MECHANICAL PROPERTIES OF PECVD BORON CARBIDE

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To the best of our knowledge, the mechanical properties of PECVD boron carbide (BC) grown using ortho-carborane as a source molecule have never been investigated before. Therefore, this thesis is an attempt to apply the bulge test and the nanoindentation technique for the mechanical characterization of PECVD BC thin films. Mechanical properties such as the Young’s modulus, hardness and residual stress were investigated. The bulge test system using an interferometry technique to measure the deflection of membrane has been designed. Commercially available LPCVD SiNₓ membrane windows were used as a substrate to deposit BC films for the bulge test. The effect of SiNₓ membrane configuration on the stability of SiNₓ/BC bi-layer membranes is also studied. The bulge test was used to investigate the residual stress in annealed BC films with two different thicknesses close to 59 and 74 nm.

The nanoindentation technique has been used to investigate the Young’s modulus and the hardness of as-deposited and annealed BC films deposited on silicon substrates. The properties of three film thicknesses close to 100, 200, and 300 nm have been investigated in each category. The compressive stress and the density of films were found to be the two important factors affecting the Young’s modulus and the hardness of BC films. The investigated properties are compared with literature values of BC films.
deposited by different forms of sputtering techniques. Spectroscopic ellipsometry was used to investigate film thickness.
This work is dedicated to my grandfather Kedarnath Aher and my grandmother Nanubai Aher.
ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

TITLE PAGE..................................................................................................................i
ABSTRACT......................................................................................................................ii
ACKNOWLEDGEMENTS.................................................................................................v
LIST OF FIGURES..........................................................................................................x
LIST OF TABLES.................................................................................................................xiii
1. INTRODUCTION .........................................................................................................1
   1.1 Boron carbide..........................................................................................................2
   1.2 Importance of the mechanical testing of thin films.................................................2
   1.3 Experimental techniques for the mechanical testing of thin films.......................4
   1.5 Literature values of the mechanical properties of boron carbide (BC) and silicon nitride (SiN_x) thin films.........................................................................................7
2. EXPERIMENTAL PROCEDURES - BC FILM GROWTH AND THICKNESS MEASUREMENTS .......................................................................................................................8
   2.1 Introduction.............................................................................................................8
   2.2 Source compound molecule...................................................................................9
   2.3 PECVD system ....................................................................................................10
   2.4 Deposition procedure ..........................................................................................12
      2.4.1 Post-deposition annealing procedure ..............................................................14
   2.5 Thickness measurement......................................................................................15
3. THE BULGE TEST FOR THE MECHANICAL TESTING OF THIN FILMS ............16
   3.1 Introduction............................................................................................................16
   3.2 The principle of bulge test.....................................................................................18
   3.3 SiN_x membrane windows ...................................................................................21
   3.4 Design layout of bulge test ..................................................................................23
3.5 Experimental setup of bulge test .................................................. 25

3.6 Design of the bulge test apparatus .................................................. 29

3.6.1 Selection of the pressure media .................................................. 29

3.6.2 Required pressure range, compressibility of pressure media and syringe stroke .................................................. 30

3.6.3 Sample mounting ................................................................. 31

3.6.4 Vibration Analysis ................................................................. 32

3.7 Experimental procedure to conduct the bulge test ............................................. 33

4. THE NANOINDENTATION TEST FOR THE MECHANICAL TESTING OF THIN FILMS ................................................................. 38

4.1 Introduction ................................................................................. 38

4.2 The Principle and Methodology ..................................................... 39

4.2.1 Amount of elastic recovery and sink-in ............................................. 43

4.3 Experimental considerations ......................................................... 43

4.3.1 Substrate effect ........................................................................ 43

4.3.2 Pile-up and sink-in ..................................................................... 44

4.3.2 Effects of micro cracks ............................................................. 45

4.3.3 Probe-tip .................................................................................. 46

4.3.4 Thermal drift, machine compliance, surface detection and surface roughness ........................................................................ 46

4.4 Experimental procedure ............................................................... 48

5. RESULTS AND DISCUSSION ................................................................. 50

5.1 Bulge test ....................................................................................... 50

5.1.1 System pressure performance ....................................................... 50

5.1.2 Analysis of fringe pattern ............................................................ 52

5.1.3 Repeatability of experimental data ................................................ 56
5.1.4 Analysis of the pressure-deflection data of a bare SiNx membrane to verify the accuracy system.................................................................57

5.1.5 Analysis of bi-layer SiNx/BC membranes to evaluate the residual stress in BC films.................................................................59

5.1.5 Experimental observations on the effects of SiNx membrane size, thickness and residual stress on the stability of a bi-layer SiNx/BC membrane....................64

5.2 Nanoindentation.................................................................................74

6. CONCLUSIONS AND FUTURE WORK .............................................86

6.1 Bulge test .......................................................................................86

6.2 Nanoindentation...............................................................................87

6.3 Future work.....................................................................................88

6.3.1 Bulge test.....................................................................................88

6.3.2 Nanoindentation...........................................................................89

7. REFERENCES ....................................................................................90

APPENDIX ...............................................................................................96

Appendix A1: Working principle of the Michelson’s interferometer ........96

Appendix A2: Alignment of Michelson’s interferometer to measure the bulge height ....97

Appendix A3: Design criteria of the pressure chamber.................................98

Appendix A4: Design criteria of the sample holder, clamping plate and assembly jig ....99

Appendix A5: Material selection for square o-rings ..................................100

Appendix A6: Selection of an epoxy ......................................................100

Appendix A7: Procedure for attaching the sample to sample holder ............100

Appendix A8: Estimating the required bulge testing pressure range ..........101

Appendix A9: Estimating the compressibility of pressure medium to build pressure ....102

Appendix A10: Estimating the required syringe stroke and number of data points ......103

Appendix A11: Selection criteria for the transducer and syringes .............104
Appendix A12: Vacuum filling procedure for the pressure chamber and the transducer
LIST OF FIGURES

Figure 1.1: Experimental techniques for the mechanical testing of thin films. .................6
Figure 2.1: PECVD system. ..........................................................................................10
Figure 2.2: An arrangement for holding the sample in chamber. ..................................14
Figure 2.3: An inside view of PECVD chamber during deposition. .............................14
Figure 2.4: A sample holder to hold 1 and 0.5 mm square SiNₓ membranes supported by
~ 2 mm square Si frame. ...............................................................................................14
Figure 3.1: A schematic of bulge test principle............................................................18
Figure 3.2: Photograph and schematic diagram of silicon nitride membrane window. ....23
Figure 3.3: A schematic of design layout of bulge test. ..............................................24
Figure 3.4: A picture of bulge test setup........................................................................26
Figure 3.5: A schematic arrangement for applying the pressure from outside and inside of
a cavity..........................................................................................................................31
Figure 3.6: A schematic and a picture pressure chamber assembly............................34
Figure 3.7: A schematic and a picture of a square ring filled with water......................36
Figure 4.1: A schematic of nanoindentation principle. ................................................9
Figure 5.1: Pressure drop at different pressures averaged over/hour intervals. ..........51
Figure 5.2: Pressure rise as a function of syringe stroke. .........................................51
Figure 5.3: A plot of ∆P₀ vs. ∆P_measured.....................................................................52
Figure 5.4: A picture of an aligned (left) and a misaligned (right) fringe pattern obtained
from a 1 mm square SiNₓ membrane.........................................................................53
Figure 5.5: A picture of a fringe pattern when the membrane is completely flat. ........54
Figure 5.6: Repeatability of experimental data...............................................................56

Figure 5.7: A typical pressure-deflection diagram of a 100 nm thick, 1 mm square SiN\textsubscript{x} membrane...........................................................................................................58

Figure 5.8: A stress-strain curve of a 100 nm thick, 1 mm square SiN\textsubscript{x} membrane. ..........58

Figure 5.9: A composite P-h response of SiN\textsubscript{x}/BC bi-layer membrane 1. .................61

Figure 5.10: A composite P-h response of SiN\textsubscript{x}/BC bi-layer membrane 2. .................61

Figure 5.11: A picture of a 200 nm thick, 1 mm square bi-layer membrane with a BC thickness of \sim 93 nm........................................................................................................63

Figure 5.12: A picture of a broken 100 nm thick, 1 mm square membrane ..................65

Figure 5.13: A picture of a wrinkled 100 nm thick, 1\times 4 mm\textsuperscript{2} rectangular membrane. ....67

Figure 5.14: A picture of a rectangular membranes showing no wrinkles upon second anneal cycle...........................................................................................................67

Figure 5.15: A picture of a wrinkled 100 nm thick, 1 mm square membrane ..................69

Figure 5.16: A picture of a flat 200 nm thick, 1 mm square membrane.........................71

Figure 5.17: A picture of a wrinkled 100 nm thick, 0.5 mm square membrane. ........72

Figure 5.18: A picture of a flat 100 nm thick, 1 mm square membrane.........................73

Figure 5.19: An area function calibration plot of Berkovich indenter. .........................74

Figure 5.20: Substrate effect of Si on the hardness and Young’s modulus of BC film as a function of displacement.....................................................................................76

Figure 5.21: A typical load-displacement diagram of as-deposited BC film ............78

Figure 5.22: A plot of hardness and Young’s modulus of as-deposited BC films as a function of film thickness. ....................................................................................82
Figure 5.23: A plot of hardness and Young’s modulus of annealed BC films as a function of film thickness. .......................................................... 82

Figure 5.24: An effect of compressive stress on the loading curve of BC film. ............... 85
LIST OF TABLES

Table 1.1: Literature values of the mechanical properties of BC films.........................7
Table 1.2: Literature values of the mechanical properties of SiN$_x$ films ......................7
Table 5.1: The residual stress and Young’s modulus values of a 100 nm thick, 1mm square membrane.................................................................................................................59
Table 5.2: The residual stress in annealed PECVD BC films.....................................62
Table 5.3: The Young’s modulus and hardness of as-deposited BC films ...................80
Table 5.4: The Young’s modulus and hardness values of annealed BC films .................80
1. INTRODUCTION

The aim of this research is to study the mechanical properties of semiconducting boron carbide (BC) thin films grown on silicon (Si) and silicon nitride (SiNₓ) substrates by plasma enhanced chemical vapor deposition (PECVD) using ortho-carborane (C₂B₁₀H₁₂, 1,2-closo-dicarbadodecaborane) as a source molecule for boron and carbon in suitable, constant ratio. This is relevant to optimizing the PECVD growth of semiconducting boron carbide for neutron detection applications particularly since mechanical stress in thick films potentially result in altered electronic properties or in delamination. The goals of the study are to determine the Young’s modulus, the residual stress, and the hardness of PECVD BC films. Both the bulge test and the nanoindentation technique were used to investigate mechanical properties of BC films.

Chapter 1 provides basic information on boron carbide, importance of the mechanical testing of thin films, different experimental techniques, and the literature values of the mechanical properties of BC and SiNₓ thin films. Chapter 2 gives information on deposition and thickness measurements of BC films. Chapter 3 provides the principle, design layout, experimental setup and the experimental procedure of the bulge test. The principle, methodology, experimental considerations and procedure of the nanoindentation test are detailed in chapter 4. Chapter 5 provides results and discussion followed by conclusions and future work in chapter 6. Appendix includes additional information related to principles, procedures and design considerations.
1.1 Boron carbide

Conventional forms of boron carbide are crystalline and known for their high hardness, high wear resistance, low specific weight [1], high stiffness, high melting point, high chemical and thermal stability [2], but are not useful semiconductors. Conventional boron carbide is the third hardest known material after boron nitride and diamond. The high thermal stability of conventional boron carbide makes it hardest material above 1100 °C [3].

The PECVD forms of boron carbide are quite different from traditional forms of boron carbide, which are not semiconductors. Semiconducting BC films are of interest for nuclear and electronic applications. As the $^{10}$B nucleus readily captures a neutron due to its large neutron capture cross-section area (~3840 barns), an important application of PECVD BC films is in neutron detectors which might be used in monitoring high security areas such as airports and nuclear power plants. PECVD BC films have been used to fabricate devices such as transistors [4], heterojunction and homojunction diodes [5], solid state neutron detectors [6], magnetic tunnel junctions [7] and, in different PECVD form, have been deposited to protect the inner surface of nuclear fusion devices [8, 9]. Due to the excellent tribological properties (i.e., high hardness), a form of BC film has the potential to replace traditional diamond-like carbon (DLC) film coatings for protecting magnetic films in computer hard disks from wear against magnetic head [9].

1.2 Importance of the mechanical testing of thin films

Thin films are extensively used for their electronic, magnetic and optical properties [10]. In addition, suitable mechanical properties are important to obtain in
order to avoid mechanical failure in service and in order to improve the reliability of thin film device. Thin films are widely used in applications such as microelectromechanical systems (MEMS), microelectronics, semiconductor devices, micro sensor devices, and data storage systems [11-13]. The strength and the stiffness are important properties of load bearing structural films, for instance, in MEMS micro-sensors. The Young’s modulus of film material can help to predict the strain in the film for a certain amount mechanical loading. As the micro-structural characteristics of thin films may be significantly different from their bulk counterparts, any assumption that the mechanical properties of materials in bulk and thin film form are the same is inappropriate. Further, mechanical testing of bulk materials yields average properties over a large volume of material, whereas thin film testing gives properties over a very small volume of material [13, 14].

Techniques such as Plasma Enhanced Chemical Vapor Deposition (PECVD), Low Pressure Chemical Vapor Deposition (LPCVD) and RF magnetron sputtering are often used to deposit thin films. Thin films deposited using these vacuum deposition techniques are often subject to internal stresses which fall into two categories - thermal and growth stresses. Due to the high deposition temperature compared to the temperature in service, thermal stresses may develop as a result of the difference between the thermal expansion coefficients of the film and the substrate material. Growth stresses are due to non-equilibrium structures created during the deposition or growth and can be either compressive or tensile. Film stress causes most of the catastrophic failures in films such as cracking and the delamination of film from the substrate. Additionally, residual stresses may be responsible for film buckling and void formation and are known to affect
electrical characteristics of semiconductor devices [13, 14]. Therefore, to improve the mechanical reliability of a device, it is important to know the residual stress in film and to ensure that the stress is sufficiently low. Hardness is an important property of wear resistant films [15]. The mechanical testing of thin films also yields information on yield strength, fracture strength, creep, and fatigue resistance [11]. If the mechanical properties of film are known, it is possible to tailor deposition conditions such as temperature, pressure, process gas ratio, substrate temperature, RF power and RF frequency until a film is deposited with the desired mechanical properties. Desired mechanical properties include good adhesion, good mechanical strength, and low residual stress [16].

1.3 Experimental techniques for the mechanical testing of thin films

Experimental techniques to obtain the mechanical properties of films are based on the principle of applying a mechanical or a thermal load (stress) on films and measuring the corresponding displacement (strain) [13]. The selection of a particular technique depends on its ability to measure the required properties. In addition, the cost and the complexity of the technique are important in selection. All experimental techniques are classified into two categories: Films on substrates and free-standing thin films [17]. Films on substrates require minimal sample preparation because the films can be tested on their substrates. The nanoindentation and the substrate curvature techniques are most common in this category. In the case of freestanding thin films, extensive sample preparation is required to make substrate-free films for testing. From this category, the bulge and the micro-tensile tests are most common [18]. The mechanical testing of films at micro- and nano-scale level have difficulties such as the sample
preparation and sample handling, as well as the ability to apply small loads and to extract stress-strain information accurately.

Substrate curvature (Fig. 1.1c) is a commercialized technique to evaluate film stress. When a film with residual stress is deposited on a substrate (usually Si), it bends elastically. As the film is much thinner than the substrate, the magnitude of bending is usually very small for relating the radius of curvature of substrate to the film stress. Therefore, it is vital to measure the radius of curvature precisely. The relationship between the stress and the radius of curvature is given by Stoney’s equation. The film strain can be varied only by varying the temperature and by measuring the resultant change in substrate curvature; it is possible to find the temperature dependence of residual stress. The technique has an advantage that even if the film thickness is known, one can evaluate the stress in film without any knowledge on the elastic properties of the film [11, 15, 19].

In micro-beam bending (Fig. 1.1d), a load is applied to the free end of free-standing cantilever made from the required material and the corresponding deflection is measured. Due to the small dimensions of beam, a high resolution force and displacement measuring system is required to obtain bending characteristics of beam. Usually, a nanoindentor is used to apply the load. The mechanical properties of the film are then found from simple elastic beam theory [11].

Similar to traditional tensile tests of bulk materials is the micro-tensile test (Fig. 1.1e). In this technique, the load and the displacement is monitored as the sample is strained between the grips. The data is easily converted into a stress-strain curve from
which the Young’s modulus and yield strength can be extracted [19]. Micro-structural changes due to the removal of film from its underline substrate, curling of the film due to the residual stress, film slippage between the grips, damage to the film while gripping, and uneven loading during the test are major problems associated with this technique [13, 20].

![Diagram showing various experimental techniques for the mechanical testing of thin films.]

**Figure 1.1: Experimental techniques for the mechanical testing of thin films.**

In the point-deflection technique (Fig. 1.1f), a small load is applied at the center of membrane (usually by a nanoindenter or an AFM tip), and the resultant deflection at the center is measured. Due to small membrane deflections, this technique is more appropriate to find the residual stress than to determine the Young’s modulus [21].
1.5 Literature values of the mechanical properties of boron carbide (BC) and silicon nitride (SiN$_x$) thin films

<table>
<thead>
<tr>
<th>Experimental technique</th>
<th>Authors</th>
<th>Year</th>
<th>Film deposition method</th>
<th>Young's Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoindentation</td>
<td>J.M. Grow et al.[22]</td>
<td>1994</td>
<td>LPCVD</td>
<td>~40-100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>A. Lousa et al. [23]</td>
<td>1999</td>
<td>Tuned RF magnetron sputtering</td>
<td>350</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Zenghui Han et al.[24]</td>
<td>2002</td>
<td>Magnetron sputtering</td>
<td>300-420</td>
<td>42.5-50.4</td>
</tr>
<tr>
<td></td>
<td>O. R. Monteiro et al.[26]</td>
<td>2003</td>
<td>Cathodic arc deposition</td>
<td>162-210</td>
<td>15.6-26</td>
</tr>
<tr>
<td></td>
<td>K.E. Lee et al.[28]</td>
<td>2004</td>
<td>R.F magnetron sputtering</td>
<td>200</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>K.E. Lee et al.[29]</td>
<td>2004</td>
<td>R.F magnetron sputtering</td>
<td>~216-250</td>
<td>~17.5-23</td>
</tr>
<tr>
<td></td>
<td>Y. Chen et al.[29]</td>
<td>2006</td>
<td>Pulsed DC magnetron sputtering</td>
<td>250 ± 50</td>
<td>30 ± 5</td>
</tr>
<tr>
<td></td>
<td>MJ Zhou et al.[30]</td>
<td>2007</td>
<td>Ion beam sputtering</td>
<td>-</td>
<td>~ 32.5-33.5</td>
</tr>
</tbody>
</table>

Table 1.1: Literature values of the mechanical properties of BC films

<table>
<thead>
<tr>
<th>Experimental technique</th>
<th>Authors</th>
<th>Year</th>
<th>Film deposition method</th>
<th>Young's Modulus (GPa)</th>
<th>Residual Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulge test</td>
<td>Tabata et al. [31]</td>
<td>1989</td>
<td>LPCVD</td>
<td>290</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Cardinale &amp; Tustison [33]</td>
<td>1992</td>
<td>PECVD</td>
<td>85-125</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Kalkman et al. [20]</td>
<td>1999</td>
<td>LPCVD</td>
<td>220±20</td>
<td>~100</td>
</tr>
<tr>
<td></td>
<td>Edwards et al.[34]</td>
<td>2004</td>
<td>LPCVD</td>
<td>257</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Rongjing Zhang [35]</td>
<td>2006</td>
<td>LPCVD</td>
<td>~250</td>
<td>~450</td>
</tr>
<tr>
<td></td>
<td>Hun Kee Lee et al. [36]</td>
<td>2007</td>
<td>LPCVD</td>
<td>232</td>
<td>64.95-94.92</td>
</tr>
<tr>
<td></td>
<td>P.Martins et al. [21]</td>
<td>2008</td>
<td>LPCVD</td>
<td>212±14</td>
<td>420±8</td>
</tr>
<tr>
<td></td>
<td>Han Li &amp; Vlassak [37]</td>
<td>2009</td>
<td>LPCVD</td>
<td>257.2±1.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>P.Martins et al. [38]</td>
<td>2009</td>
<td>LPCVD</td>
<td>217±14</td>
<td>411±30</td>
</tr>
<tr>
<td>Nanoindentation</td>
<td>Taylor [39]</td>
<td>1991</td>
<td>PECVD</td>
<td>178-271*</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Jason Gill [40]</td>
<td>1998</td>
<td>LPCVD</td>
<td>209</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Vila et al.[41]</td>
<td>2003</td>
<td>Sputtering</td>
<td>100-210</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Han Li &amp; Vlassak [37]</td>
<td>2009</td>
<td>LPCVD</td>
<td>242±0.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>P.Martins et al. [38]</td>
<td>2009</td>
<td>LPCVD</td>
<td>≥190</td>
<td>-</td>
</tr>
<tr>
<td>Microbridge test</td>
<td>Zhang et al. [42]</td>
<td>2000</td>
<td>LPCVD</td>
<td>202.57±15.80</td>
<td>291±56.17</td>
</tr>
<tr>
<td>Tensile test</td>
<td>Yoshioka et al. [43]</td>
<td>2000</td>
<td>LPCVD</td>
<td>370</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Edwards et al. [34]</td>
<td>2004</td>
<td>LPCVD</td>
<td>257±5</td>
<td>110-130</td>
</tr>
<tr>
<td>Point deflection method</td>
<td>Hong et al. [44]</td>
<td>1990</td>
<td>LPCVD</td>
<td>230, 330</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>P.Martins et al. [38]</td>
<td>2009</td>
<td>LPCVD</td>
<td>180-220</td>
<td>480±40</td>
</tr>
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</table>

Table 1.2: Literature values of the mechanical properties of SiN$_x$ films
2. EXPERIMENTAL PROCEDURES - BC FILM GROWTH AND THICKNESS MEASUREMENTS

2.1 Introduction

Semiconducting forms of BC have been grown as thin films but only by techniques (radiation- and plasma-induced deposition from suitable chemical source) that deposit the BC in conditions far from thermal equilibrium. Thin films of semiconducting BC have not yet been reported with extensive crystalline nature of traditional forms of BC. The BC films in the present research are nanocrystalline or amorphous in nature [45]. The optimal nature and growth conditions of semiconducting form of BC are not yet determined. However, it is common for thin layers of materials deposited on substrates to have properties that differ from bulk versions of the same materials.

Chemical vapor deposition (CVD) method is widely used to grow BC thin films. For electronics applications, high quality BC thin films are often deposited using CVD methods [46]. This method uses chemical vapors of source molecules and molecular gases instead of solid evaporants or sputter targets as source materials to deposit thin films. The process is called chemical vapor deposition because gases are chemically activated before or during deposition [47]. BC films can be grown from different gaseous precursors using CVD methods. Depending on the deposition conditions such as temperature, pressure, reactive gas mixture type and composition, BC films can be grown with different stoichiometries and physical properties [46]. In CVD method, these process parameters can be controlled for growing films with desired properties.
In the radio-frequency (RF) PECVD method, plasma is produced when a high frequency electric field is applied to the RF electrode in gaseous environment at low pressures. Plasma is a highly energetic ionized gas composed of ions, electrons and neutral atoms or molecules and can be used to cause chemical activation for deposition. The electrical energy is conducted throughout the body of gas by plasma electrons [47]. The energetic electrons ionize or excite carrier gas atoms (argon) and source compound molecules which enter the chamber along with carrier gas in plasma environment. BC films are grown by diffusion of excited source molecules to the deposition substrate and bombardment of the growth surface by energetic particles in plasma, principally ions.

Due to the additional energy from the plasma, PECVD BC films can be deposited at much lower substrate temperatures than would be required for thermal forms of CVD. Further, due to the possibility of using a non-volatile source compound and a non-reactive carrier gas to deposit films, the PECVD method is safe to work with [5, 46]. It important to realize that due to the difficulty of plasma modeling and of optimization of PECVD systems, most of the work reported on PECVD BC thin films is on experimental growth rate and characterization [46].

2.2 Source compound molecule

As mentioned before, the source compound molecule used in this research is ortho-carborane (C\textsubscript{2}B\textsubscript{10}H\textsubscript{12}, 1,2-\textit{closo}-dicarbadodecaborane). A boron (B) to carbon (C) ratio of 5:1 in ortho-carborane gives BC films with composition close to B\textsubscript{5}C [45]. A main advantage of ortho-carborane is that its vapors are non-toxic. Ortho-carborane used in this project was purchased from Sigma-Aldrich, St. Louis, MO.
2.3 PECVD system

The PECVD system used here is shown in Fig. 2.1. The design of a spherical shape PECVD chamber is based on the standard Gaseous Electronics Conference reference cell design [48, 49]. A 10” inside diameter stainless steel chamber has six 6” conflat flanges and eight 1.33” ports, custom fabricated by Kimbell Physics Inc., Wilton, NH. Inside the chamber are capacitively coupled parallel plate electrodes separated by a distance of about 20 mm. The top electrode is a circular shape showerhead assembly with uniformly drilled holes for introducing pure carrier gas (argon), as well as, argon gas along with source molecule vapors uniformly onto the substrate during deposition.

The bottom electrode is a 3” molybdenum plate heated radiantly by two Ushio
halogen bulbs (300W, 120V). To control the temperature of substrate, the bulb power can be varied easily by a variable autotransformer. The bottom electrode and stainless steel cylindrical barrel below it that house the bulbs are grounded by multiple copper wires to the base of the chamber. Only the top electrode is not grounded.

Radio frequency (RF) power at 13.56 MHz is applied via the top electrode and results in ionization of argon (to produce plasma) and source compound molecules and creation of other free radicals during the process of etching and deposition. The substrate temperature is measured by a thermocouple in contact with bottom electrode. A cam-controlled transfer fork mechanism is used to transfer samples via sputtering chamber to the PECVD chamber. After loading the sample, a central valve is closed to separate both chambers. Before the chamber is brought to the desired deposition pressure of carrier gas and source compound vapor, a roughing (Edwards – RV5 rotary vane pump) and a turbo pump (Leybold TMP-50) evacuates the chamber to a base pressure below $10^{-7}$ torr. The chamber can be maintained at a desired process pressure (0-1000 mTorr) by flowing argon gas and by controlling the position of butterfly valve between the chamber and the turbo pump. The pressure inside the chamber is monitored by a Baratron and a cold cathode gauge. A desired deposition pressure is set (by controlling the position of butterfly valve) and displayed by a MKS 600 series pressure controller. Low vacuum pressure monitored by cold cathode gauge is displayed by MKS 937A gauge controller. The gas flow is controlled by MKS 247 series mass flow controllers (MFC). MFC 2 controls the flow gas while etching and deposition. The gas lines can be opened or closed by needle valves.
The temperature of the PECVD chamber and the gas line system is set at 90°C with the aid of heating tape wrapped around them and with additional insulation. To avoid heat losses and temperature variations, both the chamber and the gas line system are covered by silicone foam and an aluminum foil, while some parts of gas handling lines are covered by silicone rubber tubing. The source vial is heated by silicone rubber heaters to 90°C – the usual source sublimation temperature. The temperature of chamber, gas lines, and source compound vial is controlled and monitored by Brand-Gaus temperature controller. MFC 3 controls the gas flow through source molecule vial for carrying the vapors to chamber while deposition.

2.4 Deposition procedure

To evaluate mechanical properties of as-deposited BC films by nanoindentation, the films were deposited on standard 3”, 381 ± 25 µm thick, Si wafers. These wafers were cleaned ultrasonically in the following order: acetone, methanol, and deionized water, for 5 min in each solution. Finally, wafers were cleaned in hydrofluoric acid (HF) solution for two minutes (63 g of water to 7 g of HF). The HF cleaning was not done on Si wafers supporting the membrane in chamber. As the windows were cleaned by suppliers (i.e, Silson and 2spi) to remove any organic contaminations, no further cleaning of them was performed before depositing BC films on them. To prevent the membranes from breaking or becoming wrinkled due to high compressive stress in as-deposited BC films, all BC films on membranes were annealed after deposition. Each membrane was held on a 3” Si wafer and was supported at its center by four surrounding pieces of Si wafer (Fig. 2.2). Due to the possibility of changing electrical conditions inside the
chamber, the idea of using a metal plate (i.e., stainless steel) with a square slot at its center to hold the membrane was discarded. In the present work, the same deposition conditions were used for all BC films, followed by a post-deposition annealing.

The pressure and the temperature of deposition were 200 mTorr and 350°C, respectively. Before deposition, to achieve the proximity of temperature between the sample and the bottom electrode, each sample was held at 350°C for a minimum of 2 hrs. About 45 min before deposition, heating of the ortho-carborane source molecule was started. Source molecule vapors were circulated in the gas line for ~ 1 min before deposition. As the membranes were quite clean and very thin, RF plasma etching prior to deposition was restricted to only about 1 min. For Si wafers (for as-deposited films), however, plasma etching was performed for 30 min. Immediately after etching, source molecule vapors entrained in argon gas were introduced into the plasma environment for deposition. The PECVD RF power was 30 W. A total of 10 sccm of argon gas was flowing into the chamber during deposition. Deposition rate was very low for initial 4-5 min, however, it increases afterwards to ~12 nm/min.

For membranes on a 2 mm square Si frame, a small aluminum holder (Fig. 2.4) was used to hold them during deposition. The holder with sample was placed in the place of the usual 10 mm square Si frame for the larger SiNx membranes, such as that shown in Fig. 2.2. For deposition of BC on a 3” Si wafer for nanoindentation, the entire Si wafer was held in 3” sample holder (ring) as shown in Fig. 2.2.
2.4.1 Post-deposition annealing procedure

After depositing the sample at 350ºC, the temperature was raised to 450ºC for annealing for 1 hour. The temperature was then set to 350ºC in order to allow the sample to return to this temperature over a 1 hour period. The heater was then switched off, and the sample was allowed to cool to ~126ºC (close to the temperature of chamber). Finally, the chamber heater was shut and the sample was allowed to cool to room temperature (~34ºC) in vacuum.
2.5 Thickness measurement

For convenience and accuracy variable angle spectroscopic ellipsometry was used to determine the BC thickness, as previously reported [45]. Due to the high accuracy, speed and ease in alignment, the M-2000 spectroscopic ellipsometer (J.A. Woollam Co., Inc) was used to determine film thickness. Ellipsometry data of Psi (Ψ) and Delta (Δ) spectra was obtained from visible to ultra-violet spectral range at six angles of incidence from 45º to 75º in 5º steps. By considering BC film layer as a Cauchy material, a Cauchy layer model (cauchy.mat) was used to model the experimental data. The model has default optical constants which relate closely with the optical constants of the BC films for optimal fit.

To fit the data generated by model, the BC film thickness used in modeling was varied until the data generated by the model exhibited a good fit with the experimental data. Thus, the best-fit model was used to obtain the BC film thickness. Knowledge of the approximate film thickness based on the expected deposition rate helped to fit the data faster. All parameters of the Cauchy model were used for fitting except the parameter named band edge (γ). As the Cauchy model works well for non-absorbing and transparent films, only the experimental data in spectral range from 0.75-2.1 eV was used for fitting as the BC films are considered to be transparent in this region.
3. THE BULGE TEST FOR THE MECHANICAL TESTING OF THIN FILMS

3.1 Introduction

The bulge test was one of the first techniques introduced to study mechanical properties of thin films [32]. In 1959, J.W. Beams conducted the bulge test for first time for mechanical characterization of gold and silver thin films. To find film properties, a circular freestanding film was clamped on a circular orifice and the deflection at the center was measured as a function of applied pressure [50]. The bulge test has since been successfully applied to wide range of thin film materials including metals [17, 19, 20, 51], ceramics [19, 36, 52-54] and polymers [55]. As mentioned before, it is one of the most widely used techniques to determine Young’s modulus, residual stress and even Poisson’s ratio of freestanding thin films. However, the test results are highly sensitive to the precision of measuring film dimensions, film deflection, and the overall accuracy with which the test is carried out [56].

Many individuals have contributed to improve the accuracy of data obtained from the bulge test. Itozaki [57] showed the importance of including initial height in the analysis load-deflection data. Small and Nix [58] highlighted the necessity of having a flat film before starting the test. Effects of initial film conditions such as wrinkles, initial height, and residual stress, on the bulge test data were also analyzed. Later, Kalkman et al [20] showed that it is possible to study membranes with non-zero initial height, as their specially designed setup was capable of measuring the deflection of the membrane from its curvature instead of measuring the deflection at the center of membrane. Vlassak [19] has derived analytical equations to model the elastic load-deflection behavior of square
and rectangular films. These equations are useful in predicting the pressure required for deflecting the films by reasonable amount - important in the design of bulge test apparatus. Vlassak [19] has also shown that the bending stiffness of film (up to 3 µm thick) can be neglected in the analysis due to its negligible effect on the total deflection of membrane. Vlassak [19] and Huang et al. [55] mention the rule of mixture formula (Eqs. (4) and (5) in this chapter) to test composite films. Xiang et al. [18] have given the importance of having high aspect ratio membranes. Effects of applying pressure from inside or outside of a micro machined cavity on the values of Young’s modulus and residual stress were reported by Mitchell et al. [56]. The influence of using a square or a rectangular shape sample on the bulge test results was highlighted by Hun Kee Lee et al. [36]. Due to these contributions and advancements in silicon micromachining techniques to fabricate membrane windows accurately, it is now possible to obtain reliable data from this method.

As the bulge test is performed on freestanding films, it is possible to study properties of exceptionally thin films (i.e., < 100 nm). Films should have tensile residual stress to remain flat before starting the test [19]. Due to the low bending stiffness of films, compressive stress may cause buckle-delamination or wrinkling of the surface of a film. In the former case, the film will delaminate partially on buckling [59-61] and, in the latter case, the film will buckle coherently with the substrate without any delamination [62, 63]. Films which fail to remain flat on wrinkling give meaningless data and therefore should not tested [64]. However, it is possible to test films under compressive stress by depositing them on membranes that have sufficiently a high tensile stress. In such cases, the composite membrane remains flat due to the net tensile stress [15, 19]. From the data
obtained from a composite structure, a rule of mixture formula can be applied to find the properties of each layer.

### 3.2 The principle of bulge test

A freestanding membrane is deflected by applying uniform differential pressure $P$ (sometimes $\Delta P$ in the literature) and the resultant bulge height is measured at the center of the membrane. Film properties are obtained from the pressure-deflection ($P$-$h$) data.

![Figure 3.1: A schematic of bulge test principle [65].](image)

For square shape membranes, a generalized equation to model the pressure-deflection behavior is given by Eq. (1) [19, 32], in which the suffix “s” is used to identify membranes made from SiN$_x$:

$$
P = C_1 \frac{t \sigma_s h_0}{a^2} + C_2 \frac{E_s t_s h_0^3}{(1-\nu_s)a^4} \tag{1}
$$

where $P =$ applied differential pressure ($\Delta P$) on the membrane, $h_0 =$ the membrane deflection at center, $a =$ half of the membrane width, $E_s$, $\sigma_s$, $t_s$ and $\nu_s$ are the Young’s modulus, residual stress, thickness and Poisson’s ratio of membrane (SiN$_x$), constants $C_1$ and $C_2$ are 3.393 and $(0.8 + 0.062\nu)^{-3}$ respectively and $E/(1-\nu_s)$ is the biaxial modulus.
Several other authors have suggested relatively close but different values of $C_1$ and $C_2$ ($f(\nu)$) for square membranes. For example, Maier-Schneider et al. [66] have reported the values of $C_1$ and $C_2$ ($f(\nu)$) as 3.45 and 1.994(1-0.271$\nu$) respectively. Both $C_1$ and $C_2$ depend on the aspect ratio of membranes and $C_2$ is also a function of Poisson’s ratio. To fit experimental P-h data by Eq. (1), it is important to measure the thickness of the membrane carefully and the width most precisely since it appears to the power of two and four in first and second term respectively.

The Young’s modulus and residual stress can be found by least squares fitting of Eq. (1) to the experimental P-h data. Alternatively, the Young’s modulus and residual stress can be found by converting the P-h data into a stress ($\sigma$)-strain ($\varepsilon$) curve using Eqs. (2) and (3) [67]:

$$\sigma = \frac{a^2 \Delta P}{C_3 t h_0}$$  \hspace{1cm} (2)

$$\varepsilon = C_4 \frac{h_0^2}{a^2}$$  \hspace{1cm} (3)

where $t$ = the thickness of single film or the total thickness composite structure, $C_3 = 3.04$ and $C_4 = 0.451$. The biaxial modulus and residual stress are found from the slope and the y-intercept of stress-strain curve respectively. Finally, the Young’s modulus is found from the biaxial modulus assuming a Poisson’s ratio for the film.

Since the BC film is deposited on the SiN$_x$ membrane, the P-h response is not governed solely by the mechanical properties BC films, but instead is the combined
response of both films. Thus, to find the properties of BC film alone from the P-h data of the composite SiNₓ/BC structure, a simple rule of mixture formula is used [55]:

\[ M_{\text{composite}} = \frac{t_{\text{SiN}_x}}{t_{\text{total}}} M_{\text{SiN}_x} + \frac{t_{\text{BC}}}{t_{\text{total}}} M_{\text{BC}} \] \hspace{1cm} (4)

where \( M_{\text{composite}} \), \( M_{\text{SiN}_x} \), and \( M_{\text{BC}} \) are the biaxial modulus of composite (bi-layer) structure, SiNₓ, and BC respectively and \( t_{\text{total}} \), \( t_{\text{SiN}_x} \), and \( t_{\text{BC}} \) are the thickness of composite structure, SiNₓ, and BC respectively.

\( M_{\text{composite}} \) can be found by converting the P-h data of composite structure into a stress-strain curve using Eqs. (2) & (3). The biaxial modulus of the bare SiNₓ film can be readily found before depositing the BC layer. Thus, the Young’s modulus of BC can be found from \( M_{\text{BC}} \).

Similarly, the residual stress in each film layer of composite structure is found from Eq. (5):

\[ \sigma_{\text{composite}} = \frac{t_{\text{SiN}_x}}{t_{\text{total}}} \sigma_{\text{SiN}_x} + \frac{t_{\text{BC}}}{t_{\text{total}}} \sigma_{\text{BC}} \] \hspace{1cm} (5)

The process to determine the residual stress in the BC film is similar to the process explained above. However, if the P-h response is only in the linear regime, one can find the residual stress from the P-h data in the linear regime alone using Eq. (2). If the P-h response is too small (~ 1.5 µm), one can find the residual stress by averaging the stress found from each pressure-deflection data point within this range. As the P-h data at these small deflections may not show continuous increase in stress as the strain on the film
increases, finding the residual stress by averaging it as mentioned above works well. This applies to find the residual stress in the both monolayer and the composite structure. Thus, there is no need to plot a stress-strain curve in order to find the residual stress from the y-intercept of this curve. Also, the stress-strain curve will not have a good fit at these deflections. In other words, only if the P-h curve is fully developed with a cubic regime, the stress-strain curve will have a good fit to find the residual stress and the bi-axial modulus from the y-intercept and the slope of this curve respectively. But if the stress increases sharply at small deflections in linear regime, plotting the stress-strain curve (even if the fit is poor at these deflections) for the P-h data in linear regime is more appropriate to find the approximate residual stress from the y-intercept of this curve.

Eq. (1) holds well only for relatively large membrane deflections and for the films with low residual stress (≤ 500 MPa). The deflections should be large enough for the P-h curve to enter into cubic regime. In Eq. (1), the linear and cubic terms are directly proportional and are dominated by the residual stress and Young’s modulus respectively [32, 56]. Therefore, small membrane deflections are enough to estimate residual stress from linear regime. At high deflections, when the film becomes stiff due to the contribution of the Young’s modulus, the P-h curve enters the cubic regime. Therefore, the Young’s modulus can be found accurately only with large membrane deflections.

3.3 SiNx membrane windows

For the bulge test, membrane windows (from Silson Ltd, UK and SPI Supplies Inc, PA) were used as substrates on which to deposit PECVD BC films. Both rectangular (1×4 mm²) and square (1×1 mm²) membranes from Silson Ltd. were supported by 525
µm thick, 10×10 mm² Si frame. All rectangular membranes had a thickness of 100 nm, while the square membranes had thicknesses of 100 or 200 nm. The membranes from Silson Ltd. had a low intrinsic tensile stress (~120 and 220 MPa). From SPI Supplies, 100 and 150 nm thick, 1 mm square windows and 100 nm thick, 0.5 mm square windows were used. All windows from SPI supplies were supported by 200 µm thick 2×2 mm² Si frame.

Even although rectangular windows were not found useful later due to their high aspect ratio and low intrinsic tensile stress; it is relevant to be aware of their potential advantages. A membrane with a long edge (2b), a short edge (2a), and b≥4a is considered to have central deflection close to that of an infinitely long rectangular membrane (Fig. 3.2) because the plain-strain condition holds well. When this condition exists, the strain in one direction of the film is exactly zero. The stress and strain can then be expected to remain uniform across the width. Because of this, yielding will initiate uniformly over an entire cross-section membrane, making such geometries ideal for studying the plasticity of thin films [18, 19].

As the plain strain modulus of a long rectangular membrane and the bi-axial modulus a square membrane obtained from the pressure-deflection data is given by E/1-ν² and E/1-ν respectively, the film may appear to be stiffer in the case of square membrane because its deflection depends more strongly on the Poisson’s ratio compared to a rectangular membrane. Therefore, a long rectangular can predict the Young’s modulus of the film more accurately, especially if the Poisson’s ratio of the film is not known [15, 19]. As the Poisson’s ratio of BC and SiNₓ membrane is assumed, a
rectangular membrane is more ideal to find the Young’s modulus. Also, the indentation modulus \(E/1-v^2\) found from the nanoindentation test is directly comparable to the plain-strain modulus found from the bulge test, making direct comparison of the Young’s modulus found from both techniques more appropriate. A SiN\(_x\) membrane window (Silson) with intrinsic tensile stress is shown in Fig. 3.2. For a square membrane, the only difference is \(2a = 2b\).

Figure 3.2: Photograph and schematic diagram of silicon nitride membrane window.

Due to the high mechanical strength of SiN\(_x\) membranes even at nanometer scale, it is possible to use very thin membranes as a substrate for depositing of other films [19]. If thick SiN\(_x\) membranes were used instead, then the P-h response of bare SiN\(_x\) membrane may overlap with the composite response of two films which may yield inappropriate results.

3.4 Design layout of bulge test

The bulge test apparatus used at educational and research institutes for the mechanical testing of thin films may differ in design but the basic principle is same. A schematic of bulge test design layout used in the present research is shown Fig. 3.3. It was designed, built and tested by Dhairyashil Aher. The machining of pressure chamber
was very precisely carried out by Michael Jensen and Tom Elledge of the Chemistry/Physics and Astronomy Instrument Shop.

**Figure 3.3: A schematic of design layout of bulge test.**

The main component is the pressure chamber which holds the sample and to which two syringes and a pressure transducer are attached. A film is attached to a sample holder for loading it to chamber. One of the syringes applies pressure using a syringe pump, while the other syringe, whose stroke is controlled by a micrometer head, is used for the purpose of sealing and initial alignment. The pressure transducer monitors gauge pressure with respect to time. Using a Michelson’s interferometer arrangement (See Section 3.5), the film deflection is measured with a resolution of quarter the wavelength of light (650 nm) from a monochromatic coherent light source that is used to form an interference fringe pattern (to measure deflection). A 5x objective lens is used to increase
the diameter of the laser beam, while a fringe pattern is enlarged by a plano-concave expander lens. A variable density filter matches the intensity of beam reflected from the mirror with the intensity of beam reflected from film in order to obtain a better contrast fringe pattern.

The camcorder and the transducer record fringes (and hence membrane deflection) and pressure, respectively, on same time scale. Thus, by correlating the time of deflection and pressure, the p-h data is obtained.

3.5 Experimental setup of bulge test

Appendix A1 gives the principle of a Michelson’s interferometer. For smooth and highly reflective samples an interferometer gives a better displacement resolution compared to other techniques and makes it possible to check if the membrane is flat before starting the test. However, this technique is extremely sensitive to vibrations that can easily distort the fringe pattern. Authors who have implemented an interferometry technique to measure the deflection of membrane include Vlassak [19], Gill [40], and Mitchell et al. [56]. Other techniques that have been implemented for the same purpose include scanning laser technique [20], white light interferometer microscope [38], laser nanosensor [68], an optical profilometer [69] and a laser vibrometer [36].

The configuration used in the present research was slightly modified from the basic Michelson’s interferometer in that one of the mirrors was replaced by the reflective surface of membrane. A bright laser source (class IIIa, $\lambda = 650$ nm) was used with a nominal output power of $< 5$ mW. The diameter of the laser beam was increased by a 5x
Figure 3.4: A picture of bulge test setup.
objective lens placed between the laser source and beam splitter rather than using a beam expander. A non-polarizing beam splitter provided a true 50/50 split of the light wave regardless of the incoming polarization. Fringes were viewed on a flat non-glossy white screen. The beam splitter and pressure chamber were mounted on prism table to provide a flat surface which could be adjusted along two axes over a range of 4 degrees – crucial in the alignment of interferometer. The table height was by adjusted by posts.

The mirror was mounted on a small mirror mount with two fine-resolution tilting screws for adjusting the mirror precisely in two directions during the alignment of fringe pattern. Linear translational stages gave precise linear movement to the mirror and the pressure chamber (See Appendix A1 and A2 for the principle and initial alignment of interferometer). All optical components were purchased from Edmund Optics, Barrington, NJ and OptoSigma Corporation, Santa Ana, CA.

Syringes were Hamilton’s 1700 series gastight syringes of 10 and 25 µL volumes with a stroke of 6 cm. A Teflon tip at the front end of each syringe plunger gave a leak-free seal between the plunger and syringe barrel. The syringes had a CX termination with ¼”-28 UNF male fitting for screwing them into the pressure chamber and could withstand pressures up to 1000 psi. For the loading cycle, it was possible to use a single syringe. However, in the present setup, a second syringe was used for sealing and initial alignment of fringes. The plunger of syringe for sealing purpose was modified by shortening its length to about 2.5 cm in order to help avoid buckling of the plunger to help make the system more stable. (See Appendix A11 for the syringe selection criteria).
For simplicity and reliability in pressure measurement, a GS4200-USB digital pressure transducer (Ellison Sensors International Ltd, UK) was used. Such a transducer is pre-calibrated and connects to a PC via a USB connection. The data is presented on a PC via Ellison sensors configurable software (ESI-USB) which provided the ability to measure, analyze, and record pressure directly in real time and also gave a graphical representation of pressure vs. time data. For simplicity of analysis, data were exported for use in Microsoft Excel spreadsheet program. The transducer had a maximum pressure range of 1600 kPa, with the maximum error associated with non-linearity and hysteresis being \( \pm 0.1\% \) (1.6 kPa) over full scale (FS). It could display pressure readings at minimum time intervals of 0.2 sec with 0.05\% FS repeatability, and nominally 21 bit resolution, corresponding to a pressure resolution of nominally 0.00008 kPa (1600 kpa/\(2^{21}\)). This transducer has a large internal volume of 17 mL (which should be known while designing the bulge test apparatus). It is compatible with water and has a ¼” NPT male pressure connection port.

During the loading cycle, a syringe pump (New Era Pump Systems Inc., Wantagh, NY) was used to drive one of the syringes and so to apply pressure gradually without encountering the vibrations that would occur if the pressure were applied by manually adjusting a micrometer head. The smallest displacement resolution of syringe pump is as small as 0.0024 mm/min. Fringes were recorded with a Sony model HDR-CX100 camcorder, selected for its ability to record 1920×1080 pixels high definition (HD) video at 60 frames / sec without missing any fringe movement.
The pressure chamber, sample holder, clamping plate and assembly jig (Fig. 3.6) were machined from brass due to its compatibility with the pressure medium (water) and its ease in machinability. Each sample was attached to the sample holder by a slow cure epoxy (Epolite FH-5313A-A-PAK from Andover Corporation, NH, USA) chosen to avoid curing induced mechanical stress. The clamping plate clamped the sample holder and allowed for quick loading and unloading of samples. An assembly jig was used for the alignment and attachment of sample to sample holder. (See Appendix A6 and A7 for the epoxy selection and the procedure for attaching the sample to sample holder). A square cross-section viton o-ring gave a leak-free seal between the sample and the pressure chamber (See Appendix A5 for the selection of square-ring material). All components were mounted on a steel plate supported by a granite block on a bicycle inner tube that was pressurized to damp floor vibrations (See Section 3.6.4 for vibration analysis). The setup was surrounded by a cardboard enclosure in order to minimize the distortions resulting from air movement in the lab.

3.6 Design of the bulge test apparatus

3.6.1 Selection of the pressure media

Several types of pressure media that have been used by other authors to apply differential pressure to the membrane - water [18, 19], nitrogen gas [20, 55], pump oil [8] and pressurized air [40]. The compressibility of a pressure medium determines the amount by which the medium must be compressed to obtain a desired pressure range from a certain amount of syringe stroke. Therefore, the design of the bulge test apparatus depends closely on the selected of pressure medium.
Water is highly incompressible because of its high value of bulk modulus (K), 2.18 GPa. Thus, by compressing a very small volume of water the required pressure range can be achieved using small volume syringes (such as 10 µL or 25 µL) at only a fraction of their total stroke. Water therefore enables good control of applied pressure. Most importantly, water does not react with BC and SiNₓ, making it essentially ideal for applying pressure. Distilled de-ionized water was used after degassing it by boiling on a hot plate for ~ 15 min. The jar used for boiling the water was closed with aluminum foil with a small hole in it to allow reactive gases such as carbon dioxide (CO₂) and oxygen (O) to escape. After degasification, the jar was tightly covered with aluminum foil and the water was allowed to cool to room temperature. This water treatment helps to improve the response of system to build pressure without excess system compressibility.

### 3.6.2 Required pressure range, compressibility of pressure media and syringe stroke

For a square membrane, Eq. (1) was used to predict the approximate pressure range for deflecting the SiNₓ and BC films. Other parameters in Eq. (1) were assumed from the literature. Based on the compressibility of water, the total volume of water required for the required pressure range was deduced. From the volume that was required to be compressed, the required syringe stroke and the number of data points were predicted. (For details, see Appendix A9 and A10).
3.6.3 Sample mounting

The pressure could be applied from inside or outside of the micro machined cavity of the membrane sample (Fig. 3.5). Vlassak and Nix [32] applied the pressure from inside of a cavity, while Tabata et al. [31], and Jayaraman et al. [68] applied it from outside. Mitchell et al. [56] studied the effects of sample orientation on the experimentally obtained values of Young’s modulus and residual stress using six chips of 2 µm thick 3C-SiC membranes (1 mm square). They found that the deducted residual stress did not change significantly when the pressure was applied from inside or outside of a cavity. In contrast, the Young’s modulus was 9 to 20% higher when the pressure was applied from the inside of a cavity. It was thought that the horizontal component of applied pressure on the sidewalls of a micro-machined cavity amplified the tensile stress in the film, making the effect pronounced at higher pressures. This was supported by the fact that the Young’s modulus has a larger effect on the deflection of membrane at high pressures. Since the residual stress affects initial membrane deflection at lower pressures, the cavity orientation had a negligible effect on the experimentally obtained value of residual stress.

![Diagram](image)

**Figure 3.5:** A schematic arrangement for applying the pressure from outside and inside of a cavity.
Mitchell et al [56] concluded that only if the pressure was low sample orientation does not matter. Based on their findings, it was decided to apply pressure from the outside of a cavity for the present research.

Furthermore, if the pressure is applied from outside of a cavity, the film is pushed against the SiNₓ membrane, reducing the potential for possible delamination. This would be especially important if the adhesion of a film to the substrate were poor. Also, the possibility to trap air bubbles below the membrane is more if the cavity side is placed on the square o-ring filled with water.

### 3.6.4 Vibration Analysis

The bulge test setup is required to have a good dynamic stability with a resonant frequency close to, or below, 2 Hz in order to minimize the fringe pattern response to external vibrations. Even low frequency vibrations on the platform of setup can distort the fringe pattern making it difficult to record.

A simple mass-spring oscillator has a resonant frequency given by

\[ f = \frac{1}{2\pi} \sqrt{\frac{k}{m}}, \]

where \( k \) = spring constant and \( m \) = total mass acting on the vibration damping system. Spring constant “\( k \)” is related to the force and the deflection of system by equation \( F = k\delta \), where “\( \delta \)” is the deflection. The Young’s modulus and stress are used to evaluate deflection.

To achieve the required stability, the bulge test apparatus was mounted on a bicycle inner tube filled partially filled with air. From the deflection of the inner tube
support under the weight of system, an approximate value (56928 N/m²) of Young’s modulus was calculated for the pressurized tube – about 17 times less than that of neoprene was obtained. This makes it possible to achieve desired resonant frequency. The required stability was achieved with a tube pressure of ~ 1-2 psi, with a 24”×1.75”-2.125” bicycle inner tube and a total system mass of ~ 55 kilograms acting on it.

3.7 Experimental procedure to conduct the bulge test

This procedure is laid out step by step to aid in replicating it.

i) Initial alignment of the basic interferometer to check the dynamic stability of the apparatus: After mounting on the bicycle tube, the basic interferometer (with two mirrors as reflecting surfaces) was aligned to form a circular fringe pattern (See Appendix A2 for the alignment procedure). If the fringe pattern is stable, the setup has a good dynamic stability to record fringes successfully, but if the pattern is not stable, the pressure inside the tube should be adjusted between ~1-2 psi and other factors that could cause vibrations should be checked.

ii) Pressure chamber assembly: The assembly was completed by attaching the transducer and two syringes to chamber. To obtain a good seal, the male threads of transducer were coated with 3 rounds of high density Teflon tape and square o-rings were placed between the chamber and the syringes. The transducer was screwed tightly in place, while the syringes were moderately pressed on square o-rings to avoid any damage. Syringe threads were also coated with one round of Teflon tape to hold them tightly. After the assembly was completed, the transducer and pressure chamber were filled with water. (See Appendix A12 for the filling procedure).
iii) Checking the leakage and the repeatability of system: The chamber was sealed at all four ports according to the following the procedure. Air bubbles remaining in the syringe barrel from the previous step were eliminated by removing the plungers completely and the syringes were sealed again. Then with the plunger of syringe A (at the opposite side of membrane port) inserted only ~ 1 mm into the syringe barrel to seal it, a dummy sample (380 µm thick square Si wafer attached to the sample holder - See Appendix A7 for the procedure to attach actual sample to sample holder) was placed on a square o-ring over filled with water as shown in Fig. 3.7. A polished circular Al plate, as thick as a sample holder can also be used for this purpose.

![Figure 3.6: A schematic and a picture pressure chamber assembly.](image)

The clamping plate was then slowly screwed into position until it just touched the sample holder. Then the plunger of syringe A was completely removed and quickly thereafter the clamping plate secured. Sudden rise in pressure is thus prevented by opening one of the ports to atmospheric pressure. The pressure chamber was then mounted on a prism table and the plunger of syringe B (at the opposite end of transducer) was attached via a magnet on the movable head of syringe pump and the transducer was connected to the
Finally, a small backward stroke was given to the plunger of syringe B to create ~ 1.5 cm long air bubble in syringe A. Thereafter in small steps, the plunger of syringe A was inserted back. The pressure rise (somewhere between 0-2 KPa) in each step was reduced by giving a backward stroke to the plunger of syringe B. This process was repeated until the plunger of syringe A was inserted enough to obtain a good seal. Then, the plunger of syringe A was slowly attached to the micrometer head (pressure will change by a small amount during this attachment). As air is highly compressible, forming an air bubble inside syringe A helps to avoid high pressure rise when its plunger is inserted back in steps and guarantees that the membrane is not damaged. This is especially important for membranes which could easily break if the pressure rise causes film stresses beyond their fracture strength.

With negligible leakage (pressure drop), the pressure should continuously increase with syringe stroke and should remain relatively constant when the stroke is stopped. The chamber was pressurized to different pressure intervals (upto 130 KPa), and the pressure drop was noted (See Section 5.1.1 for results and details of the leak test). Finally, to check the repeatability of data, the chamber was repeatedly pressurized to different pressure levels. With negligible pressure drop over times much greater than the duration of any bulge test, the reproducibility of data was found to be good.

iv) Sample loading and final alignment of interferometer: With a square o-ring filled with water as shown in Fig. 3.7, the possibility to trap air bubbles below the membrane after the sample is placed on it is almost negligible (Otherwise, when the pressure is applied, any air bubbles below the membrane could damage it because of the difference in surface
tension. Such membranes would also give a distorted fringe pattern that is not useful for resolving fringes). The convex shape of water on the top of square o-ring before placing the sample on it is important. As the faces of the square o-ring are parallel to the adjoining cavity, the possibility of trapping air bubbles below the membrane is negligible compared to that for standard circular cross-section O-rings. The arrangement shown in Fig. 3.7 works well for the 10×10 mm² Si frame (with a 1×4 mm² and 1×1 mm² window) were the sealing to a square o-ring is accomplished by the frame itself, but the 2×2 mm² Si frame (with a 1×1 mm² or 0.5 × 0.5 mm² window) fits inside the diameter of the o-ring and so the chamber needs to be sealed using the surrounding polished surface of the sample holder.

![Figure 3.7: A schematic and a picture of a square ring filled with water.](image)

With one additional step of alignment, the system was sealed with a membrane window in place of the dummy sample following the same procedure explained in step (iii). For the additional step, before the plunger of syringe A was inserted back in steps, the transducer was connected to the computer, the film was aligned in the interferometry setup, the chamber was clamped firmly and then finally the plunger of syringe A was attached to the syringe pump (See Appendix A2 for the alignment procedure). Care was taken to avoid any contact of syringe B with the V-groove of syringe pump, because any
such contact would transfer vibrations from the syringe pump motor to the chamber, thus distorting the fringe pattern. Finally, by adjusting optical components and the stroke of each syringe, the fringe pattern was symmetrically aligned. (See Section 5.1.2 for more details on the fringe pattern alignment). By giving the backward stroke to one of syringes, the membrane was given a small negative deflection before the pressure was applied by starting the syringe pump at a stroke rate close to 0.080 µL/min. This was done to check that the membrane could become completely flat (with entire membrane appearing bright with no fringes) and to check that the first fringe of positive displacement appeared at the center of the membrane. If both conditions were not satisfied, the pattern was re-aligned by adjusting the mirror tilt and checked once more.

v) Starting the test: Before starting the test, backlash in the syringe pump was removed. (Backlash comes from the backward stroke given to the syringe pump). Because of backlash, the pressure did not raise immediately the syringe pump was started, but as soon as the backlash was removed, the pressure rose sharply.

In analyzing fringe data, only the positive displacement after the membrane became flat was included (flat membrane represents zero displacement). The P-h data was corrected for any zero deflection pressure offset.

After the sample was tested, only the water within the square o-ring at the membrane port was replaced and the steps (iv) and (v) were repeated with the next sample. Care was taken while placing and removing the sample to avoid introducing air inside the chamber by filling the chamber with water under vacuum conditions.
4. THE NANOINDENTATION TEST FOR THE MECHANICAL TESTING OF THIN FILMS

4.1 Introduction

Companies which manufacture MEMS, microelectronics and data storage devices often use nanoindentation to measure mechanical properties of substrate-supported thin films [9, 70, 71]. Since films can be tested as deposited on substrates, this technique has advantages in minimal sample preparation and ease of sample handling and enables Young’s modulus and hardness to be found by analyzing load (P)-displacement (h) data (P-h diagram) [72]. Some nanoindenters feature load and displacement resolution of < 1 nN and 0.0002 nm respectively, making them ideal to extract P-h response of thin films. However, due to the so-called substrate effects (i.e., the deformation of substrate underneath film contributes to the measured mechanical properties of film), this technique is not so useful to measure properties of very thin films, with 100 nm considered to be the minimum useful thickness [65].

Usually, the indentation depth should be less than 10% of film thickness to avoid substrate effects [72]. However, depending on the nanoindenter noise - low noise allows experiments at very low forces – and depending on the complex elastic and plastic properties of the film and the substrate, it is possible to get reliable results for indentation depths more than 10 % of film thickness [73, 74]. Therefore, the 10 % “rule” should only be used as a guideline. If the equipment has a dynamic stiffness measurement option, the Young’s modulus and the hardness can be recorded continuously as a function of indentation depth. Both these properties will start to increase or decrease at a depth that depends on the properties of the substrate with respect to the film. This helps to
determine the maximum indentation depth at which the substrate may start influence the measurement of film properties [74].

4.2 The Principle and Methodology

An indenter of known geometry penetrates into the material surface under a chosen load and the resultant load-displacement (P-h) diagram is obtained. The information on parameters such as maximum load ($P_{\text{max}}$), maximum depth of indentation ($h_{\text{max}}$), residual depth of indentation ($h_{\text{f}}$) after reducing the load to zero and elastic contact stiffness ($S$) can be obtained directly from the P-h diagram [75].

![Figure 4.1: A schematic of nanoindentation principle.](image)

The Oliver and Pharr method is perhaps the most widely used method for analyzing the data from P-h diagram [72]. When sink-in dominates, meaning that the material bows in at the faces of indenter, this method accurately yields contact area directly from the P-h data without any need for image observation of the residual hardness impression. This method is an improved version of the earlier Doerner & Nix [76]. Using a flat punch approximation, Doerner and Nix suggested that, while the contact area remains constant during the initial stages of unloading, the unloading curve can be considered to behave linearly. Later, the experiments by Oliver & Pharr based on Sneddon’s elastic theory for indentation by an axisymmetric body of indenter [77],
showed that the contact area fails to remain constant even in the initial stages of unloading (This is especially true for hard, brittle materials, for which the contact area is expected to change upon unloading because of their large amount of elastic recovery, since such materials do not behave plastically to a significant extent). Thus the unloading curve fails to behave linearly and the unloading curve should be analyzed using a simple power law function, Eq. (6) instead [72, 77]:

\[ P = \alpha(h - h_f)^m \]  

(6)

where, \( \alpha \) and m are empirical material constants, \( h \) is the elastic displacement and \( h_f \) is the residual depth of indentation upon complete unloading. The exponent m is material dependant and falls in the range of 1.2-1.6 for indenters that behave like paraboloid of revolution [75]. The constants \( \alpha \) and m are first found by fitting the upper portion of unloading curve to Eq. (6). Usually, a fit to upper 50% of unloading curve is sufficient. Then, the contact stiffness \( S \) is found by substituting \( P = P_{\text{max}}, \ h = h_{\text{max}} \) in Eq. (6) and differentiating it with respect to \( h \). This gives Eq. (7):
\[ S = \frac{dP}{dh} = \alpha m(h_{\text{max}} - h_f)^{m-1} \] 

The contact depth \( h_c \) needed to find the projected contact area \( (A_p) \) is found from Eq. (8):

\[ h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S} \]

where \( \varepsilon \) is a constant that depends on the geometry of the indenter [77].

\( \varepsilon = 1.0 \) (Flat punch); \( \varepsilon = 0.75 \) (Berkovich indenter); \( \varepsilon = 0.73 \) (Conical indenter)

If an indenter is perfectly sharp, the projected contact area \( (A_p) \) can be calculated from an ideal area function [12]:

\[ A_p = 24.5 (h_c)^2 \]

where 24.5 is the coefficient that applies to Berkovich and Vickers indenters.

However, in repeated use, especially on hard materials, indenters fail to remain perfectly sharp because of tip blunting. Therefore, Eq. (9) needs to be corrected by tip calibration (i.e. determination of an area-function) to estimate contact area accurately at different depths, especially at small depths. Hysitron models of nanoindenters (Hysitron Inc, Minneapolis, MN) can provide an automated tip calibration following the procedure given by Oliver and Pharr [72]. The corrected area function is given by:

\[ A(hc) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + ... + C_8 h_c^{1/128} \]
where C with subscripts are constants found by curve fitting the plot of contact area (A) as a function of contact depth (hc) (A detailed procedure is outlined in Ref. [74]). For accuracy, it is important to perform this calibration over the entire expected range of indentation depths.

Since an indenter is not perfectly rigid, the Young’s modulus of the sample is found from an effective elastic modulus (E_{eff}) which combines the compliance of the indenter and sample deformation as if they behave as springs in series and so E_{eff} takes into account elastic displacements of both indenter and sample in load-displacement data [75]:

\[
\frac{1}{E_{\text{eff}}} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad \text{…………………………………………………………………………………(11)}
\]

where \( \nu \) and E are the Poisson’s ratio and the Young’s modulus of the sample and \( \nu_i \) and \( E_i \) are the Poisson’s ratio and the Young’s modulus of an indenter. For a diamond indenter, \( E_i \) and \( \nu_i \) are 1140 GPa and 0.07, respectively [78]. In Eq. (11), the Poisson’s ratio must be assumed for the film material unless it is otherwise known. After \( E_{\text{eff}} \) is determined, the Young’s modulus of film is found from Eq. (11). \( E_{\text{eff}} \) is found from the Eq. (12), which relates the contact stiffness to the projected contact area:

\[
S = \beta \frac{2}{\sqrt{\pi}} \times \sqrt{A_p} \times E_{\text{eff}} \quad \text{………………………………………………………………………………….(12)}
\]

where \( \beta \) is a correction factor that takes into account the lack of axial symmetry of indenters, and \( \beta = 1 \) (circular symmetry), \( \beta = 1.012 \) (square symmetry), or \( \beta = 1.034 \)
triangular symmetry) [79]. For a Berkovich indenter, which is a three sided pyramidal indenter, $\beta = 1.034$. An accurate value of $\beta$ for a specific indenter geometry is important, as both the deducted of elastic modulus and hardness are affected by it [75].

Finally, the hardness is found by Eq. (13):

$$H = \frac{P_{\text{max}}}{A} \quad \text{………………………………………………………………………………………………….}(13)$$

### 4.2.1 Amount of elastic recovery and sink-in

Upon complete unloading, the total amount of elastic recovery ($\Delta e$) of films can be found from Eq. (14) [80]:

$$\Delta e = \frac{h_{\text{max}} - h_f}{h_{\text{max}}} \quad \text{………………………………………………………………………………………………….}(14)$$

where $h_{\text{max}}$ = maximum depth of indentation and $h_f$ = final depth of indentation upon complete unloading.

The amount of sink-in ($h_s$) is found from Eq. (15) [75]:

$$h_s = \varepsilon \frac{P_{\text{max}}}{S} \quad \text{………………………………………………………………………………………………….}(15)$$

### 4.3 Experimental considerations

#### 4.3.1 Substrate effect

Given its importance (See Section. 4.1), the substrate effect is one of the most important considerations in testing thin films. This factor specifically limits the use of
nanoindentation to test ultra thin films, because at shallow indentation depths close to 10 nm (i.e., 10 % of 100 nm thick film), the data may be not be appropriate due to the inaccuracies that arise from sample roughness, tip rounding and equipment limitations such as depth resolution, noise, and indenter drift. As a Berkovich tip radius is at least around 50 nm, the area function can increase sharply at shallow indentation depths, giving low and inaccurate values of the Young’s modulus and hardness at these depths [76, 81, 82].

Generally, the substrate has a greater effect on the measurement of the elastic modulus than on to the hardness measurement of thin films. The best way to minimize substrate effect is to use a homogeneous film-substrate system. Further, the hardness value is more affected by substrates in the case of hard films on soft substrates compared to soft films on hard substrates [83].

4.3.2 Pile-up and sink-in

Pile-up (the blowing out of material at the surface of indenter) during the process of indentation is mainly a concern for elastic-plastic materials [75]. In the case of large pile-up, the contact area at a given depth found from the P-h diagram is underestimated from the true contact area between an indenter and a material. This inaccuracy can lead to overestimation of the hardness and the Young’s modulus found from the Oliver and Pharr method by as much as 50% [84]. Pile-up depends on the ratio of the effective modulus to the yield stress $E_{el}/\sigma_y$ and on the work hardening behavior of material. Materials with large ratio of $E_{el}/\sigma_y$ and with little or no work hardening ability generally suffer from pile-up.
Sink-in is expected for hard, brittle materials with large amount of elastic recovery upon unloading. If sink-in dominates, the Oliver-Pharr method yields accurate contact area [75, 81].

From the P-h diagram, the amount of pile-up or sink-in can easily be found from the ratio $h_f/h_{\text{max}}$, which lies between 0 to 1. The lower and upper limit means complete elastic deformation and rigid plastic behavior respectively. If the ratio is $< 0.7$, sink-in dominates (independent of the work hardening behavior of material). If the ratio remains $> 0.7$ (especially close to 1), pile-up is expected. If the ratio is close to 0.7, an image of the indent may help to find evidence of pile-up. It is noteworthy to know that the work-hardening characteristics of a material are important only if the ratio $h_f/h_{\text{max}}$ is more than 0.7 [75].

With the above facts, as BC and SiNx films are expected to show sink-in, the Oliver and Pharr method should be the most appropriate method for these materials in combination.

4.3.2 Effects of micro cracks

As BC and SiNx films are brittle, at high indentation depths (and so high loads) micro-cracks may form around the indentation. Due to energy loss during formation of micro-cracks, the load required for deformation is greater than actual load - overestimating the value of hardness [85]. Micro cracks are less likely to occur in materials showing large amount of elastic recovery. Indents should be imaged if there is suspicion of micro cracks from inappropriate results.
4.3.3 Probe-tip

Because of self-similar geometry and a constant depth-to-area ratio, a Berkovich indenter tip gives a better control on strain rate to measure the elastic modulus and hardness at small scales. Further, the experimental procedure to calibrate this tip is well-established.

4.3.4 Thermal drift, machine compliance, surface detection and surface roughness

Thermal drift (that is time-dependant deformation or creep at a certain load), can occur because of displacements due to thermal expansion or contraction of the indenter and/or the sample material during displacement measurements. Thermal drift is more severe for low melting point materials such as polymers compared to high melting point materials such as ceramics. Thermal drift rate (nm/sec) is initially found by holding a small load on the specimen for a certain amount of time and the displacements observed during this time are attributed to thermal expansion or contraction of the indenter and/or test material to find the drift rate. These displacements may be used in correction of measured displacements during acquisition of P-h data from samples. The nanoindenter used in this research, an Hysitron UBI-750 nanoindenter, has an ability to perform automated thermal drift calibration before starting the test. It is noteworthy that time-dependant displacement (creep) at maximum load is mainly a concern for soft metal films, for which this effect can be minimized by holding the maximum load constant for a certain amount of time such as ~15-20 sec before unloading in order to allow these creep related displacements to dissipate. However, for brittle ceramic films, creep related
displacements are less severe, and therefore; the unloading cycle may immediately follow the loading cycle without any dwell period if the drift change is negligible compared to the total depth of displacement.

The machine compliance ($C_m$) calibration takes into account small displacements in the test equipment which need to be corrected in order to obtain the actual displacement in the sample. It is considered good experimental practice to calculate $C_m$ even if it is less a concern in the case of small contact stiffness associated with small depths and loads.

The indenter used in the present research, a Hysitron UBI-750, has the ability to detect extremely small contact loads and so to accurately locate indenter on the film surface for subsequent displacement. As BC and SiN$_x$ films are relatively hard and brittle, locating the film surface can often be easy because these materials cause an abrupt change in contact stiffness and load.

As the indentation depth is usually very small in thin films, surface roughness becomes an important factor affecting contact area determination. High surface roughness makes it difficult to find an accurate measure of the contact area unless the indentation depth is sufficiently high compared with the surface roughness. Also, the data may scatter badly at small indentation depths. This makes it important to have a smooth surface for nanoindentation tests. The surface roughness of BC and SiN$_x$ films is close to 1 nm and so is sufficiently low to test these films successfully.
4.4 Experimental procedure

As-deposited BC films were deposited on a standard 3” Si wafer. Two pieces were cleaved from the center section of Si wafer where the thickness is approximately constant (from the same region of interference color). One of the pieces was further annealed using the procedure described in Sec. 2.4.1. Both as-deposited and annealed samples were then attached to a glass substrate as shown in Fig. 4.1. As-deposited and annealed BC films with thicknesses close to 114, 204, and 315 nm were tested. A slow cure epoxy (the same as used for attaching bulge test samples) was used to attach all samples as it becomes rigid upon drying and so contributes little to the measured compliance.

In this research, P-h data was obtained with a Berkovich diamond indenter (~150 nm radius of curvature). In total, 15 single load-unload indents were made on each sample. The nanoindenter was operated in indentation quasi-static mode to extract the modulus and the hardness of films. Sample area was defined by in-situ optical scanning. All indents were made in an area of 50 µm² after scanning this area by in-situ SPM (scanning probe microscopy) to select a defect free surface for all indents. Between each successive indent, a recommended distance of at least 20 to 30 times the maximum indentation depth was maintained. All indents were made under a displacement-control mode by restricting the maximum indentation depth to about 10 % of film thickness to avoid substrate effects. The indenter velocity was 5 nm/sec for all indents.

Following the Oliver and Pharr method, all data sets (P-h curves) were analyzed by a power law fit to the upper 50 to 98 % of unloading curves. For some indents on each
sample, the fit was more appropriate at 20 to 98% of unloading curve. The Young’s modulus ($E_i$) and Poisson’s ratio ($\nu_i$) of the Berkovich diamond indenter were assumed to be 1140 GPa and 0.07, respectively. To find their Young’s modulus, the BC films were assumed to have a Poisson’s ratio of 0.18 [46].

An indenter tip calibration (area function) was carried out by doing successive indents on fused-silica at different depths. The tip was calibrated at depths large enough to cover the entire range of depths needed to do experiments. The machine compliance was found to be 0.005 mN/nm and was corrected for in the measured displacements. Both the area function and machine compliance was found following the procedure suggested by Oliver and Pharr in Hysitron’s manual [86]. To minimize thermal drift resulting from creep and temperature changes, automated thermal drift calibration was performed for each indentation. As the thermal drift rate was negligible compared to the total displacement, a dwell period to compensate thermal drift at maximum load before unloading was omitted. By separately analyzing each of the 15 indents, an average value of the modulus and the hardness was calculated for each sample. Finally, the modulus and the hardness were reported from the mean and the standard deviation of average values of each sample.
5. RESULTS AND DISCUSSION

In this chapter, checks and calibrations are reported, followed by data and discussion on BC, in both Section 5.1 Bulge Test and Section 5.2 Nanoindentation.

5.1 Bulge test

Obtaining the most reliable mechanical data with bulge testing requires (1) that there is no unintended change in pressure over the duration of testing, (2) that the optical system is aligned with the center of the membrane, and (3) that results are repeatable.

5.1.1 System pressure performance

It is exceedingly difficult to create a system that is highly incompressible, that permits sample exchange, and that is totally leak-tight. The design to achieve incompressibility and demounting required creep-free, incompressible seals, including square section, high elastic modulus elastomers in close-fitting machined seats. With the greatest attention to surface polishing and freedom from fibers and contaminations, it was still not possible to assure that the system did not leak under pressure, but this was verified to be insignificant, as follows.

The pressure drop was estimated at different pressures up to 130 KPa – a pressure well above the maximum expected bulge testing pressure range. To conduct this leak test, a dummy sample was used. The results after monitoring the pressure drop for 1 hour at each pressure interval are shown in Fig. 5.1. No leakage was observed at low pressures
(below 25 KPa) and the pressure drop at high pressures was too small to have any effect on the compliance of system during each bulge test.

![Figure 5.1](image)

**Figure 5.1 : Pressure drop at different pressures averaged over/hour intervals.**

The pressure rise with time at constant syringe stroke (0.210 µL/minute) was checked, as shown in Fig. 5.2.

![Figure 5.2](image)

**Figure 5.2: Pressure rise as a function of syringe stroke.**
The uncertainty in pressure readings was checked at zero applied pressure to be 100 Pascal’s. Finally, a plot of $\Delta P_o$ vs. $\Delta P_{\text{measured}}$ is shown in Fig. 5.3. $\Delta P_o$ is the pressure expected if water were the only compliant material in the system and $\Delta P_{\text{measured}}$ is the pressure measured at constant syringe stoke as shown in Fig. 5.2.

![Graph](image)

**Figure 5.3 : A plot of $\Delta P_o$ vs. $\Delta P_{\text{measured}}$**

Any air bubble or other compliant material effect to first order approximation would change the slope $d(\Delta P_o)/d(\Delta P_{\text{measured}})$ by a constant factor. The curvature is perhaps explained if the syringe pump rate is affected by the changed resistance encountered as the water pressure is increased.

**5.1.2 Analysis of fringe pattern**

Fringe patterns (interference patterns) obtained from a 1 mm square SiN$_x$ membrane window are shown in Fig 5.4 for an aligned and a misaligned optical system
under a condition of positive membrane deflection. A similar fringe pattern is found for SiNₓ/BC bi-layer membranes. An aligned fringe pattern should clearly reflect the symmetry of the square membrane. The deflection at the center of the membrane was measured by counting each outward moving fringe (i.e., each bright and dark fringe that appeared at the center of an aligned fringe pattern after the membrane became flat) as the membrane deflects and multiplying that number by $\lambda/4 = 162.5$ nm. Alternatively, after the membrane became flat (bright) as shown in Fig 5.5, each bright fringe cycle at the center of the membrane was counted (during the deflection of membrane), and that number was multiplied by half the wavelength of laser light used ($\lambda/2 = 325$ nm) to find the total deflection at the center of the membrane. Each dark fringe cycle can also be counted if a flat membrane is dark.

![Fringe Patterns](image)

**Figure 5.4:** A picture of an aligned (left) and a misaligned (right) fringe pattern obtained from a 1 mm square SiNₓ membrane.

Mirror tilt was adjusted to obtain an aligned (symmetrical) fringe pattern. A symmetrical pattern assures that the system is well aligned. When the test is started with negative deflection and at the time of transition from negative to positive deflection, a well aligned system assures that the membrane becomes completely flat (i.e., entire cross section of membrane appears bright or dark depending on the sample location in the
Michelson interferometer as shown in Fig. 5.5) before the first fringe of positive deflection appears at the center.

Figure 5.5: A picture of a fringe pattern when the membrane is completely flat.

With the increase in membrane deflection, fringes near the edges of membrane become hard to resolve. But the fringes that appear at the center of membrane and matter the most are mostly visible for deflection up to a certain range. The intensity (visibility) of the center fringe, however, decreases as the deflection of membrane increases and at large deflections (when the P-h curve is in non-linear regime) the center fringe also becomes very difficult to detect. The visibility of center fringe depends on the reflectivity and the reflecting area of the membranes, which decreases at large membrane deflection. Further, the reflectivity of films is poor for films having high surface roughness, and therefore, even if the area of membrane is large, it is possible to view only few initial fringes. For 1 mm square membranes with good reflectivity, the center fringe is visible for large deflection, corresponding to pressures high enough for the P-h curve enter cubic regime. However in the case of 0.5 mm square membranes, the dimension and contrast of the center fringe became difficult to distinguish even at small initial deflections, corresponding to the linear P-h regime. The possible reason for this problem is explained in the following paragraph.
When the membrane is flat and the deflections are small, the intensity of beam reflected from the membrane is good. Thus, the intensities of beams from the mirror and the sample matches well on interference to give a fringe pattern with good contrast (fringes are clearly visible). However, the intensity of beam reflected (reflectivity) from the membrane reduces substantially (almost no visible reflection) at high deflections, and therefore, even when the intensity of beam reflected from mirror is reduced (by an optical density filter) to match it with the intensity of beam reflected from film, it becomes very difficult to obtain a fringe pattern with good contrast to resolve fringes. Membranes with small area suffer more from this problem were the intensity of beam reflected from the membrane is reduced at much smaller deflections compared to large size membranes. The reflectivity of the membrane must be decreasing with increasing deflection because the light starts to travel back at a wider angle after getting reflected from the sloped section of bulge. Further, because of the self-interference or diffraction of light reflected from the sloped section of bulge, secondary fringes appear concentric to the center fringe [87]. The intensity of center fringe is less affected compared to the outer fringes because more light travels back (from film) perpendicular to the surface of beam splitter after getting reflected from the top center section of bulge where the slope is close to zero.

The accuracy of load-deflection data closely depend on how accurately one determines the membrane is flat before noticing the first fringe of positive displacement. As the initial membrane deflection is mostly dominated by residual stress (which do not have a prominent effect compared to the Young’s modulus in resisting bulge), initially the membrane deflects rapidly (at low very pressures) causing the fringes to move quickly. But as the deflection increases, the film stiffness (Young’s modulus) starts
contribute to the deflection and the impact of residual stress on the deflection starts to decrease. Therefore, as the film becomes stiffer to deflect at high deflections, fringes will start to move slowly. Therefore, before starting the test, the syringe stoke should be set to move fringes as quickly as possible at a speed decent enough to record them successfully (Initially if the fringes move slowly, their speed will decrease further as the deflection increases). This minimizes total time for running the test. If the test takes more time, the experimental errors associated with temperature variations (thermal drift) due to the heating of transducer electronics, changes in the room temperature, atmospheric pressure etc., may tend to increase.

5.1.3 Repeatability of experimental data

Pressure-deflection curves obtained for a bare SiN\textsubscript{x} membrane from three loading cycles are shown in Fig. 5.6. It is evident that the reproducibility of data obtained from the system is good. This is important to minimize the uncertainty in results.

![Pressure-deflection curves](image)

**Figure 5.6:** Repeatability of experimental data.
For both loading cycles the film shows a completely elastic behavior with no signs permanent plastic deformation. As a matter of fact, only if the sample deforms elastically over an entire range of deflection, repeatability of data from the same sample can be achieved. Finally, a good repeatability of data mainly comes from the ability of transducer to measure the pressure with minimum uncertainty, an accurate deflection measuring system such as interferometer, a good vibration damping system and the skill of user to accurately analyze pressure readings and the recordings of fringes to obtain pressure-deflection data.

5.1.4 Analysis of the pressure-deflection data of a bare SiN_x membrane to verify the accuracy system

As the mechanical properties of LPCVD SiN_x membranes are well know, the bulge test was first conducted on a bare SiN_x membrane to find any discrepancies between the experimentally obtained properties and the literature. A typical pressure-deflection diagram of a 100 nm thick, 1 mm square membrane is shown in Fig. 5.7.

The deflections were large enough for the P-h curve to enter the cubic regime. The P-h data was then converted into a stress-strain curve (Fig. 5.8) using Eq. (2) and (3). The residual stress was found from the y-intercept, while the bi-axial modulus was found from the slope of the stress-strain curve. Finally, the Young’s modulus was found assuming a Poisson’s ratio of 0.27 for LPCVD SiN_x [88].
Figure 5.7: A typical pressure-deflection diagram of a 100 nm thick, 1 mm square SiN$_x$ membrane.

Figure 5.8: A stress-strain curve of a 100 nm thick, 1 mm square SiN$_x$ membrane.
Experimentally obtained mechanical properties are given in Table 5.1.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Residual Stress (MPa)</th>
<th>Biaxial Modulus (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>127.73 ± 13.88</td>
<td>442.53 ± 35.85</td>
<td>323.04 ± 31.87</td>
</tr>
</tbody>
</table>

**Table 5.1: The residual stress and Young’s modulus values of a 100 nm thick, 1mm square membrane**

Within the accuracy of our measurements, the residual stress and the Young’s modulus match well with the literature [31, 32, 34, 35, 89]. It therefore shows that the bulge test system designed here is capable of producing reliable results. Although it may be difficult to view fringes beyond this deflection range, testing the membrane beyond this range can further increase the contribution of Young’s modulus to the deflection of membrane. This will help to minimize uncertainty in the value of Young’s modulus.

### 5.1.5 Analysis of bi-layer SiNx/BC membranes to evaluate the residual stress in BC films

BC films with two different thicknesses (below 100 nm) were tested. The configurations of bi-layer membranes are given below:

**Bi-layer membrane 1:**

- Substrate: 201 nm thick, 1 mm square membrane supported by 10 mm square Si frame (from Silson Ltd).
- Mean residual stress in SiNx membrane: 229 ± 6.21 MPa.
• BC film thickness: ~ 59 nm.

• Total thickness of bi-layer membrane: ~ 260 nm.

**Bi-layer membrane 2:**

• Substrate: 200 nm thick, 1 mm square membrane supported by 10 mm square Si frame (from Silson Ltd).

• Mean residual stress in SiNₓ membrane: 229 ± 6.21 MPa.

• BC film thickness: ~ 74 nm.

• Total thickness of bi-layer membrane: ~ 274 nm.

The composite P-h response of bi-layer membrane 1 and 2 is shown in Fig. 5.9 and 5.10 respectively.

As the residual tensile stress of bi-layer membrane with a thicker BC film decreases due to the increase in compressive stress as the thickness of BC film increases, the pressure required for the deflection of bi-layer membrane 1 is more than the bi-layer membrane 2. This is because the bi-layer membrane 1 imposes more resistance to bulging due to its high residual tensile stress.

The residual stress in BC film is obtained by applying the mixture law using Eq. (5). The residual stress in bi-layer membranes (composite structures) is obtained from the linear regime of P-h response by averaging the stress estimated by Eq. (2) for each pressure-deflection data points within the linear regime. The residual stress is reported by
Figure 5.9: A composite P-h response of SiN$_x$/BC bi-layer membrane 1.

Figure 5.10: A composite P-h response of SiN$_x$/BC bi-layer membrane 2.
taking the mean of residual stress values obtained from three trials. The results given in Table 5.2 indicate that the compressive stress in annealed BC films increases as the thickness increases. This finding strengthens the assumption made in the discussions of nanoindentation results that the compressive stress likely increases with the increase in film thickness.

In case of bi-layer membrane 1, the compressive stress in BC film is higher than the tensile stress in SiNₓ membrane. However, the composite structure remained flat (with no wrinkles), because a 200 nm thick SiNₓ membrane should impose about 4 times more constraint (as per Eq.(17)) for wrinkles to form than a 100 nm thick SiNₓ membrane. This also means that a thicker SiNₓ membrane helps to maintain mean residual tensile stress in the composite structure. The same is true for bi-layer membrane 2. The composite structure remained flat in each case because the residual tensile stress in each of the composite structures was large enough to prevent them from wrinkling. But if the thickness of BC film increases further, the compressive stress in it will increase and therefore, the residual tensile stress in composite structure will decrease further and become too small to prevent the composite structure from wrinkling. To verify this fact, a

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Bilayer membrane</th>
<th>Total thickness of Bi-layer membrane (nm)</th>
<th>Thickness of SiNₓ film (nm)</th>
<th>Thickness of BC film (nm)</th>
<th>Residual stress in SiNₓ film (MPa)</th>
<th>Mean residual stress in Bi-layer membrane (MPa)</th>
<th>Mean residual stress in PECVD BC (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>032211</td>
<td>1</td>
<td>~260</td>
<td>201</td>
<td>~59</td>
<td>229 ± 6.21</td>
<td>120 ± 2.23</td>
<td>-248 ± 9.60</td>
</tr>
<tr>
<td>031611</td>
<td>2</td>
<td>~274</td>
<td>200</td>
<td>~74</td>
<td>229 ± 6.21</td>
<td>66 ± 1.57</td>
<td>-376 ± 5.83</td>
</tr>
</tbody>
</table>

Table 5.2: The residual stress in annealed PECVD BC films.
bi-layer membrane with ~ 93 nm thick BC film deposited on a similar substrate used for bi-layer membranes 1 and 2 is shown in Fig. 5.11. It is clearly evident that the wrinkles appear because of the increase in compressive stress as the thickness increases. In this case, as mentioned before, the residual tensile stress in the composite structure became too small to prevent it from wrinkling.

As the BC films deposited on SiNₓ membranes were annealed, a similar type of annealing was done on the SiNₓ membranes following the procedure given in Sec. 2.4.1 (this annealing cycle also includes the heating of membrane for 2 hrs at 350°C and plasma etching of ~ 1 min). As annealing can affect the residual tensile stress in SiNₓ membranes, the residual tensile stress of annealed SiNₓ membrane was used in the mixture formula.

Figure 5.11: A picture of a 200 nm thick, 1 mm square bi-layer membrane with a BC thickness of ~ 93 nm.
5.1.5 Experimental observations on the effects of SiN$_x$ membrane size, thickness and residual stress on the stability of a bi-layer SiN$_x$/BC membrane

To obtain a flat, unbuckled, wrinkle free SiN$_x$/BC bi-layer membrane (composite structure); it is important to select a SiN$_x$ membrane with adequate size (i.e., width, length), thickness, and intrinsic residual tensile stress. A flat membrane is the primary requirement for conducting the bulge test successfully. With the deposition conditions mentioned in Sec. 2.4, the adhesion of BC is very good on SiN$_x$. Thus, there is no need to have a thin adhesive layer of some other material, say Cr, between BC and SiN$_x$. With no adhesive layer, sample preparation and data analysis time is significantly reduced.

To have a fair comparison on the stability of membranes with different configurations, BC deposition time of was kept minimum (~5-10 min) to avoid large thickness variations.

Post-deposition annealing of as-deposited BC film was required on all SiN$_x$ membrane configurations. Without annealing, due to the high compressive stress in as-deposited BC film, membrane broke in the chamber while cooling it to room temperature. For example, a broken 1 mm square membrane is shown in Fig. 5.12. Upon breaking, to relax the compressive strain, the composite membrane got bend in downward direction below the membrane as shown in Fig. 5.12. This type of behavior upon breaking is typical for a compressively stressed structure. (i.e., if the composite structure breaks due to the high tensile stress, one could expect it to bend in upward direction above the membrane). This was the first evidence of high compressive stress in as-deposited BC
films. To clarify our understanding, when a bare SiN$_x$ membrane with residual tensile stress was broken, the membrane showed similar evidence as mentioned for a high tensile stress composite structure.

**Figure 5.12: A picture of a broken 100 nm thick, 1 mm square membrane**

Post-deposition annealing helped to prevent all membrane configurations from breaking. This is because annealing helps to relax compressive stress in an as-deposited BC films. However, if the BC film is deposited on SiN$_x$ membrane with inadequate configuration, even post-deposition annealing cannot help to avoid the membrane (with certain configurations) from wrinkling upon removing it from chamber (Fig. 5.13 and 5.14). This is when the size, thickness and the level of residual tensile stress in the SiN$_x$ membrane become vital to avoid wrinkles. Composite structure doesn’t break when wrinkles occur, but buckles coherently with the substrate (SiN$_x$ membrane) with no signs of delamination (Fig. 5.13) – a common characteristic of wrinkles.

To see the effect of annealing cycle on a bare SiN$_x$ membrane, it was subjected to a similar annealing cycle without depositing BC film on it. Upon removing the membrane from chamber, it remained stable and never got wrinkled due to the intrinsic tensile
stress. Also, as nitride films do not have tendency absorb any water molecules from air, the stress level can be expected to remain stable in these films.

Fig. 5.13 (sample no. 030310) shows a wrinkled 100 nm thick rectangular membrane (1×4 mm$^2$). After removing the membrane from chamber, it showed first few wrinkles after ~ 36 hrs. Few wrinkles were first seen at the center of the membrane and their number got slowly increased in the lateral direction over a period of next 6 hrs. This type of behavior is most likely due to the dynamic change in the compressive stress of BC film upon exposing it to ambient conditions. Wrinkles moved in lateral direction (with each wrinkle parallel to the width of membrane), because of the fact that the membrane is less robust in that direction helping it to relax the compressive strain in entire membrane.

An interesting observation was made when this wrinkled rectangular membrane was annealed again. Upon annealing the sample for two hours at 350°C, wrinkles were still present. After this when the maximum annealing temperature was set to ~ 575 °C, wrinkles started to gradually vanish at ~ 440 °C. All wrinkles were gone, by the time maximum set annealing temperature was reached. Without any hold time at the maximum temperature, the sample was cooled down to ~ 125°C in an argon gas pressure of 200 mTorr. Further cooling to the room temperature was done in vacuum. The temperature was gradually lowered during the whole cooling cycle. Upon removing the sample from chamber, a stable wrinkle free composite membrane was obtained. This observation further fortifies the fact that the BC film wrinkled coherently with SiN$_x$ membrane without any buckle-delamination. After completing this second anneal cycle,
no wrinkles formed on this sample for the about next 5 months. Ref. [90] shows a similar type observation but on different set of materials (120 nm polystyrene film deposited on 1 mm thick PDMS substrate). In their study, the polystyrene film developed compressive stress during the cooling stage due to the difference in thermal expansion coefficients of two materials. Due to the compressive stress, polystyrene film formed wrinkles which got vanished upon annealing the sample again.

**Figure 5.13:** A picture of a wrinkled 100 nm thick, 1×4 mm² rectangular membrane.

**Figure 5.14:** A picture of a rectangular membranes showing no wrinkles upon second anneal cycle

A possible explanation for a probable dynamic change in the compressive stress of BC film can be explained from the fact, that the PECVD BC has a tendency to absorb oxygen and carbon molecules from air when exposed to ambient conditions [8]. Because of this, the BC film will try to swell. But as the swelling is constrained by SiNₓ membrane, the compressive stress in the BC film increases and ultimately the film wrinkles coherently with SiNₓ membrane to relax the compressive strain. It was found that BC films deposited on a 100 nm thick, low stress rectangular and square SiNₓ
membranes (from Silson) were susceptible to this type of failure. This is because, when there is dynamic change in compressive stress of BC film, these SiNₓ membranes provide insufficient constraint to prevent the BC film from wrinkling.

Upon annealing the wrinkled sample, it is believed that the absorbed molecules including the hydrogen molecules were removed from the BC film resulting into the formation of stable B-C bonds. Ref. [45] points out that high temperature annealing can substantially lower the concentration of hydrogen in BC films by breaking B-H bonds. Further, it was shown that after the high temperature (875 K) annealing of PECVD BC films, no further change in the composition of films (deposited on the Si substrates) was observed due to the formation of stable B-C bonds [8]. Also, the increased composition of carbon molecules upon exposing the PECVD BC film to air returned to the original composition after annealing. Thus, when the impurities get removed by annealing, there is a strong possibility that the BC film will try to shrink. Again, because of the constraint from SiNₓ membrane to shrink, the compressive stress is diminished as the SiNₓ membrane is trying to impose tensile stress on BC film. These could be the factors which may have attributed to get a stable composite membrane upon annealing the wrinkled sample for second time. However, wrinkles occurred on this sample again after ~ 5 months in a similar way as shown in Fig. 5.13.

Fig. 5.15 illustrates a wrinkled 100 nm thick, 1 mm square membrane. After removing the sample from chamber, first few wrinkles occurred at all four edges after ~ 2 hrs. Similar to the rectangular sample, wrinkles occurred on this sample because of the lack of constraint from substrate (SiNₓ membrane) to prevent the BC film from
wrinkling. As the square membrane is equally robust in all directions (because of equal side dimensions), the entire membrane got uniformly wrinkled soon after the initial traces of wrinkles were seen.

Figure 5.15: A picture of a wrinkled 100 nm thick, 1 mm square membrane

On the BC which got deposited on thick Si supported SiNₓ substrate surrounding the membrane, no wrinkles or delimitation was ever observed for both as-deposited and annealed BC films. This is because, even if the as-deposited BC film is under a high compressive stress or there is a dynamic change in the compressive stress of annealed BC film, thick substrates impose enough constraint to prevent wrinkles or buckle-delamination from happening. SiNₓ membrane is only 100 - 200 nm thick, but as it is supported on 0.36 - 0.525 µm thick Si substrate, it can be considered as a thick substrate surrounding the membrane. Thus, the issue of wrinkling is only a concern on SiNₓ membranes due to their extremely low bending stiffness compared to thick substrates. The next paragraph explains why thick substrates impose enough constraint to prevent the BC film from wrinkling.
Wrinkling occurs when the compressive stress in the film exceeds the critical stress for wrinkling to happen. The critical stress is given by an Eq. (16) [91]:

\[
\sigma_w = \frac{E_f}{4} \left( \frac{3E_s}{E_f} \right)^{2/3}
\]

Where \(E_f\) and \(E_s\) are elastic modulus of the film and the substrate respectively. With \(E_f(BC)\) and \(E_s(SiNx)\) equal to \(\sim 70 \text{ GPa}\) and \(\sim 240 \text{ GPa}\) respectively, \(\sigma_w = 82.76 \text{ GPa}\). As no wrinkles ever occurred on as-deposited and annealed BC films deposited on the adjoining Si supported SiN\(_x\) substrates, an estimated \(\sigma_w\) should be extremely high compared to the compressive stress in as-deposited BC films and the maximum dynamic change in the compressive stress of annealed BC films for the wrinkling to happen on SiN\(_x\) supported on thick Si substrate.

Eq. (16), however, may not hold true for membranes because it does not take into account the thickness of the substrate. Membranes are extremely thin free-standing structures and have an extremely low bending stiffness. As a result, even if the compressive stress in the BC film is less than the critical stress for wrinkling to happen, wrinkles can easily occur on membranes (with certain configurations), but not on the mentioned thick substrate. Therefore as mentioned before, when a compressively stressed film is deposited on the membrane, the size, thickness and the level of intrinsic tensile residual stress in the membrane becomes more crucial.

With post-deposition annealing of BC film deposited on a 200 nm thick, 1 mm square membrane, no wrinkles formed on the sample (Fig. 5.16) after exposing it to ambient conditions.
This sample is a typical example of how the membrane thickness matters to prevent the composite membrane from wrinkling. From Eq. (17) [92],

\[
\sigma_x + \frac{a^2}{b^2} \sigma_y = 1.1 \frac{E t^2 a^2}{1 - \nu^2} \left( \frac{3}{a^4} + \frac{3}{b^4} + \frac{2}{a^2 b^2} \right)
\]

where, \(\sigma_x\) and \(\sigma_y\) = compressive force acting uniformly on the edges “a” and “b” respectively, of a square or a rectangular plate (clamped at all edges), \(E\) = Young’s modulus, \(t\) = thickness, and \(\nu\) = Poisson’s ratio, a thicker (200 nm) membrane should impose about 4 times more constraint to wrinkling compared to a similar 100 nm thick, 1 mm square membrane from Silson. Also from Eq. (17), a rectangular membrane because of its large length of edge “b”, is less robust and therefore more prone to form wrinkles.

From the viewpoint of Eq. (17), selecting a membrane with adequate length of edges can make it substantially robust. Theoretically, the membrane with edges \(a = b = 0.5\) mm, should be \(\sim 4\) times more robust than a similar 200 nm thick membrane and \(\sim 8\) times more robust then a similar 100 nm thick membrane. With additional high residual tensile stress, this membrane can only become more robust (the importance of using high
residual tensile stress membranes is explained in following paragraphs). In reality, however, a 100 nm thick, 0.5 mm square membrane with a low residual tensile stress from 2spi got wrinkled after ~1 day (Fig. 5.17). As these membranes can be expected to be much stronger than the other large size membranes with similar tensile stress, wrinkling of these membranes was highly surprising. However, the time to form wrinkles was much longer (~ 24 hrs) compared to the sample (Fig. 5.15) which showed wrinkles after ~ 2 hrs. It means more than the aspect ratio, the lengths of the edges “a” and “b”, along with the membrane thickness are more important to make it more robust.

Figure 5.17: A picture of a wrinkled 100 nm thick, 0.5 mm square membrane.

The membrane shown in Fig. 5.18 (from 2spi) has a tensile stress of ~290 MPa. So even if the size of this membrane is similar to other two 1 mm square membranes from Silson, due to the high tensile stress in these membranes, the net tensile stress in the composite structure remains high enough to prevent the BC film from wrinkling (even if there is a possible dynamic change in the compressive stress of BC film).
A membrane with proper configuration should therefore make a bi-layer SiNₓ/BC membrane more robust, however; these membrane configurations may not work to obtain a flat bi-layer membrane with thicker BC films. In few cases, a better membrane configuration can only make wrinkles to appear after more time compared to the membrane with a weak configuration. An example of this is given in the explanation of 0.5 mm square window. As the sample shown in Fig. 5.18 is flat for more than 4 months, high residual tensile stress seems to be the most important membrane configuration to obtain a stable SiNₓ/BC bi-layer membrane.

Therefore, a user while selecting the membrane may look for one of the above mentioned conditions or it is even better to select a membrane satisfying all of the above mentioned favorable conditions for preventing the bi-layer SiNₓ/BC membrane from wrinkling. This is especially important as the thickness of BC film increases.

There is also a possibility of change in the compressive stress of BC film (which may form wrinkles) due to the difference in thermal expansion coefficient of BC and SiNₓ material. If the difference was significant the membrane may wrinkle in the chamber itself while cooling it to room temperature. This was not observed in any of the cases.
5.2 Nanoindentation

Indenter tip calibration is important for estimating mechanical properties accurately from the nanoindentation test. Fig. 5.19 shows an area function calibration plot of Berkovich indenter. From the comparison of ideal and calibrated (corrected) area function of a Berkovich indenter, it is evident that without calibration the contact area can be significantly underestimated over the entire range of displacements. This can greatly inflate the true values of hardness and Young’s modulus due to their direct dependence on the accurate evaluation of contact area.

![Figure 5.19: An area function calibration plot of Berkovich indenter.](image)

As it is important to calibrate area function over the entire expected indentation depths, the area function was tailored in the indentation depth range of 10 to 100 nm. The area function curve was extrapolated below and beyond this range and was further
corrected from an uncorrected area function by eliminating bad data points (the data points which showed large deviations in the values of reduced elastic modulus and hardness of fused silica which was used for the calibration). This correction further improves the accuracy of contact area especially for the displacements greater than 20 nm as shown in Fig. 5.19. Thus, the corrected area function was used to evaluate film properties.

All discussions and the possible conclusions on results are applicable only to the thickness regime investigated.

Fig. 5.20 illustrates the influence of substrate effect of Si on the hardness and Young’s modulus of BC film as a function of indentation depth. With both the hardness and Young’s modulus rising with the increase indentation depth, the substrate effect of Si on the mechanical properties BC films is clearly visible. It shows that the BC films are softer and less stiff than the Si substrate. Substrate effects are visible at displacements as small as 9-10% of film thickness. As shown in Fig 5.20, at indentation depths greater than ~10 % of film thickness, both the Young’s modulus and hardness sharply increase showing the substrate effect of silicon on the measured properties of BC films. At a displacement of ~80% of film thickness, both the hardness and Young’s modulus of film approaches the literature values of hardness (~13 GPa) and Young’s modulus (~165 GPa) of Si. This also means that the area function was well-defined. The film hardness measurements are almost identical over the depth range of 10-12 nm (9.5-10.3% of film thickness). This reflects that the substrate effect is minimal at these depths. Around the
same range, the Young’s modulus is also not much affected within the accuracy of our measurements.

![Graph showing Young's Modulus and Hardness vs Indentation Depth](image)

**Figure 5.20:** Substrate effect of Si on the hardness and Young’s modulus of BC film as a function of displacement.

A sharp increase in the value of Young’s modulus at indentation depths above 10 nm can be attributed to the fact that the measurement of Young’s modulus is more affected than the hardness by the presence of the hard substrate. This is because the elastic field under an indenter is a long range field that extends into the substrate and is not restricted within the film itself, especially for very thin films [83]. Therefore, with increasing film thickness, one can expect to see the effect of substrate stiffness on the measured value of Young’s modulus to decrease. This fact is supported with results showing maximum standard deviation of Young’s modulus for thinnest film and a sharp
decrease in standard deviation with increasing film thickness. On the other hand, within 10-12 nm depth range, the value of hardness saturates due to minimal substrate effect. This is possibly due to the fact that for a soft film on hard substrate, plastic deformation is mostly contained within a film [83]. However, in the present work, the effect of substrate hardness on the film hardness was seen at indentation depths well below the film/substrate interface probably due to the lack of plastic deformation in BC films. Thus, the indentation depth between 9.5 to 10.3% of film thickness is ideal to evaluate mechanical properties of BC films.

At low indentation depths (i.e., ~8.6% of film thickness) the area function rises sharply which can lead to the underestimation of hardness and Young’s modulus of film. To support this fact, the difference in the contact area at 8.6 to 9.5% of film thickness is quite small (639 nm²), but there is a substantial difference in the maximum load of about 20 μN (H=P_max/A) at these depths (P_max is the maximum load and A is the contact area at the maximum indentation depth). Also, the change in stiffness is only about 0.68 μN/nm. Thus, due to an overestimation of contact area at low depths, both properties can be underestimated. Further, because the hardness varies as A^{-1}, the effect of incorrect contact area on hardness is more pronounced than the effect on the Young’s modulus, which varies as A^{-1/2}. The effect is visible in results with a low value of hardness (~4.39 GPa) compared to the Young’s modulus at ~8.6 % film thickness.

The following discussion relates to the findings given in Table. 5.3 and 5.4. Fig. 5.21 shows a typical load-displacement diagram of as-deposited BC film.
The deformation is mostly elastic because of the small amount of hysteresis between the loading and the unloading curve. Using Eq. (14), the total amount of elastic recovery upon unloading for as-deposited and annealed BC films was about 93 and 95% respectively. Thus, the BC films exhibit excellent elasticity, with only about 5% of permanent plastic deformation taking place.

Using Eq. (13), the maximum amount of sink-in for all as-deposited and annealed BC films was about half the maximum indentation depth. The ratio of \( h_f/h_{max} \) has a value of \(~0.06\) and \(0.008\) for as-deposited and annealed BC films respectively. Annealed films show \(~7.5\) times more sink-in compared to the as-deposited BC films. This indicates that annealed films have better elasticity. This ratio of \( h_f/h_{max} \) is well below the transition point of 0.7 above which the pile-up can be expected. Further, the ratio of \( E/H \) is \(~13\)
and 12.6 for as-deposited and annealed films, respectively. This ratio is also very small compared to other soft materials that are expected to show pile-up. For example, the ratio of \( E/H \) for aluminum can be as high as 100. Therefore, as expected for ceramic films, the possibility of pile-up can be discarded. The unloading curve was well defined by a power law fit that was used in evaluating the values of hardness and Young’s modulus.

Assuming a Poisson’s ratio of 0.18 [46] for boron carbides, the Young’s modulus and hardness of as-deposited and annealed BC films with three different thicknesses are shown in Table. 5.3 and 5.4 respectively.

Because of the errors associated in the case of evaluating the Young’s modulus accurately, the thinnest films were not used to estimate average Young’s modulus of all samples in respective categories. The average Young’s modulus and hardness of all film thicknesses is \(~72\) and \(6\) GPa for as-deposited films and \(~74\) and \(6\) GPa for annealed films. Thus, within the accuracy of our measurements, the effect of annealing does not seem to be pronounced on the Young’s modulus or on the hardness of films.
<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Young’s modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Indentation depth (% of film thickness)</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>86.26 ± 5.19</td>
<td>5.16 ± 0.13</td>
<td>9.6</td>
</tr>
<tr>
<td>205</td>
<td>71.74 ± 4.13</td>
<td>5.95 ± 0.28</td>
<td>9.7</td>
</tr>
<tr>
<td>317</td>
<td>71.74 ± 2.05</td>
<td>6.97 ± 0.28</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 5.3: The Young's modulus and hardness of as-deposited BC films

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Young’s modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Indentation depth (% of film thickness)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>76.9 ± 3.63</td>
<td>4.40 ± 0.13</td>
<td>10.2</td>
</tr>
<tr>
<td>209</td>
<td>72.36 ± 3.60</td>
<td>6.02 ± 0.49</td>
<td>9.5</td>
</tr>
<tr>
<td>320</td>
<td>77.23 ± 3.01</td>
<td>7.65 ± 0.30</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 5.4: The Young’s modulus and hardness values of annealed BC films
For reference, the modulus of glass and aluminum (~70 GPa) are close to the values of modulus reported here. Also, the hardness of glass (~7 GPa) is very close that reported here.

A plot of hardness and Young’s modulus of PECVD as-deposited and annealed BC films as a function of film thickness is illustrated in Fig. 5.22 and 5.23 respectively. As discussed before, a high Young’s modulus for thinnest films (114 and 117 nm) can be most likely attributed to an experimental error rather than the true Young’s modulus of these films. Between a 200 and 300 nm range of film thickness, discrepancy in the value of Young’s modulus is very less. Thus, for thicker films, it is possible to find the Young’s modulus with a negligible experimental error. In the view of results discussed so far, the Young’s modulus of thinnest films may most probably fall in or near a range of 68 to 72 GPa. Thus, if this is true or the Young’s modulus of thinnest film is not considered, the Young’s modulus of as-deposited films remain relatively constant as a function of film thickness. For both as-deposited and annealed BC films, the hardness seems to increase linearly as a function of film thickness. Possible reasons for this type of change in the hardness are discussed in the following paragraphs.

From the discussions on the effects of SiN_x membrane size, thickness, and residual stress on the stability of a bi-layer SiN_x/BC membrane (See Section 5.1.5), it is evident that as-deposited PECVD BC deposits have intrinsic compressive stress which can be relaxed by post-deposition annealing. By definition, hardness is the measurement of resistance to deformation. As the membranes wrinkled more easily with thicker BC
Figure 5.22: A plot of hardness and Young’s modulus of as-deposited BC films as a function of film thickness.

Figure 5.23: A plot of hardness and Young’s modulus of annealed BC films as a function of film thickness.
films deposited on them, likely with an increase in thickness the compressive stress in BC films increases. A sample with compressive stress is more difficult to deform compared to a sample with tensile stress in it. This is because the compressive stress helps to resist deformation contrary to the tensile stress which tends to encourage it. Therefore, with the increase in compressive stress as the film thickness increases, the hardness tends to increase.

Compressive and tensile stress effects on the determination of Young’s modulus and hardness from an analysis nanoindentation load-displacement data have been reported before [84, 93]. In Ref. [93], an Al 8009 sample was examined in order to study the effects of residual stress on the Young’s modulus and hardness by analyzing the load-displacement data. T.Y. Tsui et al. [93] found that, with increasing compressive stress, material pile-up became pronounced and therefore the contact area found using the Oliver and Pharr method was increasingly under-predicted. Therefore, both the Young’s modulus and hardness were over estimated. To support the fact that the contact area was under estimated due to pile-up, T.Y. Tsui et al. [93] took an optical image of contact areas to find actual contact area. As the actual contact area was unaffected by the level of stress (compressive or tensile), both the inferred Young’s modulus and hardness showed no dependence on stress. Further, the difference in the value of the actual contact area and the contact area found using the Oliver and Pharr method became closer with increasing tensile stress due to the decrease in amount of pile-up. Therefore, due to the inability of the Oliver and Pharr method to estimate the contact area accurately when pile-up occurs, both the Young’s modulus and hardness were over estimated in the study by T.Y. Tsui et al. [93]. It was clear that the compressive stress made both values to
increase, but this increase was due to the pile-up and not due to the actual increase in
hardness due to the increase in compressive stress.

From the results presented here for BC films, pile-up is not expected due to their
low $h/h_{\text{max}}$ (well below the 0.7) and $E/H$ (≈ 14) ratios. Second, for as-deposited BC films
(not considering the 114 nm film due to a possible experimental error due to the substrate
effect), only the hardness changes but the Young’s modulus does not. For annealed BC
films, there is a change in the Young’s modulus along with that in the hardness, possibly
due to an increase in film density upon annealing (explained later). This is contrary to the
results in Ref. [93], where both values are reported to increase with an increase in
compressive stress due to pile-up. But when sink-in effect dominates (as for BC films),
the Oliver and Pharr method is reported [75] to estimate accurate contact area from the
analysis of load-displacement data. From the viewpoint of these observations, the
increase in compressive stress must be increasing the resistance to deform films, and
therefore; indeed the hardness of films must be increasing with increasing compressive
stress (with an increase thickness) as sink-in dominates.

Ref. [84] points out that with the increase in compressive stress, the loading curve
may gradually shift towards left. In the present work, a similar shift in the loading curve
of 316 nm film relative to the loading curve of 205 nm as-deposited BC film in shown in
Fig. 5.24. This further fortifies the fact that the compressive stress may be increasing with
the increasing thickness.

Finally, the indication of increase in Young’s modulus and hardness of annealed
BC films shown in Fig. 5.23 (not considering the thinnest film due to the possible
experimental error) is probably due to the increase in density of BC films upon annealing. An increase in film density of PECVD BC due to the formation of stable B-C bonds upon annealing has been reported before [45]. It is notable that annealing relaxes compressive stress and so the hardness of annealed BC films can be expected to be less than as-deposited BC films. However, this is not the case and therefore, the increase in film density upon annealing may be the contributing factor for the increase hardness of annealed BC films.

![Loading curve of BC films](image)

**Figure 5.24:** An effect of compressive stress on the loading curve of BC film.
6. CONCLUSIONS AND FUTURE WORK

6.1 Bulge test

A bulge test system has been successfully designed for the mechanical testing of thin films. Due to the intrinsic compressive stress in PECVD BC films, sample preparation was one of the main problems encountered in conducting a bulge test on BC films. The residual compressive stresses were found from the linear bulge test pressure-deflection response to be -248 ± 9.60 and -376 ± 5.83 MPa for BC film thicknesses of ~59 and ~74 nm. However, wrinkles developed in BC film (~93 nm thick) / SiNx (~200 nm thick) membrane pair - strong evidence of the increase in compressive stress with increase in film thickness was found, but not useful for evaluation of the residual stress in the BC film.

The bulge test results are sensitive to the accuracy of measuring geometric parameters such as the film thickness and the membrane width, and the ability to measure the deflection and pressure accurately. The interferometry system offers good displacement resolution, but the clarity of fringes, especially at high film deflections is greatly affected by the film roughness and window size. As the SiNx membrane windows were used as a substrate to deposit BC thin films, it is important to select these membranes with adequate tensile stress, size and shape to obtain a stable SiNx/BC bi-layer membrane for the bulge test. From the present experience of depositing PECVD BC films on SiNx membranes, it seems only annealed BC films of few hundred of nanometers have potential to be tested by the bulge test. High tensile stress (~450-500
MPa), 1 mm square SiNₓ membranes are more suitable to deposit BC films compared to the low tensile stress large or small size membranes.

Overall, with a proper understanding of sample preparation, experimental limitations and possible causes of errors, the bulge test can be successfully applied for the mechanical characterization of PECVD BC films.

6.2 Nanoindentation

The nanoindentation test was successfully performed to find the Young’s modulus and residual stress of as-deposited and annealed BC films. In each category, three film thicknesses close to 100, 200 and 300 nm were tested. All film properties were extracted at about 10% of film thickness. Substrate effect was more pronounced for the film with smallest thickness; however, it was minimal for thicker 200 and 300 nm films.

As the problems (i.e., wrinkling, buckling, delamination) arising from compressive stress in BC films are eliminated due to the use of thick Si substrate (i.e., 356 µm) for depositing BC films, this technique can be employed to test both as-deposited and annealed BC films and shows a great potential to test BC films at micron scale. The average Young’s modulus and hardness of all film thicknesses was ~ 72 and 6 GPa for as-deposited films and ~ 74 and 6 GPa for annealed films. PECVD BC films have excellent elasticity of ~ 95%.

From the literature values of mechanical properties of different types of BC films (See Table 1.1), the Young’s modulus and hardness of PECVD BC is less than the BC films fabricated from different forms of sputtering techniques (i.e., the hardness is ~ 3 to
8 times less, while the Young’s modulus is ~ 2.5 to 6 times less). Only the Young’s modulus (40-100 GPa) of LPCVD BC is comparable to the Young’s modulus of PECVD BC. Also, the Young’s modulus of PECVD BC is ~ 6 times less than the bulk form of BC ($E_{\text{bulk BC}} = 420$ GPa).

The Oliver and Pharr method works well to analyze nanoindentation load-displacement data of BC films. To evaluate accurate mechanical properties it is important to calibrate the instrument properly, especially the area function of Berkovich indenter. Further, it is vital to define area function over the entire expected indentation depth.

For as-deposited BC films, the Young’s modulus showed no dependence on film thickness, while the hardness showed small increase with increasing thickness likely due to the increase in compressive stress of film as the thickness increases. For annealed BC films, both the Young’s modulus and hardness showed a small increase with increasing thickness likely due to the increase in film density upon annealing.

Overall, if the instrument is well calibrated, the nanoindentation technique can be successfully implemented to study the mechanical properties of PECVD BC thin films.

6.3 Future work

6.3.1 Bulge test

To find the Young’s modulus of BC films from the bulge test, bi-layer SiN$_x$/BC membranes should be tested in the cubic regime of P-h curve. The effects of varying important deposition parameters such as the deposition pressure, RF power and RF frequency on the stability of SiN$_x$/BC bi-layer membranes should be studied. By
changing these parameters, the intrinsic compressive stress in BC films may be reduced. Ref. [16, 47] gives further details on these and some other important CVD deposition parameters. Using high tensile stress (~ 450-500 MPa), 1 mm square SiNₓ membranes, it is possible to check the maximum thickness of annealed BC films that can be tested by the bulge test. Also, using these high stress membranes, it is possible to check if the bulge test can be applied to test as-deposited BC films with thicknesses of at least few tenths of nanometers. Further it possible to investigate if the residual stress and the Young’s modulus are different at the center and the edge of 3” Si wafer.

6.3.2 Nanoindentation

If there are no issues associated with the delamination of BC films on glass substrate, it can be used as a substrate to deposit BC films as the mechanical properties of both materials are close to each other. This can substantially minimize substrate effect, especially on the obtained value of Young’s modulus. It can also be interesting to check the mechanical properties of BC films at micron scale. Fracture toughness of BC films can also be investigated.
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APPENDIX

Appendix A1: Working principle of the Michelson’s interferometer

A modified diagram of Michelson’s interferometer is shown in Fig. A1. The laser beam is split by a 50/50 beam splitter and the resultant two coherent beams travel in two different, but nearly equal paths to the film and the mirror. The film and the mirror surface reflect the beams back to the beam splitter were they recombine. Due to the deflection of film, there is a change in the optical paths of two beams because of which an interference pattern formed. Depending on the distance travelled by the two beams, the fringe pattern shows constructive (bright spots) or destructive interference (dark spots) at the center of the pattern.

As the membrane deflects, a new central fringe is formed and the previous one moves outwards. As the beam travels to the film surface and is reflected back, each bright or dark fringe cycle represents the displacement by half the wavelength of laser light used ($\lambda/2$). Thus, the bulge height can be obtained by counting the total number of bright and dark fringes and multiplying that number by ($\lambda/4$).
Appendix A2: Alignment of Michelson’s interferometer to measure the bulge height

1) Check if the laser beam is perfectly parallel with the optical platform (X-axis). A ruler can be used to check if the laser beam height is consistent with the platform. Also check if the laser beam is perpendicular to the y-axis of the platform.

2) The beam splitter was mounted with a laser beam striking its front surface at the center. To assure if the laser beam was perfectly perpendicular to the front surface, the beam splitter was tilted for allowing the back reflection from it to go inside the laser bore.

3) The mirror was mounted as one of the reflecting surfaces of interferometer. Mirror tilt was adjusted till the back reflection from it goes inside the laser bore. Also, the laser spots reflected on the screen from the beam splitter and the mirror were merged together.

4) A film loaded to the pressure chamber acts as a second reflecting surface of interferometer. Again, to assure if the beam was perfectly perpendicular to the surface of the film, the chamber position was adjusted to allow the back reflection from the film to go inside the laser bore. The reflected laser spot from the films surface on the screen was merged with the previously merged laser spots from the mirror and the beam splitter. For the optimum performance, the distance of the beam splitter from both the film and the mirror was approximately same (within ~1 mm). Fringes became wide if the distance is exactly same, but with increasing difference in distance, fringes appear to be narrower.

5) A 5x objective lens was inserted between the laser pointer and the beam splitter to increase the diameter of beam. The beam now covered the whole membrane area and an
interference pattern was seen on the screen. Depending on the membrane shape, the interference pattern can either be square or rectangular in shape.

6) The pattern was enlarged further by placing an expander plano-concave lens between the beam splitter and the screen. The system was then sealed as explained in the procedure to conduct the bulge test in Sec 3.7. Mirror tilt was adjusted further to get a symmetrical fringe pattern about the center of the membrane. Finally, if the reflections from the mirror are partially blocked, one can notice this symmetry with respect to the bright spot reflected from the membrane. Each time when the chamber was loaded with a new film, only the steps from 4 to 6 were repeated again.

**Appendix A3: Design criteria of the pressure chamber**

To improve the compliance of the system, the main design criterion was to have the total volume of cavity inside the pressure chamber as small as possible for having a better control to build the pressure efficiently. A majority of total water volume was contained within a cavity of transducer. The total volume of water, including the volume of water inside the cavity of transducer and square o-rings is important while designing the pressure chamber to build the maximum expected pressure. The chamber should quickly allow loading and unloading of samples. Machine threads of the pressure chamber should be precisely machined for the screwing of transducer and syringes without any leakage. Further, the square o-ring seats should be smooth without any scratches. The seats can be polished by one micron aluminum powder applied on a soft balsa tree.
Appendix A4: Design criteria of the sample holder, clamping plate and assembly jig

The sample holder is a circular disc with a center slot approximately equal to the backside opening of a rectangular or a square membrane (Fig. 3.6). Slot dimensions were such that the support of the Si substrate was maximized and it was possible for the laser beam to cover the whole membrane area.

The clamping plate should quickly allow for loading and unloading of samples. It should have a center hole for passing the laser beam on the membrane. For minimizing the torque on square o-ring while clamping, the clamping holes should be in line with the center of the cross-section of square o-ring (at membrane port).

Assembly jig (Fig. 3.6) was used for attaching the sample to the sample holder. It should quickly align the membrane with the slot in the sample holder. For accommodating 525 µm thick, 10 mm square Si frames, the jig has a 0.3 mm deep, 10 mm square slot it. A circular hole in square slot prevents the membrane from damage. The assembly jig used here is only capable of aligning membranes on 10 mm square Si frames. After applying a small amount epoxy around the slot in sample holder, a sample with ~ 2 mm square Si frame (with a 1 mm square membrane) was aligned manually on the sample holder with the help of tweezers. Without using an assembly jig, it takes more time to attach samples manually.
Appendix A5: Material selection for square o-rings

An elastomer with high stiffness shows less creep and is hard to deform at high pressures. Impermeability of elastomer is also important as even a small amount of water loss can make it difficult to build pressure - degrading the compliance of system. These material characteristics were necessary to build pressure efficiently. Compatibility with pressure medium and the ability to withstand operating temperatures were other important characteristics. Square o-rings made from Viton satisfied these material characteristics.

Appendix A6: Selection of an epoxy

Quick cure epoxies take ~ 5-30 min to cure completely. High cure rate can alter the initial stress in the film especially if the epoxy is applied directly on the substrate supported film on the membrane side. Further, if the epoxy cures quickly, it makes it difficult for aligning the sample (membrane) properly with the slot in the sample holder. Most importantly, the epoxy should be waterproof and should maintain its strength in the presence of moisture. For these reasons, a slow cure epoxy with a cure schedule of 12 hours at room temperature was used and was applied on the window side.

Appendix A7: Procedure for attaching the sample to sample holder

By weighing, an epoxy was prepared with a resin to hardener ratio of 6:1. The ratio was properly maintained for adequate bonding. The assembly jig was cleaned with methanol before placing the sample on it. The sample was held with tweezers from top while applying epoxy at the edges of the frame. A small amount of epoxy was sufficient
and the care was taken to avoid the epoxy from flowing onto the membrane when the sample holder was placed on the sample for alignment. In other words, epoxy should be applied away from the cavity at the edges of the frame. After placing the sample holder on sample, the slot in the sample holder was aligned with the membrane. For all samples, it was important for aligning the slot in the sample holder properly with the membrane. Approximately 12 hours were allowed for curing.

Appendix A8: Estimating the required bulge testing pressure range

Using Eq. (1), an approximate total pressure for the deflection of a square membrane in the cubic regime was predicted. As the pressure is inversely proportional to “a” to the power of two and four in the first and the second term respectively in the Eq. (1), the total pressure required to deflect the membrane by a certain amount changes dramatically as the “a” changes. The total pressure was predicted for the deflection of ~30 µm for bare SiNₓ membranes (100 and 200 nm thickness) as well as for BC films with thicknesses up to 600 nm. To obtain a fully developed P-h curve, the maximum assumed deflection was more than enough for the P-h curve to enter the cubic regime. The width (2a) of the membrane was assumed to be 1 mm. All other terms in Eq. (1) were assumed from the literature. The system, however, was designed to build pressure many times higher than the actual predicted pressure. This also helps to successfully test bi-layer SiNₓ/BC membranes in case they require very high pressures.

Depending on the true mechanical properties (i.e., the Young’s modulus and the residual stress) of the film, in reality the actual pressure required for the testing of films may be many times less than the actual predicted pressure. But the design of the system is
good as long as the system is capable of building more pressure than the actual pressure required for testing the films and the transducer is capable of measuring low as well as high pressures with good resolution.

From the predicted pressure range, it was possible to select a pressure range for the transducer. A transducer was selected with a pressure range of 0-16 barg. There were two reasons for selecting a transducer with pressure range many times higher than the actual required pressure: First, it is possible to test thicker films and use windows with smaller widths and second, as this transducer is required to be filled with water under vacuum; a high pressure range can prevent it from the possible damage when the pressure close to the zero absolute pressure (vacuum pressure) is formed inside it before filling it with water.

**Appendix A9: Estimating the compressibility of pressure medium to build pressure**

The bulk modulus (K) of the pressure medium (Water: 2.18 GPa) decides the amount by which the pressure medium is required to be compressed for achieving the desired pressure range. For this estimation, the total volume of water (inside the pressure chamber, transducer, and square o-rings) should be known. The total volume was found to be ~ 19.32 mL. For instance, the approximate volume of water that is required to be compressed for achieving the maximum pressure of ~100 KPa is:

\[
= \frac{\text{Maximum pressure}}{\text{Bulk modulus of pressure medium}} \times \text{total volume}
\]

\[
= \frac{0.0001}{2.18} \times \text{total volume}
\]
= 0.88 μL.

Similarly, this amount can be calculated for other pressures.

**Appendix A10: Estimating the required syringe stroke and number of data points**

From the estimated compressibility of pressure medium to achieve the desired pressure range, it is possible to select a syringe with an appropriate volume and estimate the syringe stroke required to build pressure. To apply pressure it was decided to use a 25 μL syringe with a total stroke of 60 mm. There were two reasons for selecting this syringe: First, the volume of syringe is sufficiently more than amount of fluid that is required to be compressed. Second, compared to 10 μL syringes, the required stroke rate can be small for 25 μL syringes as the amount of fluid compressed per increment is large to build the pressure (small stroke rates can minimize the vibrations of syringe pump). For instance, for compressing (displacing) ~ 0.88 μL water, a syringe stroke of ~ 1.6 mm was required. This calculation was based on the fact that the syringe delivers 25 μL over a stroke of 60 mm. During the deflection some amount of fluid is occupied in the diaphragm of the transducer and membrane. As per Ellison sensors, a maximum of 0.33 μL was occupied in the diaphragm and our calculations show ~0.024 μL was occupied in the membrane at the maximum membrane deflection of ~30 μm. An additional syringe stoke of ~ 0.6 mm is required for these volumes. Therefore, the total stroke of syringe is sufficient to apply pressure successfully. A syringe pump was selected accordingly with a good displacement resolution as it is important to build pressure gradually (especially low pressures).
As mentioned before, sufficient number of data points is mainly a concern for small initial deflections as the pressure required at this stage is extremely small. Also, for very thin films the pressure required for small initial deflections will decrease further. But with a resolution of ~ 0.00008 KPa, the transducer is capable of giving enough number of data points for both small and large membrane deflections even if the required pressure is very small compared that predicted.

Appendix A11: Selection criteria for the transducer and syringes

A transducer should have a high resolution to obtain sufficient number of data points. This is especially important to test very thin films; because, compared to thick films they require less pressure for the maximum deflection. Also, the pressure required for the initial film deflection is very low which demands for a transducer with high resolution to obtain sufficient number data points. If a transducer has an internal cavity, its volume should be known. Further, it should be company calibrated, easy to configure, and its output should be easy monitor and record.

The selection of syringes was based on three basic requirements: First, syringes should have small volume with sufficient stroke to apply pressure uniformly with each small increment of syringe plunger and at the same time, total syringe volume should be sufficiently more than the total amount of fluid that is required to be compressed to build the required pressure. Second, syringes should have a small diameter for minimum push force and third, syringes should be gastight for adequate sealing.
Appendix A12: Vacuum filling procedure for the pressure chamber and the transducer

As the transducer has a large internal cavity of ~ 17 mL (Fig. A2), it was necessary to fill it under vacuum. Also, the transducer has a small size pressure port, so without vacuum water did not flow inside the cavity as the surface tension of pressure port walls acting on the water column was greater than the weight of water. Using an adapter at membrane port, the pressure chamber assembly was connected to the vacuum pump (Fig. A3). The vacuum filling procedure guarantees that the cavity inside the transducer including the cavity of pressure chamber is filled with water without introducing any air bubbles.

1) After closing the valve B, the hose was slowly filled with water and the care was taken to avoid any air bubbles to get trapped in it while filling. Once the hose was filled, the valve B was slightly opened and then closed to allow some water to flow through it. This was done to remove any air bubbles from the inside section of valve B.

2) The complete pressure chamber assembly was connected via adaptor to the vacuum filling setup. A Buna-N ring placed at the end of adaptor sealed it efficiently with the chamber. Adaptor threads were covered with Teflon tape for adequate sealing.

3) The vacuum pump was started and the valve A was slowly opened to create vacuum inside the cavities of the pressure chamber and the transducer.

4) When the absolute pressure reached close to zero, a vacuum close to 100% was formed inside the cavities. At this point, immediately after closing the valve A, the valve B was
opened to fill the cavities with water under vacuum. Finally, the transducer showed pressure close to the atmospheric pressure (1 bar) after filling.

Figure A2: A schematic of a transducer having a large internal cavity.

Figure A3: A schematic and a picture of apparatus for filling the transducer and pressure chamber under vacuum.