressed as:

$$b(x) = \frac{b_o}{\sqrt{L}} \sqrt{L-x}$$  \hspace{1cm} (3.1)
Figure 3.12: The “blister” defect is modeled as a parabolic beam of width $b(x)$.

Now, we can calculate the deflection of this parabolic beam, $w$:

$$w(x = a) = \frac{4PL^3}{Et^3b_o} \left[ 16 + 30\left(\frac{a}{L}\right)^2 - 40\left(\frac{a}{L}\right) \right] \frac{16}{5} \sqrt{\frac{L - a}{L} (1 - \frac{a}{L})^2}$$

We can use this relation from eqn. 3.2 at $a = L$, to calculate the “extent” of blistering in the MLD coating. We assume a load, $P = 1$ mN, deflection of the blister, $w \sim 0.25 - 0.40\mu m$ (from Figures 3-6 and 3-8), $b_o \sim 8 - 15\mu m$ (guided by SEM images such as shown in Figure 3-10) and elastic modulus.
for the multilayer, \( E \sim 82 - 105 \) GPa (see chapter 2 for details) and use this is to calculate the extent of blister cracking, \( t \), in the MLD coating. This analysis leads to the estimate \( t \sim 4 - 4.8\mu m \).

This is an important result since it shows that this thickness calculated for a particular instance of nano-indentation is consistent in order of magnitude with the thickness of the multilayer (\( \sim 5\mu m \)). Not only does this validate our results of nano-indentation at the low loads (1 mN) but also gives us a sense of the depth of cracking in the MLD from the “blister” defect. Our calculations are verified by cross-sectioning a blister defect using focused ion-beam (FIB) imaging technique. The result is shown in Figure 3-12. Clearly, our numerical results are in excellent correlation with the pictorial evidence from the SEM image.

The FIB image shown above also revealed the “blister” defect fracture mechanism and was used to develop a fracture mechanics model to explain the delamination and fracture of the MLD [13].

Also observe that for a given “blister” defect, the length, \( L \) is known and therefore, the term \( (4PL^3)/(Et^3b_0) \) in eqn. 3.2 is constant. We can now analyze how \( (4PL^3)/(Et^3b_0) \) depends on \( a/L \). It is also useful to compare this calculated deflection for a parabolic beam (shown in eqn. 3.2) to the case where the width, \( b \) is uniform at \( b_0 \).
Figure 3.13: FIB image of a cross-sectioned “blister” defect on a MLD (∼ 5µm thick) reveals the extent of cracking ∼ 4µm, thus verifying our numerical results of t ∼ 4 − 4.8µm.

This is given as:

$$w(a)_{\text{uniform}} = \frac{4PL^3}{Et^3b_o\left(\frac{a}{L}\right)^3}$$

Plotting this dependence, see Figure 3-14, allows us to analyze the effect of the parabolic profile on deflection of the modeled beam. A further extension
of this model might involve a position-dependent thickness, that is, $t(x)$.

Figure 3.14: $w(a)$ is seen to have a (small) dependence on the parabolic profile of $b(x)$.
3.5 Conclusions

Nano-indentation is a useful technique for mechanical characterization of defects on thin films. Here we investigate the “blister” defect, a micron-scale delamination artifact observed on MLD coatings following acid cleaning processes. The following main conclusions are drawn:

1. Different blisters (either on the same sample or different samples) may show different magnitudes of compliance under similar testing conditions at low loads, but the general behavior across each blister is similar.

2. Maximum compliance is always seen in the “extended region” of the blister, furthest from the blister’s initiating nodule/scratch.

3. Differences in indentation behavior between samples during CSM testing may be related to coating age.

4. Using a simple numerical model based on low-load (1 mN) indentation experiments on the blisters, we calculated the extent of “blistering”, \( t \sim 4 - 4.8\mu m \). This was verified through FIB images of the cross-section of the defect (Figure 3-12).

5. The cross-section images in the SEM proved critical in understanding the “blister” defect forming mechanism and led to a fracture mechanics model to explain the delamination of the MLD [8].
Figure 3.15: Coating design for run 44T0954.
Figure 3.16: Coating design for run 20T1056.
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Chapter 4

Nano-scale separation of ductile and brittle deformation in patterned high-aspect ratio silica using nano-indentation

4.1 Introduction

Indentation (both at the micro- and nano-levels) is a useful technique that can be used to observe and determine the overall deformation of surfaces. Of interest to us are both bulk glass surfaces [1] and patterned surfaces [2, 3] where indentation may be employed to study the contributions of plastic deformation and fracture in the overall mechanical response. This experimental approach has allowed for the measurement of important mechanical properties such as hardness (measure of ductility in glass), elastic modulus and fracture toughness (measure of brittleness in glass).

Lambropoulos et al. [1], from the perspective of precision optics manufacturing, explained the interaction of the grinding tool and the optical surface under deterministic micro-grinding conditions by adapting a micro-
indentation model. This model not only mimicked sub-surface damage on the surface (bulk optical glass) from the tool (determination of depths of radial cracks under an indenter) but also accounted for the material removal (depths of lateral cracking from indentation). This study concluded that elastic, plastic and fracture properties of glasses must all be used to establish a correlation with the surface quality resulting from deterministic micro-grinding operations and the mechanical properties. It is important to emphasize that grinding operations (and, micro-indentation) include both formation of a plastic zone and a complex cracking system. This work was useful in understanding the micro-mechanics of deterministic micro-grinding and addressed ductile-brittle transition estimates on bulk optical glass by correlating ductile and brittle length scales with the measured mechanical properties. The model clearly hinged on the development of a plastically deformed zone under the indenter. As such, for any flat surface, one cannot isolate the two material responses of ductility and brittleness from one another by using micro-indentation as any cracking in a bulk, flat surface is closely related to surface plastic deformation.

However, recent work in nano-indentation shows that it might be possible to isolate ductility from brittleness when studying surface patterns other than flat surfaces. To understand ductile-brittle transition and study them as isolated from one another, it is preferred to use uniaxial yield stress and not hardness for glass deformation [4]. The concept of hardness is convenient and practical (involves only small amount of test material) but it is not
fundamental and its measurement involves a complex 3-D stress distribution under an indenter. As such, the uniaxial yield stress (simple stress state) is a preferable property to use although direct measurement is difficult in brittle materials (fracture will precede yield under uniaxial conditions in the absence of a confining medium). The Hill model [5], which simulates the growing zone of deformation under the indenter as an expanding cavity under internal pressure (representing the average indenter pressure, $p$ or the hardness, $H$) is associated with the current radius of the cavity and the radius of the elastic-plastic boundary which in turn is related to the uniaxial yield stress ($\sigma_Y$), Poisson ratio ($\nu$) and the Young’s modulus ($E$). This leads to:

$$\frac{(E/H)}{3(1-\nu)} \frac{1}{(\sigma_Y/H)} = e^{\frac{-1}{3} \left( \frac{3/2}{\sigma_Y/H} \right)}$$

(4.1)

It should be noted here that there is no fracture whatsoever in this correlation which originally was developed for metals. However, this model allows, for a given glass, the determination of the corresponding uniaxial yield stress. Lambropoulos calculated $\sigma_Y$ for a number of optical glasses. Examples include BK7 with $\sigma_Y = 3.2 \pm 0.2$ GPa and fused silica with $\sigma_Y = 4.6 \pm 0.5$ GPa.

Nano-indentation and/or uniaxial compression of patterned surfaces manufactured using techniques such as focused ion beam (FIB) milling and lithography [6] have shown tremendous potential in isolation of the ductile response
of the material from its brittle response. These studies prominently feature the uniaxial compression of metallic micro- and nano-pillars \([3, 7, 8, 9]\) produced by FIB milling with diameters ranging from 75 nm - 7.5 \(\mu\)m (aspect ratios of 3:1 to 6:1). Such structures are used to study the ductile deformation of metals, specifically size effects and their dependence on properties such as yield strength, but, of course, fracture is not prominent in metals.

Lacroix et al., have recently reported experiments on micropillars of amorphous silica by subjecting them to uniaxial compression \([10, 11]\). These micropillars, made by reactive ion etching (RIE) of amorphous silica wafers, have either a square cross-section (6 x 6 \(\mu\)m) and are about 13 \(\mu\)m tall or have a circular cross-section (3.1 \(\mu\)m diameter and 4.75 \(\mu\)m high). Their findings indicate that silicate glasses are very suitable for micropillar compression because the ratio of the yield stress to Young’s modulus is comparatively high as compared to a typical metal like aluminum. They also demonstrated the experimental conditions under which plastic flow can be obtained in compression of these pillars without its catastrophic failure and accompanied only by minor, well defined radial crack patterns. These findings conclude that plastic flow in these micropillars takes place at a von Mises stress of 6.5 - 7.0 GPa which matches the intrinsic tensile strength measured on pristine silica fibers.
4.2 Materials and Methods

4.2.1 Fabrication of MLD gratings

The multilayer dielectric (MLD) gratings used in OMEGA EP’s pulse compressors are surface relief gratings, composed of an MLD mirror with a periodically grooved top diffraction layer. The MLD high reflector is a quarter-wave stack of alternating low and high refractive index layers on a glass substrate, typically hafnia ($HfO_2$) and silica ($SiO_2$) coated onto BK7 glass. The grating is patterned by small-beam interference lithography (SBIL) [6] and etched into the top silica MLD layer via the grating manufacture process [12, 13] shown in Figure 4-1. During the final step, aggressive chemical cleaners such as acid piranha are used to strip away residual photoresist, antireflective coating (ARC), and other debris from the grating surface. The grating’s surface structure, shown in Figure 4-2, is a periodic pattern of (tapered) parallel walls and grooves. For the grating sample used in this work, the silica walls were approximately 440 nm tall, with a slightly tapered geometry ($\sim 250$ nm wide at the base and $\sim 160$ nm wide at the top).

4.2.2 Nano-indentation of patterned silica

A MTS nano-indenter XP fitted with a conical tip (60° included angle, 1 μm tip radius) was used in this work. The system was calibrated by performing nano-indentation on fused silica. The response was measured by indenting at
very low fixed loads. By varying the location of nano-indentation one can isolate ductility from brittleness. This is not possible in flat, bulk glass/ceramic materials or in metallic nano-pillars (ductile deformation). By centering an indent on a “wall” we can induce plastic deformation of the SiO$_2$ (ductile response) whereas an off-center indent can fracture the “wall” from the base (brittle response).

Figure 4.1: Schematic (adapted from Smith et al. [12] and Ashe et al. [13]) showing grating manufacture process used at PGL. The grating is patterned using SBIL, undergoes two reactive ion beam etching (RIEBE) processes to etch away ARC and shape the pillar geometry, and finally it is chemically cleaned to strip photoresist, ARC and debris.
Therefore, to obtain “centered” indents our aim was to strike a single pillar per indent, without disturbing any neighboring pillars. Due to the limited imaging capabilities of the instrument and given the sub-micron scale of the pillar structures, it was not possible to resolve the impressions made by the indenter using the nano-indenter’s built-in microscopy; instead, the sample had to be transferred to a scanning electron microscope (SEM) to observe the indents and pillar damage. Therefore, the indenter was programmed to indent in an array fashion so that the set of indents could be found easily.
in the SEM and to increase the probability that at least some of the indents would hit a single pillar. “Off-centered” indents that result in fractured silica walls are useful too; based on the degree of off-center, these indents can be used to invoke either a pure brittle response (calculate fracture strength of silica at nano-scale) or, a mixed ductile-brittle response (explained in chapter 5). This is illustrated in Figure 4-3. Therefore, nano-indentation over a range of indentation loads can be used to transition from ductile deformation (centered indent) to ductile-brittle mixed deformation (off centered indent) and finally to complete brittle deformation (off centered indent), all by simply displacing the location of the nano-indenter tip on the surface of the grating structure.

Figure 4.3: Controlled nano-indentation can invoke 3 different responses in MLD gratings. These are ductile, ductile-brittle mixed and fracture (pure brittle); also discernable by looking at their respective load-displacement curves.
4.3 Results

4.3.1 Experiments

MLD grating samples were indented in an array fashion at loads of 0.4 and 0.5 mN to generate “centered” and “off-centered” indents. This is shown in Figure 4-4. Clearly, many indents resulted in fracture of the grating walls to tangential force from the indenter tip and some are observed in a state of ductile deformation at the same load. A “centered” indent was one in which the indenter tip was aligned almost perfectly on top of a grating wall and deformation occurred without the damage extending to the adjacent sidewall. Off-centered indents, at the same loads, resulted in toppling of the silica walls and produced scalloped features. High magnification images of the individual indents shown in Figure 4-5 and 4-6 highlight these phenomenon. All experiments reported in this chapter were performed on the sample grating piece.

The responses of indents, both “centered” and “off-centered” (or, catastrophic), were registered using their respective load-displacement curves (Figure 4-7). Data for the SiO₂ grating pillars were also compared to the response for bulk fused silica under the same indentation conditions (0.5 mN load). The data showed that, for the same load, the “centered” indents on the silica pillar saw displacements that were nearly 4 to 5 times greater than the displacement recorded for bulk silica. For the “off-centered” indents that
Figure 4.4: Indents were generated in an array to invoke ductile and brittle response in the silica walls at loads of 0.4 mN and 0.5 mN. “Centered” indents were confined to a single wall whereas the “off-centered” indents caused fracture in adjacent walls too. Reprinted from Mehrotra et al. [14] with permission from Cambridge University Press.
Chapter 4. Nano-scale ductile and brittle deformation in silica

Figure 4.5: “Centered” indents made at 0.4 and 0.5 mN show deformation on a single silica wall.

Figure 4.6: “Off-centered” indents at 0.4 and 0.5 mN loads show catastrophic damage to the silica walls. The damage extends to three grating walls.

knocked over the pillars, the total indenter displacement was approximately the same as the height of the grating pillar (~ 440 nm) and included a plateau region where the indenter traveled about 300 nm into the sample with no increase in loading, presumably following mechanical failure of the pillar.

It must be noted that in the experiments described so far, we have not attempted to control the degree of off-centered in the indents that resulted in a
Chapter 4. Nano-scale ductile and brittle deformation in silica

Figure 4.7: Load-displacement curves for indentation on “pillars” at 0.4 and 0.5 mN loads. Comparison to bulk fused silica is also shown.

catastrophic response simply because of lack of instrumentation limitations. But this is an important consideration especially since it is our understanding that a low amount of off-set will result in a mixed ductile-brittle response. This is seen to be of importance when discussing how nano-indentation can be used to explore a connection with laser-induced damage thresholds of these gratings in the next chapter. Therefore, in an attempt to address this we collaborated with a researcher, Dr. Jeffrey Wheeler (now at Eidgenössische Technische Hochschule (ETH) Zurich), at Swiss Federal Laboratories for Materials Science and Technology (EMPA) in Switzerland who performed in-situ SEM nano-indentation. Using this capability, he was accurately able to control the off-set for each indent and produced “centered” and “off-centered” indents with varying off-sets. The measured load-displacement curves are re-
ported in Figure 4-8(a) and maximum load for each offset is plotted in Figure 4-8(b). This is also shown in Figure 4-9 in the series of SEM images that show a complete transition from an indent with no off-set to an indent that is completely “off-centered”.

Figure 4.8a: Load-displacement curves from in-situ SEM indentation performed at EMPA show the changes in nano-mechanical response of the sample as offset is changed from 0 nm (centered indent) to 200 nm (fully off-centered indent).
Figure 4.8b: Maximum load corresponding to each offset distance for indents in Figure 4-8(a).

4.3.2 Numerical simulations

Early-stage simulations were performed in COMSOL® to verify our experimental data performed at 0.5 mN for “centered” indents only. This was achieved by creating a 2-D axisymmetric finite-element model corresponding to an indentation depth of \(\sim 170\) nm (seen in load-displacement curves in Figure 4-7). The measured value of maximum von-Mises stress is \(\sim 4.5\) GPa and is shown in Figure 4-10.

Next we developed a much more detailed model in ABAQUS® both in 2-D and 3-D space that would allow us to analyze both “centered” and “off-centered” indents. The 2-D model was developed as a plane-strain analysis using 18,675 CPE4 elements (four-node bilinear plane strain quadrilateral).
Figure 4.9: SEM images of in-situ nano-indentation shows the transition from a “centered” indent in (a) to completely “off-centered” in (f). Damage evolves as the offset goes from 0 to 200 nm.
Figure 4.10: 2-D finite-element analysis (FEA) of a “centered” nano-indentation experiment corresponding to conditions generated at a load of 0.5 mN.

Highly refined meshing is used near the area of contact with a progressively coarser mesh employed as we move away from the zone of maximum deformation (grating walls and the top few layers of the grating). As an example the set-up for the centered indent is shown in Figure 4-11.

The identical set-up was used to simulate off-centered indents except that the indenter tip was moved from being aligned on top of a single silica wall
Figure 4.11: Meshing and set-up of a 2-D plane-strain simulation for a “centered” indent.
to exactly in between 2 walls. Simulations corresponding to penetration depth of 170 nm resulted in the following results. Von-Mises stress for the “centered” indent, shown in Figure 4-12, was observed to be $\sim 4.7$ GPa at the top of the wall where the indenter made contact. Since, the “off-centered” indents involved fracture of the grating walls, maximum principal stress (at 170 nm indentation depth) were plotted in Figure 4-13 and observed to be $\sim 3.1 - 3.6$ GPa.

Figure 4.12: “Centered” indent at a penetration depth of 170 nm shows a von-Mises stress of $\sim 4.7$ GPa in the region of contact (top of the wall).
Figure 4.13: “Off-Centered” indent at a penetration depth of 170 nm shows a maximum principal stress of $\sim 3.1 - 3.6$ GPa along the walls of the grating and at the base.

Clearly, 2-D modeling is not sufficient to explain the experimental results especially for the off-centered nano-indentation tests. The result in Figure 4-13 shows the possible locations where fracture could originate (zones of concentration of maximum principal stresses) in an “off-centered” indent but this is also a function of the amount of off-center. Hence, the problem was modeled in 3-D space using a total of 82,368 elements (C3D8 – hexagonal, 8-node linear brick). The centered indent corresponding to penetration depth of 170 nm (guided by the experiments performed at load of 0.5 mN) is shown in Figure 4-14. The plotted von-Mises stresses are seen to be maximum at the top of the grating wall ($\sim 3.5 - 4.5$ GPa) where the indenter tip made contact. It must be noted that these stresses are plotted after the indenter tip
was retracted from the surface of the grating so Figure 4-14 truly represents the residual stresses and reveals the deformation (in the form of “stretching”) that is reminiscent of the SEM images (Figure 4-7) from the experiments.

Figure 4.14: Von-Mises stresses corresponding to a nano-indentation experiment performed at a load of 0.5 mN. The maximum stresses are observed at the top of the grating wall.

Similarly, finite-element analysis was performed for “off-centered” indents at varying degrees of off-center and at different penetration depths. This was done to simulate the in-situ SEM experiments performed at EMPA. The SEM images (Figure 4-9) clearly emphasize the important of offset distance but fracture would depend on the load applied. Since we are trying to understand
fracture through the off-centered indents, the maximum principal stresses are plotted for off-centered indents for 3 different offsets - 25%, 50% and 100% (indenter tip aligned between the two grating walls) and are shown in Figures 4-15(a), (b) and (c).

Figure 4.15a: 25% off-centered indent at a penetration depth of 100 nm. It is evident that this amount of offset is not enough to affect the adjacent silica wall. The maximum principal stresses generated are concentrated on the wall that made contact with the indenter tip. As a result there is mainly plastic deformation (represented by the “stretching”) and possibly some fracture at the base of the wall.
Figure 4.15b: This figure shows the maximum principal stresses plotted on the grating’s surface after nano-indentation was performed at an offset distance of \( \sim 120 \text{ nm} \) from the central axis of the grating wall and is referred to 50% off-centered indent. Clearly, at a modest penetration depth of 100 nm, the damage has extended to the adjacent silica wall as well. The wall on the left, where contact is first made, also experiences some initial plastic deformation (“stretching”) but soon high levels of stress (\( \sim 4.5 \text{ GPa} \)) become concentrated at the base of the wall.

Next we evaluated the effect of varying the penetration depths at a fixed offset distance. This analysis is helpful in understanding the evolution of damage in the grating structure as the indentation progresses. Specifically, we will discuss the results of a 100% or, fully off-centered indent at penetration depths of 50 nm, 100 nm, 170 nm and 250 nm. This is shown in Figures 4-16(a), (b), (c) and (d) respectively.
Figure 4.15c: Completely or, 100% off-centered indent at a depth of $\sim 100$ nm produces similar damage on the adjoining wall.
Chapter 4. Nano-scale ductile and brittle deformation in silica

Figure 4.16a: 100% off-centered indent at a 50 nm penetration depth.

Figure 4.16b: 100% off-centered indent at a 100 nm penetration depth.
Chapter 4. Nano-scale ductile and brittle deformation in silica

Figure 4.16c: 100% off-centered indent at a 170 nm penetration depth.

Figure 4.16d: 100% off-centered indent at a 250 nm penetration depth.
4.4 Discussion

4.4.1 "Centered" indents: Extraction of nano-scale yield strength of silica

The indentation loads (0.4 mN and 0.5 mN) for the experiments were selected so that the indentation transverse extent would be larger than the pillar width (about 150 nm at the top), larger than the pillar height (about 440 nm), and the indent depth less than the pillar height so as to minimize the effect of the underlying MLD. These conditions are expected to essentially create a mostly uniform state of stress under the indent.

The results presented in Figure 4-7 were in accordance with expectations: the bulk material, which is fully constrained in the plane perpendicular to the indenter’s path, experiences a much higher triaxial stress when indented as compared to a grating pillar, which is only constrained in the normal direction and in a single transverse direction.

The geometry of the grating pillars does not allow the use of the Oliver-Pharr method [15] to evaluate the nano-indentation response. We therefore adopt a stress-strain model [3] to explain the measured nano-indentation response. From the SEM images in Figure 4-5 it is evident that there is no fracture whatsoever in the indentation response from “centered” indents. Therefore, the imposed condition for a given indentation load P over a projected area of width w and length a can be given as:
\[ \sigma_{zz} \approx -\frac{P}{wa} \]

(4.2)

Figure 4.17: Illustration showing the indentation response of the grating pillar as explained by our stress-strain model.

Also, we assume that \( \epsilon_{xx} = 0 \) (constraint on strain in x direction) and \( \sigma_{yy} = 0 \) (stress assumed to be zero in y, since the grating pillar is quite narrow). Thus the elastic solution, valid for small loads, predicts the principal stresses to be \( \sigma_{max} = \sigma_{yy} = 0, \sigma_2 = \nu \sigma_{zz} < 0 \), (where \( \sigma_2 \) is the intermediate principal stress) and \( \sigma_{min} = \sigma_{zz} < 0 \), where \( \nu \) is Poisson ratio. From Tresca’s yield criterion, the initial yield will occur when \( |\sigma_{zz}| = P / wa = \sigma_Y \), where \( \sigma_Y \) is the yield stress. A von-Mises analysis gives yield when \( P / wa = 1.07 \sigma_Y \). The fully plastic solution invokes the flow rule for perfectly plastic materials which relates the strain tensor increments \( d\epsilon \) with the deviatoric stress tensor \( S \) as \( d\epsilon_{xx} = \lambda S_{xx}, d\epsilon_{yy} = \lambda S_{yy}, \) and \( d\epsilon_{zz} = \lambda S_{zz} \), where \( \lambda \) is a constant of proportionality. The principal stresses are then calculated to be \( \sigma_{max} = \sigma_{yy} = 0, \sigma_2 = (\sigma_{zz}/2) < 0 \), and \( \sigma_{min} = \sigma_{zz} < 0 \). Tresca’s
yield criterion again predicts $|\sigma_{zz}| = P/wa = \sigma_Y$ and the von-Mises criterion predicts that $P/wa = 1.15 \sigma_Y$.

On analyzing the nature of the plastic strains from this simple model, we find that $d\epsilon_{xx} = 0$, $d\epsilon_{yy} = -(\lambda/2)\sigma_{zz} > 0$, and $d\epsilon_{yy} = (\lambda/2)\sigma_{zz} < 0$. These strains correspond to compression in the $zz$ direction and expansion in the $yy$ direction, illustrated in Figure 4-17, as observed in SEM images (Figure 4-5).

The plastic analytical solution predicts that the yield stress is 4.5 GPa ($P = 0.5$ mN) and 4.6 GPa ($P = 0.4$ mN). This numerical model neglects the shear stresses. Of course, such stresses are present, but they are much lower than the normal stresses for the geometry considered here.

A 2-D elastic-plastic finite element model (Figure 4-10) was used to match experimental observations (maximum penetration of 180 nm at load of 0.5 mN for a valid indent) and pillar geometry while leaving the pillar yield stress as a free variable. Such matching led to a value of 4.1 GPa for the yield stress. The FEM analysis also revealed that the largest stress component was $\sigma_{zz}$, and that $\sigma_{xx}$ amounted to about 50%-60% of $\sigma_{zz}$, while $\sigma_{xz}$ (the shear stress) amounted to about 20% of $\sigma_{zz}$. The plastic strains were (-180%) in the $zz$ direction, (+210%) in the $yy$ direction, and (-30%) in the $xx$ direction; the plastic engineering shear strain amounted to 28%. Therefore, excellent correlations were established with our analytical model.

Finite-element analysis performed in ABAQUS® in 2-D and 3-D, shown in Figures 4-12 and 4-14 respectively, clearly show that our simulations cap-
ture the deformation seen in the “centered” indents – “stretching” around the top of the grating wall where contact was made with the indenter tip. The maximum von-Mises stress observed in this region and thus the yield stress is $\sim 4.5 - 4.7$ GPa. This is in agreement with results of previous simulations as well as our simple analytical model. Due to lack of any fracture around the indentation area in Figure 4-5, this response is inferred as pure ductile deformation; this phenomenon is typical of metals but rarely seen in a bulk brittle material such as silica. This measurement is unique since we have now shown that glass (silica) can show plastic deformation without any fracture but at the nano-meter level. This novel response is observed in nano-patterned surfaces (diffraction gratings) and is different from nano-indentation response in bulk materials in which the surrounding material constrains the material deformation. Here the relatively small thickness of the walls allows for the “stretching” behavior imparting huge, metal-like strengths to brittle silica.

Given the complex distribution of stress fields under an indenter, it is preferable to use uniaxial yield stress rather than the hardness to quantify the mechanical response of these structures. We adopt the model of Hill [1, 4, 5] (explained in section 4.1) to study how the uniaxial yield stress can be related to the measurable mechanical properties such as Young’s modulus, Poisson ratio and hardness of the material. Therefore, given a measured hardness $H$, Young’s modulus $E$, and Poisson ratio $\nu$ for glass we can calculate the corresponding uniaxial yield stress $\sigma_Y$.

For fused silica using $H = 8.5$ GPa, $E = 72$ GPa and $\nu = 0.17$, the $\sigma_Y$ is
found to be \( \sim 4.4 \) GPa which is in excellent correlation with our measurements. It must be noted that there is no fracture in this correlation at all. The effect of Poisson ratio is shown in Figure 4-18.

Figure 4.18: Correlation of \( \frac{\sigma_Y}{H_v} \) with measured hardness and Young’s modulus for \( \nu = 0.1, 0.2 \) and 0.3. Notice that the hardness \( H_v \) is measured using a Vickers indent.
4.4.2 "Off-centered" indents: Extraction of nano-scale fracture strength of silica

It is shown in the previous section how “centered” indents can be used at appropriate loads to invoke ductile deformation in a nominally brittle material such as silica allowing us to calculate nano-level yield strength of silica. “Off-centered” indents (Figure 4-6), on the other hand, are intimately associated with fracture. Naturally, this leads to an attempt to calculate the fracture strength of the silica walls at the nano-scale.

To analyze fracture of the silica wall we will first develop a simple analytical model in order to identify the relevant quantities that are important, and then proceed to a detailed numerical model.

We employ first a simple analytical model to hypothesize the fracture mechanism, that is, how the silica walls “topple” as in Figure 4-6 and eventually calculate fracture stresses.

Analysis of the fracture patterns can be approached by viewing the fractured walls as a loaded cantilever plate. As the spherical nano-indenter tip (1μm) descends and contacts both the grating walls (off-centered indent results in contact with 2 walls), a transverse force \( F_x \) develops in addition to the normal force \( 2F_y \) applied by the tip (Figure 4-19).

As long as the line of action of the resultant force \( F \) intersects the base between points C and D, the stress at D is mostly compressive, hence does not induce fracture. When the line of action of the force \( F \) reaches point C, then the grating wall will fracture and “topple”, consistent with images in
Chapter 4. Nano-scale ductile and brittle deformation in silica

Figure 4.19: Hypothesis on the fracture mechanism of the grating walls.

Figures 4-6 and 4-9 (b)-(f). This hypothesis also includes the length of the fractured structure (into the plane of paper for Figure 4-18 or the length of the scalloped wall in Figure 4-20).

Based on the geometry in Figure 4-19 (derived from Figure 4-2) and guided by SEM image in Figure 4-20, the typical dimensions for this calculation are as follows: a $\sim 150$ nm (top of the grating wall); b $\sim 250$ nm (base of the grating wall); L $\sim 440$ nm (height of the grating wall); t $\sim$ dimension into the plane of the grating wall representing the length of the fractured grating wall, shown as ‘aa’ ($\sim 2000$ nm) or ‘bb’ ($\sim 700$ nm) in Figure 4-20;
Figure 4.20: SEM images of broken grating walls help in calculation of fracture stress at the base of the wall. The dimensions ‘aa’ and ‘bb’ are $\sim 2000$ nm and $\sim 800$ nm respectively.

$\theta \sim \arctan[\frac{L}{(a+b)/2}] \sim 65.6$ degrees; guided by load-displacement curves shown in Figure 4-7, we choose $F_y \sim 0.3 \text{ mN}/2 \sim 1.5 \times 10^{-4}$ N at failure of the wall (example of a load where fracture is initiated in the indentation experiment). Also, $\tan \theta = \frac{F_y}{F_x}$ and the indentation load applied, $P = 2 F_y$.

We now calculate the total stresses at the “foot” of the wall (point D in Figure 4-19). The compressive stress at D due to the normal component of force is $F_y/b_t$. Additionally, there is a tensile stress at D due to bending
Chapter 4. Nano-scale ductile and brittle deformation in silica

and is given as \(6 F_s L/(t b^2)\). Therefore, total stress acting at the “foot” of the grating wall (point D) is given as:

\[
\sigma_D = \frac{6 P}{2 \tan \theta} \frac{L}{t b^2} - \frac{P}{2 t b}
\]  

(4.3)

Using \(t = a \sim 2000 \text{ nm}\), we estimate \(\sigma_{\text{fracture}} \sim 1.1 \text{ GPa}\). However, careful examination of the SEM image in Figure 4-19 suggests that there is a possibility that fracture could originate when \(t = b \sim 700 \text{ nm}\). The corresponding fracture stress in this case is \(\sigma_{\text{fracture}} \sim 3.3 \text{ GPa}\). Although this calculation suggests that fracture stress of silica is \(\sim 1.1 - 3.3 \text{ GPa}\), more detailed finite-element simulations were used to account for the initial contact of the nano-indenteter tip and the ‘soon-to-fracture’ grating wall (observe the compressed/deformed region represented by ‘bb’ in SEM image Figure 4-20) and the fact that the grating wall is supported by a compliant “base” at CD (Figure 4-19) rather than a rigid support as we have used in our analysis so far. We next discuss the results of a detailed numerical model.

Figures 4-16 (a) - (d) show the evolution of maximum principal stresses in the grating structure under a nano-indentation load corresponding to different penetration depths (from 50 nm to 250 nm) for a fully “off-centered” indent. It must be noted that there is no fracture built in this finite-element model and, therefore, guided by the analytical analysis and fracture mechanism hypothesis discussed previously, we will account for maximum principal
stresses at the base of the grating wall to estimate fracture stress in these silica walls. It is seen that as the penetration depth changes from 50 nm to 250 nm, the contact area on the grating walls drastically increases which also suggests that length dimensions of the scalloped features - ‘t’ (seen as broken walls for example in Figure 4-6) also increase. This, in turn, means that maximum principal stresses seen at the base of the grating walls also increase. For the case of penetration depth of 50 nm, the contact area is small (compare to ‘bb’ in Figure 4-20) and the maximum principal stress at the “foot” of the grating wall is \( \sim 0.8 - 1.2 \) GPa. As penetration depths increase, the stresses increase and cause the silica walls to overcome “stretching” alone and “topple” over. The excessive “stretching” of the walls in Figures 4-16 (c) and (d) will correspond to fractured walls with \( t \sim ‘aa’ \) (refer to Figure 4-20). Here the maximum principal stress at the “foot” of the wall is observed to be \( \sim 2.5 - 3.5 \) GPa.

Thus the numerical model establishes the nano-scale fracture stress for silica as \( \sim 0.8 - 3.5 \) GPa. Once again, excellent correlation is seen with our simple analytical model. An important observation here is that these levels of fracture stress in a brittle material like silica are atypical (for reference, the nominal strength of fused silica is 50 - 100 MPa) and are thought to be due to the accommodating nature of the silica walls achieved by the initial “stretching” and then fracture. Again, this behavior seen here is exclusive to patterned surfaces because bulk brittle materials cannot “stretch” before fracture, and therefore, have low strengths.
4.5 Conclusions

We have shown in this chapter that by employing carefully controlled nano-indentation (“centered” versus “off-centered” indents) on meta-surfaces such as patterned gratings, it is possible to isolate ductile deformation from brittle fracture at nanometer scale in a nominally brittle material like silica (the main component of glass). This approach leads to three unique responses in these MLD gratings: 1) characteristic fracture response we typically associate glass with, 2) a mixed response with both glass and metal like behavior (ductile + fracture), and 3) pure “metal-like” or ductile deformation. This is illustrated in Figure 4-21. Results from location-specific nano-indentation supported by simple analytical models and detailed 3-D FEA lead to the following conclusions:

1. Glass (silica), a material that is brittle by nature with strengths \(\sim 50\) - \(100\) MPa, is observed to be ductile in the \(50\) - \(100\) nm regime. This is due to the “stretching” behavior, normally associated with metals, and lends glass counter-intuitive fracture characteristics at the nm-scale. It is this “stretching”, seen as pure ductile deformation (Figure 4-21), that leads to strengths \(\sim 4.5\) GPa (calculated as yield strength) which is comparable to strengths of metals. Therefore, surface meta-geometry (use of patterned surfaces) can be exploited to suppress fracture, even in brittle materials, and lead to increase in strength of the material.
2. A fracture mechanism for “toppling” of the silica walls during off-centered indents was hypothesized. Using this we estimated the fracture strength of silica (glass) $\sim$1.1 - 3.3 GPa. We know glass to fracture very easily due to the microscopic structural flaws present at its edges. These flaws lend glass its characteristic low strengths from the macro-scale down to the micro-scale but here at the nm-scale we measure very high fracture strengths. It is known that strength is a function of flaw size in a material ($\mu$m to mm dimensions) and the greater the flaw size (nm to $\mu$m dimensions), the lower are the measured strengths. Here in our material, the geometry has nm-level dimensions which is of the same order of magnitude as defects/flaws in the grating structure (see Chapter 5 for detailed explanation of defects on the grating structure). Therefore, we surmise that this leads to high values of fracture strengths in glass.
Figure 4.21: The 3 unique responses to nano-indentation performed on a MLD grating helps in analyzing ductility and fracture separately; this is otherwise not possible in bulk materials. At the nano-scale, glass (silica) shows uncharacteristically high strengths (1- 4 GPa) because in the form of a patterned surface it can accommodate stresses by “stretching” like metals.
References


Chapter 5

Nano-mechanics of laser-induced damage in optical MLD gratings

5.1 Introduction

We seek to understand how a nano-mechanical test can be used to generate metrics to complement laser-induced damage testing (LIDT) measurements and show that differences in optical performance of the gratings (arising from changes in cleaning process and/or fabrication methods) can be related to its mechanical reliability.

Multilayer-dielectric (MLD) pulse compressor gratings are critical components used in the high peak-power laser system’s amplification systems and have been a focus of recent research and development efforts because of their low damage thresholds [1, 2]. At the Laboratory for Laser Energetics (LLE), the peak power capability - and thus the overall performance of the petawatt-class OMEGA EP laser system is limited by the laser damage resistance of diffraction gratings in the chirped-pulse amplification (CPA) pulse
compressors for each beam line [3, 4, 5, 6]. Increasing the damage thresholds of these components is therefore an important objective. Howard et al. [7] developed a low-temperature chemical cleaning approach to improve the performance of these MLD gratings and demonstrated that grating coupons that were cleaned using the optimized method consistently met OMEGA EP requirements on diffraction efficiency (> 97%) and 1053 nm laser-damage resistance at 10 ps (>2.7 J/cm²). They also observed that for the highest-damage-threshold samples there were minimal laser-conditioning effects and suggested a transition from a contamination-driven laser-damage mechanism to defect-driven damage for well-cleaned components. These metrics (diffraction efficiency and laser-induced damage thresholds) compose what will be referred to as optical testing hereafter. Such optical testing is the most common way used to characterize the performance and, hence the quality of a MLD grating that has been cleaned for use in a high-power laser system.

There is some concern that cleaning procedures and/or the fabrication techniques for gratings can mechanically weaken the fragile grating pillars, possibly affecting the grating’s resistance to laser damage and, therefore, warrant mechanical characterization. The development of a methodology for monitoring a grating’s mechanical properties will enable a better understanding of the fabrication and cleaning process, and point to appropriate modifications that will preserve or enhance the grating’s integrity. Nano-indentation of MLD gratings [8] discussed in the previous chapter is our adopted approach and the indents that invoke fracture of the silica walls are
now treated in detail.

Both tests (laser damage and nano-indentation), although vastly different in nature and implementation, inherently measure the performance of the grating (optical versus mechanical). Fracture, due to concentration of mechanical stresses is an intimate part of these measurements. Therefore, it is imperative and almost intuitive to explore mechanical testing (nano-indentation) as means to complement and even precede optical testing to establish the “quality” and performance of a MLD grating sample. Our thinking here is guided by the observation that both optical fields (electric, magnetic) and mechanical fields (stress, strain), when interacting with the grating geometrical features and with defects and inhomogeneities, will show significant concentrations.
5.2 Materials and Methods

5.2.1 Fabrication of MLD gratings

The MLD grating manufacturing process is detailed extensively in published literature [7, 8, 9] and is also discussed in the previous chapter. We summarize here the main steps for completeness.

The first step is to deposit the multilayer dielectric (MLD) coating on the glass substrate (fused silica or BK7) by reactive evaporation at 200°C. This was a 4.8 μm thick modified quarter-wave thin film stack [10] with hafnia (HfO$_2$) and silica (SiO$_2$) used as the high and low-index materials, respectively. Hafnia layers were deposited from a hafnium metal source using an oxygen backfill pressure of 2.0 x 10E-4 Torr, while the silica layers were deposited from the oxide without an oxygen backfill (See Oliver et al. [10] for a discussion of coating development for OMEGA EP gratings). Then a bottom antireflective coating (BARC) layer (organic polymer) may be applied to the multilayer mirror in order to mitigate standing-wave effects [9] during small beam interference lithography (SBIL) process. The part is then coated with photoresist, and interference lithography is used to pattern the grating (grooves, 1740 lines per mm).

The grating is then subjected to reactive ion-beam etching (RIBE) processes to etch the BARC and top MLD layer which leaves the silica wall geometry. Finally, organic residues (including BARC and photoresist layers,
and environmental contamination) and inorganic residues (including metallic contaminants and oxide debris) are stripped away in a final cleaning process that is explained next. The grating’s surface structure is a periodic pattern of parallel grating lines (pillars) and grooves. For the grating sample used in this work, the pillars were approximately 440 nm tall, with a slightly tapered geometry (∼250 nm wide at the base and ∼150 nm wide at the top).

5.2.2 Optimized procedure for cleaning MLD gratings to maximize laser damage thresholds

Cleaning experiments were performed on small-scale MLD grating coupons for this study. 100 mm diameter, 3 mm thick, round hafnia/silica MLD gratings were broken into eight equally sized, wedge-shaped coupons. All cleaning experiments described in this chapter were performed on un-cleaned gratings with BARC and photoresist still intact (that is, they were not subjected to any photoresist stripping or cleaning operations other than those described here). Un-cleaned gratings can be easily distinguished due to their characteristic brown and hazy appearance attributed to the reactive ion etching step and is seen to disappear when a grating was well cleaned.

Acid piranha, the most widely used chemical cleaning at higher temperatures [9], could not be used exclusively for our low temperature (40°C) process; a multistep technique is warranted to ensure a wide range removal of performance-limiting contaminants. This cleaning methodology is discussed in Howard’s work [7, 8, 9, 10, 11] and was adapted by improvising on ex-
isting literature for cleaning gratings (such as [9]) and semiconductor wafer processing. It is split in two parts: partial clean consisting of six steps and a final clean which includes a plasma step. This is summarized in Table 5.1.

The first two steps of the partial clean consist of using acid piranha to strip photoresist, BARC, and carbonaceous etch residues. The piranha strip is then followed by plasma cleaning in room air to clear away partially removed organic matter especially BARC which is known to “flake off” [2] and not dissolve in the acid piranha. The third step in the partial cleaning process is an ionic clean with a standard clean 2 (SC-2) solution - a mixture of hydrochloric acid and hydrogen peroxide commonly used in the microelectronics industry to remove metallic contamination from silicon wafers. Howard et al. [2, 7] justified the inclusion of an ionic clean to remove molybdenum, a metal, detected on (un-cleaned) grating samples through x-ray photoelectron spectroscopy (XPS) measurements. The ionic clean is followed by another plasma treatment to clear away light organic matter collected on the sample. The final step in the partial clean is a buffered oxide etch (B.O.E), which reduces grating duty cycle and eliminates any remaining contaminants on the grating by removing a thin layer of silica [12]. The final clean is a third plasma treatment, which cleans the surface by removing light organics. This can be either an air plasma [7] or an oxygen plasma (conventionally used in grating cleaning procedures). As shown later, this choice can have a decisive effect on the laser damage threshold attained by a grating sample.

Plasma cleaning (in all the steps) was performed using the Harrick Plasma
Chapter 5. *Nano-mechanics of laser damage in optical gratings* 128

Cleaner and PlasmaFlo gas mixer add-on (for the oxygen plasma only). The Pyrex glass chamber was used in the plasma cleaner. Settings on the plasma cleaner and PlasmaFlo were adjusted so that a blue or pink glow was viewed for oxygen and room air plasma cleaning respectively.

5.2.3 Laser damage testing – set-up, process and parameters

Damage testing was carried out at LLE’s damage testing facility on the short-pulse (10 ps) system with operating capabilities in both air and high-vacuum (4 x 10E-7 Torr). The MLD grating samples studied here were tested in air and used s-polarized light at 1053 nm at an incident beam angle of 61° with an irradiation spot size of 370 μm (e⁻¹ in intensity) in the far field. Beam analysis and fluence calculations were performed using the Ophir-Spiricon commercial laser beam profiler. Laser-damage assessment was performed in situ using a white-light imaging system (~100x magnification). Damage was defined as a feature on the sample’s surface that was not observed before laser irradiation [11, 13]. Damage thresholds are reported as beam normal fluences. An example of damage site on grating 566-5 is shown in Figure 5-1.

Our damage tests employed the N-on-1 regime performed in air. Particulars of this testing regime and others, such as 1-on-1, can be found in literature [14]. N-on-1 (stepwise ramped fluence) testing is conducted by irradiating the sample site at a fluence which is well below the 1-on-1 threshold
### Table 5.1: Cleaning process for the MLD gratings used in this work.

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Chemical Process Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>15</td>
<td>5:1 Piranha spray</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>15</td>
<td>2:1 Piranha spray</td>
</tr>
<tr>
<td>3</td>
<td>23</td>
<td>10</td>
<td>Air plasma-6.8 W power</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>10</td>
<td>1:1:6 SC-2 no stir soak</td>
</tr>
<tr>
<td>5</td>
<td>23</td>
<td>10</td>
<td>Air plasma-6.8 W power</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
<td>5</td>
<td>2800:1 BOE soak</td>
</tr>
<tr>
<td>7</td>
<td>23</td>
<td>15</td>
<td>Air plasma-6.8 W power</td>
</tr>
</tbody>
</table>

**Partial Clean**

**Final Step**

OR

Oxygen plasma-6.8 W power
for 10 shots. If no damage is detected, the same site is irradiated with five more shots at a slightly increased fluence. This is continued until damage is observed in white light, at which point the damage onset fluence is recorded as the N-on-1 threshold for that site. The N-on-1 test is repeated for five sites on each MLD grating sample to generate an average and a standard deviation, which are reported as the N-on-1 threshold and measurement error, respectively. The diffraction efficiency (DE) of each grating sample was measured, in five different locations, with a 5 mm diameter beam incident at $72^\circ$ on the sample surface.
5.2.4 Nano-indentation of MLD gratings

A MTS Nanoindenter XP fitted with a conical tip (60° included angle, 1 μm tip radius) was used in this work. The system was calibrated by performing nanoindentation on fused silica. Due to the limited imaging capabilities of the instrument and given the sub-micron scale of the pillar structures, it was not possible to resolve the impressions made by the indenter using the nanoindenter’s built-in microscopy; instead, the sample had to be transferred to a scanning electron microscope (SEM) to observe the indents and “wall” damage. Loads in the range of 0.1 to 0.5 mN were used and three types of indents could be produced by simply displacing the location of the indentation tip on the grating - centered, partially off-centered and mostly off-centered indents. The details of the indentation are described in the results section.
5.3 Experimental results

5.3.1 LIDT results for gratings as a function of the cleaning processes

In this study, the fabrication method of gratings is the same across the 3 samples. They are 13P-11-56/#566-3, 13P-11-56/#566-5 and 5P-12-56/#644-1; ‘13P’ and ‘5P’ denote coating runs, ‘11’ and ‘12’ denote the year of manufacture and ‘56’ represents the size of the coating chamber. The cleaning procedures detailed earlier are used to prepare these gratings before they are subjected to laser-induced damage testing (LIDT). The details and the subtle differences in the cleaning methods for our samples is tabulated in Table 5.2. For purposes of brevity, the grating samples will be addressed as #566-3, #566-5 and #644-1 hereafter.

Table 5.2: Summary of LIDT results for gratings and specific cleaning methods used.

<table>
<thead>
<tr>
<th>Grating#</th>
<th>Cleaning process description</th>
<th>DE Results %</th>
<th>N-on-1 (J/cm²); air</th>
</tr>
</thead>
<tbody>
<tr>
<td>13P-11-56/#566-3</td>
<td>Partial + Air</td>
<td>97.3 ± 0.2</td>
<td>3.66 ± 0.51</td>
</tr>
<tr>
<td>13P-11-56/#566-5</td>
<td>Partial + O₂</td>
<td>97.3 ± 0.5</td>
<td>4.30 ± 0.25</td>
</tr>
<tr>
<td>5P-12-56/#644-1</td>
<td>Partial + O₂</td>
<td>97.9 ± 0.5</td>
<td>1.82 ± 0.08</td>
</tr>
</tbody>
</table>

Two of the gratings (#566-3 and #566-5) that originate from the same coating run were processed together until the cleaning step. The third grating
specimen (#644-1) was fabricated a year later using an identical coating process (5P-12-56).

5.3.2 Nano-indentation data - concept of minimum deflection to fracture

Nano-indentation tests were performed on all 3 grating samples at loads of 0.1, 0.2, 0.3, 0.4 and 0.5 mN. For each sample and at each load, 9 indents were made at locations several microns apart. The aim here was to make as many de-centered indents as possible. As mentioned in detail elsewhere [8, 15], the centered indents are useful in measuring the yield strength of silica at nano-scale corresponding to this unique geometry. Off-centered indents on the other hand, are inherently related to fracture of the grating walls which can now be used to explore a connection with laser-induced damage testing (associated with fracture as well).

Figure 5.2: Three distinct nano-indentation responses are seen in MLD gratings.
Therefore, after performing indentations on the samples, we analyzed each corresponding load-displacement curve to separate the off-centered indents from centered ones. An example is shown in the figure below for sample 566-5 indented at a load of 0.2 mN. Three distinct load-displacement curves representing centered, partially (or, very slightly) off-centered and mostly off-centered indent are shown. Clearly, the centered indent looks similar to an indent in a bulk material [8, 15] and has no silica wall fracture associated with it. The difference, however, from bulk nano-indentation is that in bulk nano-indentation the surrounding material laterally constrains the material deformation. In grating (“wall”) nano-indentation, such lateral constraint is reduced due to the small thickness of the silica wall. The other two curves, showing the off-centered indents, include fracture which is seen by the sudden break in the curve (leads to a “plateau”) followed by loading again. The SEM images shown in Figure 5-2 illustrate these differences well.

For purposes of extracting a metric that can be useful in analyzing mechanical performance of gratings that can then be compared to their optical performance (LIDT) we located the point of initiation of fracture for each of the load-displacement curves. This is illustrated in Figure 5-4 for grating 566-3 at a load of 0.2 mN. The location of point of initiation of fracture (penetration depth, \( \Delta \)) for each indent depends on the amount of de-centering and naturally this is different for each indent (see Figure 5-4). But in order to evaluate the grating as a whole at that particular load we chose the smallest penetration depth across all indents to represent the value at which fracture
Figure 5.3: Load-displacement curves of nano-indentation on gratings.

is initiated. In this example (Figure 5-4), the penetration depth of 81 nm is weakest site for failure under a nano-mechanical load of 0.2 mN and will be designated as $\Delta_{\text{minimum}}$. Similarly data can be collected across all the 3 grating samples for the load range of 0.2 - 0.5 mN.

We chose to consider only indents made at loads varying from 0.2 to 0.5 mN as indentations made at 0.1 mN load did not yield any discernible instances of fracture.
Figure 5.4: Location of initiation of fracture is measured using the load-displacement curves for off-centered indents made on the MLD gratings.

5.3.3 Relation of nano-indentation-induced fracture and laser-induced damage threshold

The penetration depths corresponding to the weakest sites for initiation of fracture ($\Delta_{\text{minimum}}$) at each load are plotted against the measured values of LIDT for each grating sample and shown in Figure 5-5.
5.3.4 Relation of yield stress and laser-induced damage threshold

Using the methodology discussed in literature [8] based on the geometry of the grating walls (width at the top of the wall, ‘w’ $\sim 150$ nm) and contact area, ‘a’ (function of radius of indenter, ‘R’ and load applied, ‘P’) defined at the time of initiation of fracture corresponding to $\Delta_{\text{minimum}}$, we can determine the yield “strength” of the grating and plot it against measurements of LIDT. The yield strength is a stress found for the maximum load and the impression area. This is calculated as follows:

$$ Contact \ area, \ a = \sqrt{2 \ R \ \Delta_{\text{minimum}}} $$

(5.1)
Chapter 5. Nano-mechanics of laser damage in optical gratings

\[ \text{Yield strength, } \sigma_Y = \frac{P}{2a w} \]  

(5.2)

The exacted yield stress is correlated to the laser-induced damage threshold in Figure 5-6.

Figure 5.6: Relationship of LIDT and minimum depth of penetration into the MLD grating needed to initiate fracture.
5.3.5 Thickness discontinuity observed in grating walls from cleaning and their measured LIDT (J/cm$^2$)

Observations from several SEM images such as ones shown below reveal a direct correlation between the sizes of the undulations, seen as disfigurement at the top of the grating walls (circled in the Figures 5-7(a) and (b)) and the measured LIDT. It is seen that stronger undulations are associated with gratings that performed poorly in the optical testing, yielding lower values of laser damage thresholds. Such surface defects (numerically modeled in the next section) can be expected to play an important role in determining the “quality” of the particular grating since they would concentrate electric fields and mechanical stresses associated with nano-indentation. Hence, they are important consideration to our experiments.

Figure 5.7: Relationship of LIDT and minimum depth of penetration into the MLD grating needed to initiate fracture.
5.3.6 Pores/surface heterogeneities observed on the grating floor

Another type of surface defects or heterogeneities observed are nano-sized (10 - 100 nm diameter) pores on the base or the “floor” of the grating as shown in Figure 5-8. This observation was consistent for each grating type used in our experiments. Once again, these defects can be expected to act as regions of concentration of optical as well as mechanical stress fields and impact the performance of the particular grating. Therefore, it is necessary to take a closer look at these regions especially during mechanical testing.

Figure 5.8: Pores on the “floor” of the grating structure can lead to reduced LIDT of the grating.
In summary, the MLD gratings, after cleaning treatment, are observed to have two distinctive types of surface defects from SEM images – disfiguration along the top of the “wall” (also referred as undulations) in Figure 5-7 and pores (Figure 5-8) in the “floor” of the grating structure. These defects are thought to be regions of concentration of both mechanical and optical fields and are, therefore, important features to be included in our numerical modeling.
5.4 Numerical Simulations

Numerical ‘experiments’ were performed using the commercial finite element package, ABAQUS® (version 6.14-1). Guided by 2-D finite-element analysis (FEA) performed previously ([8] and chapter 4 of thesis), the nano-indentation experiment was modeled as a 3-D problem using a total of 82,368 elements (C3D8 - hexagonal, 8-node linear brick) for the grating structure as shown in the figure below. The indentation region is significantly smaller than the size of the sample modeled and therefore this area of large deformation is modeled using a highly refined mesh as compared to regions surrounding it (Figure 5-9). This also is seen to decrease the computational cost associated with executing the analysis.

The grating structure is defined as an elastic-plastic material composed of silica with an underlying layer of hafnia ($\sim$ 130 nm) as shown in Figure 5-10. The elastic modulus of silica was selected as 95 GPa [16] and a Poisson ratio of 0.17. Isotropic hardening was implemented to model plasticity in the material corresponding to a yield stress of 2.8 GPa (based on the work described in Chapter 4). Hafnia was modeled as an elastic material with Young’s modulus of 130 GPa and Poisson ratio of 0.25. The indenter tip (diamond, elastic modulus $\sim$ 1400 GPa) is modeled as an analytical rigid body as we do not expect it to deform during the experiment.

The nano-indentation problem was set-up for simulation in 4 different ways as seen in Figure 5-11. Since the purpose of this work is to correlate
optical and mechanical damage fields in testing of gratings we will consider FEA of off-centered indents only, namely the 25%, 50% and fully-decentered models (details of the centered model are discussed in the previous). Our goal is to simulate the nano-indentation testing as well as mechanical stresses generated in optical tests in the form of radiation pressure. These analyses can then be used to evaluate the different regions in a grating structure where stresses are concentrated.

Figure 5.9: Finer meshing is used in the region of contact of the indenter tip on the grating structure.
Figure 5.10: Grating was modeled as an elastic-plastic material with silica “walls” and one hafnia layer of the MLD coating. The height of the grating is 440 nm, and the spacing is 500nm.

In the following section, we use FEM to describe effects of discontinuities and of deformation on the stresses created by nano-indentation, and by the pressure exerted during laser damage testing.

5.4.1 3-D FEA of a 50% off-centered indent

It has been experimentally observed (see Section 4.3.1) that a high degree of indenter tip off-center coupled with a relatively deep penetration depth (> ~150 nm) of indenter tip corresponds to catastrophic indents on the grating structure. For purposes of simulating nano-indentation experiments exclusively reported earlier, “slightly”-to-“mostly” off-centered indents are expected to be more useful since they include effects of both ductility and
brittle deformation. These numerical experiments are modeled as a 25% or a 50% off-centered set-up.

Figures 5-12 (a) - (d) show the evolution of damage for a 50% decentered indent as the depth of penetration of the indenter tip is increased from 50 nm to 250 nm (which is the full indentation depth). The regions of highest concentration maximum principal stress are seen in the regions of the grating wall that are “stretched” at lower penetration depths. As greater penetra-
tion depths of 170 nm and 250 nm are reached, the highest concentrations of maximum principal stress also extend to the adjacent wall since it is now, too, in significant contact with the indenter tip. This not only causes both the walls to “stretch” excessively but also affect the “foot” of the wall which is also observed to concentrate maximum principal stress. It should be noted here that we have not modeled crack growth in this simulation and therefore, it is highly likely that excessive “stretching” seen in off-centered indents corresponding to high depths of penetration would indeed fracture the silica walls. In summary, the sequence of events in off-centered indent consists of mechanical stretching of the grating top, followed by load sharing with neighboring gratings, and by load transmission to the base of the grating.

Figure 5.12a: Damage is restricted to a single wall for penetration depth of 50 nm. The height of the grating is 440 nm, and the spacing is 500 nm.
Figure 5.12b: As penetration depth is increased to 100 nm, damage extends to the adjacent wall.

Figure 5.12c: At penetration depth of 170 nm there is significant damage on the adjacent wall.
Figure 5.12d: At full penetration depths of 250 nm, both walls will fracture indicated by the build-up of tensile maximum principal stress along the walls.

5.4.2 Radiation pressure

Radiation pressure is the mechanical pressure applied by the laser illuminating the grating during the laser damage threshold tests. The laser is focused on the gratings approximately at an angle of 60 degrees from the normal of the grating wall. It is calculated as follows:

\[
 p_{\text{rad}} = \frac{I}{c} (1 + R) \tag{5.3}
\]

where \( p_{\text{rad}} \) is the radiation pressure, \( I \) is the intensity of the laser beam, \( R \) is the reflectance of the MLD structure and \( c \) is the speed of light. Fluence (known) is defined as:
Chapter 5. Nano-mechanics of laser damage in optical gratings

\[ \text{Fluence} = \frac{\text{Laser pulse energy [J]}}{\text{Area of beam [cm}^2\text{]}} = 4.63 \, J/cm^2 \]  
\hspace{5cm} (5.4)

Therefore,

\[ \text{Intensity [I]} = \frac{\text{Laser peak power [W]}}{\text{Area of beam [cm}^2\text{]}} = \frac{\text{Fluence J/cm}^2}{\text{Pulse duration[s]}} = 4.63 \, E + 11 \, J/s \, cm^2 \]  
\hspace{5cm} (5.5)

and, as a result,

\[ p_{rad} = \frac{4.63 \, E + 11 \, J/s \, cm^2}{2.998 \, E + 10 \, [cm/s]} \left(1 + 0.04\right) = 15.51 \, MPa \]  
\hspace{5cm} (5.6)

3-D FEA shows that when this calculated value of pressure is applied at the given angle on the grating walls, the highest value of maximum principal stress is positive (that is, tensile) and concentrated at the base or the “foot” of the grating wall (Figure 5-13). The highest maximum principal stress as seen in the analysis is \( \sim 63 \, MPa \). As a figure of merit, and only for comparison, the fracture strength of bulk fused silica is in the range of 50 -
100 MPa. It is worth noting here that a 2-D analysis also could have been adopted for this simulation.

![Simulation showing mechanical contribution of radiation pressure](image)

Figure 5.13: Simulation shows that the mechanical contribution of radiation pressure exerted on the gratings is concentrated at the base of the walls. The height of the grating is 440 nm, and the spacing is 500 nm.

### 5.4.3 2-D FEA of gratings (penetration depth = 50 nm, 100% off-centered) - geometric discontinuities

**a. Effect of thickness discontinuity**

The 3-D FEA discussed in the previous two section makes an important assumption - the shape of the grating is perfect; we have modeled ideal
Chapter 5. Nano-mechanics of laser damage in optical gratings

gratings. Although not realistic, it is computationally efficient especially for a 3-D model. In this section, we take into account some of the inhomogeneities that are encountered with gratings that can potentially act as regions to concentrate mechanical stresses in a nano-indentation test and have a direct impact on its laser damage threshold.

The off-centered nano-indentation experiment is modeled as a plane-strain simulation in 2-D and is meshed using 42,828 CPE4 elements (4-node bilinear plane strain quadrilateral). Highly refined meshing is used near the area of contact with a progressively coarser mesh employed as we move away from the zone of maximum deformation (grating walls and the top few layers of the grating). The grating structure is modified to a) include the effects of thickness discontinuity evident as disfigurement of the grating walls (undulations shown in SEM images in an earlier section), and b) nanometer sized surface pores. The results from the simulation are shown below and are compared to those from an ideal grating structure – illustrated in Figures 5-14 (a) and (b).

It is clearly seen that for a penetration depth of only 50 nm the “disfigured” grating concentrates max principal stresses at the “foot” of the grating wall as well as the along the undulation (peak stress ∼3GPa), whereas there is no significant accumulation of stresses along the wall of the ideal grating shape.

In addition to the stress concentration along the foot of the grating, the thickness discontinuity includes an additional effect, reminiscent of concent-
trated plastic shear deformation (shear banding).

The plastic strain (maximum principal component) for ideal and disfigured gratings at a penetration depth of 50 nm is plotted in Figures 5-15 (a) and (b), respectively. This helps further assess the areas of the grating structure that are exposed to stress concentration in a nano-indentation test. It is seen that there is a “banding” effect in the upper region of the grating wall where it makes contact with the indenter tip. This “band” or, the region under plastic strain, is significantly evolved in the disfigured grating as compared to the ideal grating structure.

Figure 5.14a: Ideal grating (no defects) - no significant accumulation of stresses at 50 nm penetration depth.

We next proceed to model inhomogeneities, such as pores, on the floor of the grating.
Figure 5.14b: Disfigured grating shows accumulation of stresses at 50 nm penetration depth.

b. Effect of inhomogeneities (pores)

A nm-sized inhomogeneity, such as a pore, is shown in Figure 5-16. A closer look at the surface pore (100 nm) on the grating “floor” reveals that it is also a region of concentration of the highest levels of maximum principal stress (∼3 GPa) in a nano-indentation test (Figure 5-16). This indicates that the area around a surface pore, which is expected to concentrate electrical fields during optical testing, is not only exposed during mechanical testing but, in fact, concentrates high levels of stresses that can prove to be catastrophic.
Chapter 5. Nano-mechanics of laser damage in optical gratings

Figure 5.15a: Plastic strain depicted as a shear band is not prominent except in the area of contact with the indenter tip.

Figure 5.15b: Shear band due to the plastic strain is prominent due to the disfigured shape of the grating modeled and extends across the top width of the grating wall.
Figure 5.16: Concentration of high levels of tensile stress at the pore on the grating “floor” from nano-indentation testing.
5.5 Discussion

5.5.1 Effect of cleaning procedures on LIDT

The cleaning procedure is widely reported to have a significant impact on the damage threshold of these pulse compression gratings [9, 11]. Numerous studies dedicated to studying the effects of various effects of cleaning processes (Piranha at different temperatures, Nanostrip) [17, 18, 19, 20, 21, 22] on the threshold at 10 ps, 1053 nm show that efficiency of the process (measured by reduction in traces of photopolymers and organic contaminants after cleaning) is linked to the LIDT measured for the grating.

For our purposes subtle differences in cleaning processes, shown in Table 5.2, such as use of air plasma over oxygen plasma cause significant changes in the measured LIDT for the respective gratings. Specifically, this is the only difference between gratings #566-3 and #566-5 (which were processed identically until this point) and yet the latter performed much better in optical testing (LIDT 4.3 ± 0.25 J/cm²). The same is true in comparing #566-3 and #644-1. So it must be emphasized that these differences in cleaning procedures might seem insignificant but they apparently lead to critically different optical performances.

It must be noted that although we have shown that changes in cleaning methods have led to vastly different values of measured LIDT, this is not the main purpose of this study and is discussed elsewhere [2, 7, 11].
5.5.2 Thickness undulation and concentration of mechanical fields

Guided by SEM images (in Figure 5-7) and LIDT data there is an apparent relationship between shape of the top of the grating wall and the optical performance of the grating. We summarize this relationship as:

a. Undulations can amplify E field intensification in those regions leading to higher damage probability

b. 2-D FEM results show higher stress concentrations, shear band development in a disfigured grating for the same penetration depths \( \sim 50 \text{ nm} \)

The primary purpose of the simulations in the previous section was to identify the regions of the grating structure that are affected in a nano-indentation test and then use these regions to compare nano-indentation to the results from a laser damage threshold test or an optical test. Specifically, for a 50% off-centered indent, the 3-D finite-elements model in Figure 5-12 shows that the highest levels of maximum principal stress are concentrated in the “stretched” part of the wall at lower levels of penetration depth. This region can be thought as the site of initiation of fracture in the nano-indentation experiment and the indentation depth at which the maximum principal stress exceeds the fracture stress of silica corresponds to the location of the point of initiation of fracture (compare to \( \Delta_{\text{minimum}} \) indicated in load-displacement curves, see Figure 5-4). In this case the indentation depth is in the range between 50 nm and 100 nm which corresponds well with experimental data. As indentation depths increase, fracture becomes imminent.
and is suggested by the spatial increase in “stretched” regions of the grating wall as well as adjoining areas where stress is concentrated - “stretched” region in the adjacent grating wall and “foot” of the grating.

It is widely reported in literature [10, 23, 24, 25, 26] that in a laser damage threshold test the damage to the MLD grating appears to start at the upper edge of the silica walls. This is where the modulus of the square of the electric field is highest. SEM images of our gratings (Figure 5-7), obtained after cleaning, show distinctive disfigured regions at the top of the grating wall which in some cases have thinned the gratings to a great extent. Guided by these SEM images and LIDT data there is an apparent relation between the shape of the top of the grating (or, severity of undulations created) and the respective values of damage threshold measured in optical testing. Gratings with smaller amounts of thickness disfigurement are associated with higher values of laser damage thresholds. This is interpreted by the fact that any inhomogeneity along the top of grating wall will amplify the catastrophic effects of the laser energy used to irradiate these gratings.

Now that we have established that analyzing these undulations is an important aspect of understanding why gratings behave differently in laser-induced damage testing, we discuss how nano-mechanical testing of these silica walls can be used in understanding their performance. For a penetration depth of 50 nm, it is observed in the 2-D finite-element model that the two highlighted regions in the figure for the ideal (Figure 5-14(a)) and disfigured grating (Figure 5-14(b)) concentrate the highest levels of maximum
principal stress. Observe the area around the top of the grating wall; it is clear that for a given penetration depth the disfigured grating experiences much higher levels of stress ($\sim 2.5$ GPa) as compared to an ideal grating in the same region ($< 1$ GPa). This shows that mechanical stresses are amplified greatly for a disfigured grating and as the severity of undulations increases it can be expected that stresses would also increase ultimately leading to a mechanical failure of the grating wall.

Plastic strains are also useful in understanding deformation of these gratings and it is seen that during the nano-indentation test there develops a “shear band” as contact proceeds. Figures 5-15 (a) and (b) show a comparison between the “shear bands” of an ideal and disfigured grating structures respectively. Clearly, the “banding” effect is more severe in case of the grating with an undulation and extends across the width of the wall along the region where it is disfigured. Strains as high as 45% are seen in regions away from the contact area and are highlighted in the figure. The shear band in the ideally shaped grating is contained mostly within the area that is in contact with the indenter tip.

It must also be noted that the penetration depth chosen here (50 nm) to model the nano-indentation stresses in the grating is similar to the values of $\Delta_{minimum}$, from the load-displacement curves, which represents the point of initiation of fracture. Therefore, it can be inferred that under nano-mechanical testing, the gratings with more severe undulations will fracture before gratings that are relatively free of these features. This result is critical
in explaining that gratings with a lower $\Delta_{\text{minimum}}$ have a lower laser-induced damage threshold (LIDT) as reported in section 5.3.3 and shown in Figure 5-5. Also, it is worthwhile to make note that these simulations highlight that a nano-mechanical test exposes regions of the grating structure that are imperative to its laser threshold performance statistics.

### 5.5.3 Surface heterogeneities on the grating “floor”

It is known that defects on the surface of an optical structure can contribute substantially to deterioration of their laser-induced damage performance [27, 28, 29, 30] by enhancing localized absorption effects [31]. In this work, for the gratings we have studied, the surface heterogeneities are manifested in the form of localized pores and are a strong indicator of the quality of the grating surface.

SEM images of our cleaned gratings (Figure 5-8) show the presence of these surface pores on the “floor” of the grating structure. These pores, 10 - 100 nm in diameter, are thought to be associated with the fabrication process discussed earlier. Of course, there is also the possibility that these defects arise from cleaning techniques. The pores act as absorbing sites for damage initiation. In an optical test, temperature evolves by thermal diffusion-based model [32]. The implication is that this will lead to a lower laser damage threshold value for the grating sample. Therefore, to correlate mechanical and optical “stress fields” that govern the failure of these gratings such sites must be incorporated.
2-D FEA analysis (Figure 5-16) shows that in a nano-indentation test, not only are these sites subjected to mechanical stress but in fact, are seen to exhibit very high values of maximum principal stress (\( \sim 3 \) GPa). These stresses are positive, that is, tensile in nature and can lead to fracture/damage to the grating in this region. This is a clear indication that nano-mechanical testing exposes such nano-sized pores on the surface of the grating and, naturally, the higher the density of such heterogeneities, the higher the spatial extent of the stress build-up on the grating floor and therefore, lower mechanical strengths. Once again, this is evidence that nano-indentation measurements expose regions on the grating structure similar to an optical test.

### 5.5.4 Radiation pressure

The mechanical component of radiation pressure is primarily dominant at the base of the gratings and can act as source of amplification of electric fields in that region.

The value of maximum principal stress observed at the base of the grating wall (\( \sim 63 \) MPa) is significantly lower than the fracture stress of the silica walls but it must be noted here that the purpose of the simulation is to show the regions of the concentration of mechanical stress. Of course, this analysis does not include any thermal stresses generated during the laser damage testing. These regions of concentration of highest levels of maximum principal stress (“foot” of the wall) are consistent with the observed failure pattern of the gratings in optical testing and indicated in the SEM image in
Figures 5-17(a). It is seen in the images that most of the grating walls have either “melted” due to exposure to high temperatures or have mechanically “uprooted” at the base of the grating wall. This mechanism of failure is consistent with the results of the finite-element analysis and lends validity to the simulation. Therefore, mechanical stress from a nano-indentation test, as well as an optical test (radiation pressure) are observed to lead to similar response at the base of the grating wall. There is another failure pattern visible (Figure 5-17 (b)) in the form of “chipping” at the top of the grating wall. This is well documented in literature [1, 26] but is beyond the scope of this work.

5.5.5 Correlation of optical and mechanical tests (LIDT and $\Delta_{\text{minimum}}$)

Figure 5-5 shows LIDT for the three differently cleaned gratings against $\Delta_{\text{minimum}}$ at various loads used to perform the nano-indentation measurements. It is apparent that there is a strong linear dependence of $\Delta_{\text{minimum}}$ on the measured LIDT ($\text{J/cm}^2$). LIDT increases with increasing values of $\Delta_{\text{minimum}}$, that is, the more “brittle” a grating, the lower its damage threshold. This correlation is novel and important for two different reasons. First, it provides us with a quantitative metric which can be used to predict optical performance of gratings based on nano-mechanical tests alone. Simply put, a grating that shows an earlier initiation of fracture in an off-centered nano-indentation test (tracked using load-displacement curves) has more like-
Figure 5.17a: Stresses concentrated at the base of the grating walls during an optical test cause “uprooting” as seen here. Thermal stresses cause “melting” of the material.

lihood to be associated with lower value of laser-induced damage threshold as compared to a grating that could absorb more mechanical stress before initiation of fracture. Second, this result can also be extended to correlate yield stress in these gratings (at the time of first fracture) to their respective laser damage thresholds. The relation of LIDT and yield stress in Figure 5-6 indicates that a grating with a higher laser-induced damage threshold will have a lower value of yield stress. This means that for decreasing yield strength, the grating is more ductile or can absorb more mechanical energy
Figure 5.17b: “Chipping” mechanism of failure in gratings after a laser damage test.

before it fractures. In summary, gratings with higher ductility demonstrate higher LIDT.

It is also worth noting that from, Figure 5.5, the correlating lines, when extended, have intercepts near zero. Of course all gratings have a non-zero LIDT; however, this observation indicates that, if the deflection $\Delta_{\text{minimum}}$ to fracture, is practically nil, then the resulting LIDT also vanishes. Such correlation of fracture and LIDT is in agreement with the discussion in this section.

We now proceed to discuss first-principles-based dimensionless metrics for
correlating our results between nano-indentation and optical performance. Our goal is to cast our results in a way that may extend their range of validity to experimental conditions other than the ones we have used here. In essence, we are seeking appropriate ways to cast our experimental results in a dimensionless form.

Higher ductility in grating structures can be thought in terms of “stretched” zones as indicated in finite-element simulations (Figure 5-12 (c)). This “stretching” before initiation of fracture in an off-centered indent is attributed to the (tangential) stress (hoop) exerted by the indenter. This phenomenon is broadly analogous to an internally pressurized cylinder. The pressure causes the cylinder to expand or “stretch” and we can calculate a hoop stress ($\sigma_{\theta\theta}$) and strain ($\varepsilon_{\theta\theta}$) associated with it. The stress is a function of the pressure (force applied by indenter), radius of the cylinder (amount of off-center in nm of the indenter) and thickness of the cylinder (width of the top of the grating wall). The fracture strain is calculated for the penetration depth ($\Delta_{minimum}$) at which “stretching” leads to initiation of fracture. The hoop strain can be estimated from the definition of strain and is depicted in Figure 5-18. The estimate is:

\[
\epsilon_{\theta\theta} = \frac{u_r}{L} = \frac{\Delta_{minimum} \tan \theta}{L} = \frac{\Delta_{minimum}}{\sqrt{R_{ind}^2 - L^2}}
\]  
(5.7)
Chapter 5. Nano-mechanics of laser damage in optical gratings

Figure 5.18: Geometry of grating in contact with nano-indenter tip used to calculate fracture strain.

This dependence is shown to contain the minimum depth of penetration so as to initiate fracture ($\Delta_{\text{minimum}}$). We can now normalize $\Delta_{\text{minimum}}$ to $\varepsilon_{\theta\theta}$ in the plot of LIDT vs $\Delta_{\text{minimum}}$.

We also need to normalize laser-induced damage thresholds to some nominal threshold fluence. One way to do this is to consider that the mechanism of laser-induced damage during an optical test is due to thermal stresses exceeding or equaling the strength of the material, or reaching some critical temperature. It is reported in [32] that the damage in the optical material is established once temperature of the defect-surrounding material reaches its melting point. Therefore, threshold fluence as a function of this critical temperature (melting point of the optical material which in our case is silica) can be now calculated in equation 8.
Chapter 5. Nano-mechanics of laser damage in optical gratings

\[ F_0 = \frac{3.1 \, T_{cr} \, K_h \, \sqrt{\tau}}{\gamma \, \sqrt{D}} \]  \hspace{1cm} (5.8)

where:

- \( F_0 \) is the threshold damage fluence;
- \( T_{cr} \) is the critical temperature or, the melting point of silica \( \approx 1900 K \);
- \( K_h \) is the thermal conductivity = 1.4 W/ (m K);
- \( \tau \) is the pulse duration = 10 ps;
- \( D \) is the thermal diffusivity (for silica) = 0.0075 cm\(^2\)/s; and
- \( \gamma \) is the absorptivity at 1053 nm = 10 E-3;

The result is that \( F_0 = 2.8 \) J/cm\(^2\).

Therefore, the LIDT of the gratings can be normalized to \( F_0 \). The dimensional plot shown earlier in Figure 5-5 is re-plotted in Figure 5-19 by using dimensionless quantities. Normalizing the \( \Delta_{minimum} \) and LDT has the advantage that the new plot is truly non-dimensional and can be used to predict the trend that, for increasing fracture strains, the normalized laser-induced damage fluence will also increase. Again, notice that the correlating straight lines essentially pass through the origin.
Figure 5.19: Normalized plot showing the dependence of damage thresholds on fracture strain developed in gratings during nano-indentation testing.
5.6 Conclusions

A novel analysis has been presented to show that nano-indentation testing, supported by SEM images and finite-element simulations, can be effectively used to interpret the “quality” of a grating post cleaning. The most widely accepted metrics to rate the performance of MLD gratings used in high powered laser systems are expressed through optical tests in the form of LIDT and diffraction efficiencies (D.E.). Not only do nano-mechanical tests naturally complement laser damage testing by providing a fracture-derived metric ($\Delta_{\text{minimum}}$) that distinguishes between grating samples based on their propensity to fracture, but also exposes identical regions of the grating structure to stresses as in a laser damage test. The analogy is illustrated in Figure 5-20. Therefore, we have argued that nano-mechanical testing carried out in the proposed way (that is, identifying the weakest mode of the grating deformation) can be implemented as a rapid first test to predict how MLD gratings will perform when subjected to more rigorous and specialized optical tests such as laser damage testing.

In the Figure 5-20 below, we summarize schematically the analogy between stress/strain field concentration and electromagnetic field concentration.

The following main conclusions can be made from this study:

1. Subtle changes in grating cleaning techniques lead to significant changes in the measured LIDT.
2. Our work shows a strong correlation between the nano-mechanical fracture-based metric, $\Delta_{\text{minimum}}$ and laser-induced damage threshold measured through optical testing for the grating samples tested. It is observed that a smaller value of LIDT is associated with a smaller $\Delta_{\text{minimum}}$ or simply, a grating that has a tendency to fracture easily in a nano-indentation test will most likely have the lowest laser damage threshold.

3. LIDT decreases as the measured yield stress for the grating samples increase. In other words, the less deformable gratings lead to reduced LIDT.

4. The presence and size of undulations, or surface heterogeneities, on the grating structure have a direct impact on how the grating performs in both mechanical and optical tests. A grating with severe disfigurement at the top of the wall is more likely to have a low value of LIDT as compared
to a grating that was relatively free of this artifact.

5. Off-centered nano-indentation and laser-induced damage threshold measurements expose the same regions of the structure of the MLD grating and therefore, can be seen as complementary tests.

In summary, we have presented a novel way of using nano-indentation testing, electron microscopy and finite-element simulations to interpret the laser-induced damage thresholds of optical gratings.
References


Chapter 6

Summary and Recommendations for future work

6.1 Summary of main results

Nano-structured optical materials such as amorphous silica diffraction gratings on multilayer dielectric (MLD) thin films have been lauded for emerging as critical components and performance enhancers in high-power laser applications such as in inertial confinement fusion experiments. Our work focuses on using nano-indentation, electron microscopy and finite-element (2D and 3D) simulations to study nm-scale structures such as gratings and thin films. With these tools we measure and observe the nano-mechanical material properties (elastic, plastic, and fracture) of nm-level features along with their associated defects in important optical components that include single layer oxide films, multilayers comprised of oxide layers, and optical diffraction gratings. These nm-level features are of the order 100 - 500 nm. Following is a high-level overview of our main results:
Separation of nanoscale brittle and ductile deformation in patterned amorphous silica optical surfaces using nano-indentation – induced unique indentation response in optical gratings, revealing that elasticity, ductility and fracture at the nm-level can be studied separately, in contrast to flat surfaces of brittle materials where deformation and fracture are coupled.

Nano-mechanics of laser damage in optical diffraction MLD gratings – employed nano-indentation as a diagnostic tool to co-relate laser damage performance of gratings (silica walls) that were cleaned using different techniques, to nano-mechanical fracture produced in nano-indentation testing. For the first time we demonstrated the relation between laser-induced damage resistance and nano-mechanical robustness in these important optical nano-structures.

Failure analysis and nano-mechanical characterization of MLD thin films – characterized “blister” defects, generated by cleaning methods, to understand the failure and fracture mechanisms of multilayered optical oxide thin films. Electron microscopy, focused ion-beam (FIB) milling and atomic force microscopy were used to identify the true geometries of “blisters” as well as for developing models of mechanical response to explain the cracking mechanism leading to “blister” formation.
6.2 Recommendations for future work

6.2.1 Multi-layer thin films under different environmental conditions

Optical multilayers are grown by evaporation under vacuum conditions, but often used and handled under ambient conditions. It is well known that humidity may contribute significantly in the generation of large compressive stresses [1, 2, 3], which themselves are coupled with the onset of laser damage. The incorporation or expulsion of water vapor is a diffusion-driven mechanism and is complicated because of two factors: (a) different oxides have different maximum solubility of water (and diffusion coefficients) and, (b) presence of extensive grain boundaries within each layer in the multilayer which are due to the evaporation growth conditions and provide an escape route for diffusion to take place. It is, therefore, necessary that these multilayers be tested in various conditions of humidity to determine how the mechanical behavior of these thin films change as the humidity levels change. Such a study based on nano-indentation will also be useful for modeling the interaction of water vapor with the oxide layers in the multilayer.

Currently, set-up for performing such tests is not available at the university and therefore we collaborated with a group out of England led by Prof. Ian Ashcroft (University of Nottingham). Multilayer (hafnia-silica system) samples of thickness 5μm were sent for nano-indentation under controlled atmospheres with relative humidity (RH) levels of 23, 50% and 80%. The
data generated (displacement of the indenter tip in the film, modulus and hardness) clearly was dependent on the RH% used. These results are summarized in Figure 6-1. Results obtained from Ashcroft lab are also compared to data generated in our lab at ambient conditions on the same multilayer (around the same time). It should be mentioned that sample was held at a particular humidity for at least 10 hours before actual nano-indentation testing was started.

We also investigated the nature of the load-displacement curves for different loads at humidity level 81%. The plot (Figure 6-2) shows a “step” kind of a behavior which is very prominent at the higher load of 400 mN (penetration depth $\sim$50% of film thickness). On closer analysis it is observed that the number of “steps” ($\sim$25) closely matches the number of layers in the multilayer (28 layers). This is clearly a result of alternating layers of hafnia and silica absorbing moisture at different rates and amounts.

The load-displacement curve shown in the preliminary work (Figure 6-2) represents the response of the hafnia-silica multilayer when indented at different loads in an atmosphere with 80% RH. The loading part of the curve shows a “stepped” response with each kink in the curve almost corresponding to each individual layer in the multilayer (28 layers, $\sim$5 $\mu$m). This unique nature of the curve is very clear and prominent at loads of 400 nm which correspond to a penetration depth of $\sim$3.2 $\mu$m. As mentioned earlier, capabilities to perform such tests currently do not exist at the university and this data was generated in collaboration with Loughborough University, UK.
Figure 6.1: Comparison of nanoindentation data obtained at various RH% from Ashcroft lab. Clearly the higher humidity levels have a marked difference on the mechanical properties of the multilayer. Data from England is also compared to data from our lab.
Figure 6.2: Load-displacement curves generated (Ashcroft lab) at different loads for the multilayer held at RH $\sim$80%. The plots show a “step” type behavior that can be correlated to the number of layers in the multilayer tested.

Guided by this very interesting result future work would involve collaboration with Micromaterials Inc, UK (a nanoindenter manufacturing firm) to perform humidity based testing on our multilayer and individual layer thin film samples. The motivation to perform these tests has been mentioned earlier but what is equally important in understanding the effect of humidity on the mechanical response of these multilayers is the response of the individual layers under identical conditions that compose these multilayers. Therefore,
we propose that future research include testing of individual layers (of similar thicknesses as in multilayers) and correlating their mechanical response with that observed for the entire multilayer. Also, future work would explore the changes in mechanical response of a multilayer deposited using a plasma assist e-beam evaporation process and the effect of a “water-stop” layer such as alumina in the stack.

The specific aim of these experiments would be to measure the mechanical properties (Hardness \([H]\), elastic modulus \([E]\)) and record the load-displacement curves as a function of \(\%\) Relative Humidity \((RH)\) for a specified load range for all the thin film samples (multilayers and individual layers) using a standard Berkovich nano-indenter tip. The procedure that will be followed for testing in different humidity conditions is to measure \(E\) and \(H\) for the specified load range at lab conditions, that is, without imposing any special humidity or temperature conditions and then at different levels of \(\%\) RH. Each of these tests should be performed on a different piece of the (same) multilayer or the single layer. Also, it is recommended that for each test the sample must be maintained at that value of \(\%\) RH, for which it will be tested, inside the indentation chamber for at least 10 hours to ensure desired (and uniform) levels of moisture throughout the sample. Initial testing should be performed on the following samples: 3 multilayers \((\text{HfO}_2\text{-SiO}_2, \text{HfO}_2\text{-SiO}_2/\text{plasma assist e-beam}, \text{HfO}_2\text{-SiO}_2/ \text{with Al}_2\text{O}_3 \text{stop layers})\) and 3 individual layer thin films \((\text{HfO}_2, \text{SiO}_2 \text{and Al}_2\text{O}_3)\).

Through these experiments one can hope to achieve the long term goal of
understanding the mechanism of water vapor interaction in these high laser
damage threshold oxide multilayers.

6.2.2 Application of indentation on patterned optical surfaces: strength and robustness of very thin finished glass edges

Perfectly centered indentation on grating walls gives rise to the idea of indentation of very thin glass edges possibly to predict the strength and therefore lifetime of optics manufactured using very thin glass. The most important difference in the application of indentation to these two problems is the distinction between the length scale involved – analysis of gratings are prominently on the nanometer scale whereas indentation of very thin glass edges (∼0.1-0.3 mm thick) will operate (at least) on the micrometer scale.

Prediction of lifetime by determination of strength of thin glass is a very important problem in optics manufacturing. These very thin edges are finished using grinding (Figure 6-3) or very rarely, polishing techniques. These processes introduce flaws in glass referred to as chips (Figure 6-4) which determine the overall strength of the glass part.

For future work we suggest use of (nano- and micro-) indentation techniques on very thin glass edges to study the impact of chips on measuring the strength of glass. The important parameters here would be adequate selection of the indenter tip to match the thickness of the glass edge and the “condition” of the finished edge. In our previous work the condition of the
Figure 6.3: Load-displacement curves generated (Ashcroft lab) at different loads for the multilayer held at RH ~80%. The plots show a “step” type behavior that can be correlated to the number of layers in the multilayer tested.

surface of the silica grating walls was not very critical as all grating walls were manufactured identically but in glass edges the finishing process could be very different depending on the end application. Therefore, this work will incorporate these parameters into modeling the indentation response of very thin glass edges.
Figure 6.4: Load-displacement curves generated (Ashcroft lab) at different loads for the multilayer held at RH $\sim$80%. The plots show a “step” type behavior that can be correlated to the number of layers in the multilayer tested.
References

