Investigation Of Reactively Sputtered Silicon Carbon Boron Nitride (sicbn) Thin Films For High Temperature Applications

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INVESTIGATION OF REACTIVELY SPUTTERED SILICON CARBON BORON NITRIDE (SiCBN) THIN FILMS FOR HIGH TEMPERATURE APPLICATIONS

by

ARUN VIJAYAKUMAR
M.S.E.E., University of Central Florida, 2003

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the School of Electrical Engineering and Computer Science in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

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2007

Major Professor: Kalpathy B. Sundaram
ABSTRACT

The increasing demand for efficient energy systems in the last decade has brought about the development of advanced sensor systems that utilize advance detection methods to help in preventive maintenance of these essential systems. These usually are needed in hard to access environments where conditions are extreme and unfit for human interaction. Thin film based sensors deposited directly on the surfaces exposed to harsh environments can serve as ideal means of measuring the temperature of the component during operation. They provide the basic advantage of proximity to the surface and hence accurate measurement of the surface temperature. The low mass size ratio provides the additional advantage of least interference to system operation. The four elements consisting of Si, C, B, and N can be used to form binary, ternary and quaternary compounds like carbides, nitrides, which are chemically and thermally stable with extreme hardness, thermal conductivity and can be doped n- and p-type. Hence these compounds can be potential candidates for high temperature applications. This research is focused on studying sputtering as a candidate to obtain thin SiCBN films.

The deposition and characterization of amorphous thin films of silicon boron carbon nitride (SiCBN) is reported. The SiCBN thin films were deposited in a radio frequency (rf) magnetron sputtering system using reactive co-sputtering of silicon carbide (SiC) and boron nitride (BN) targets. Films of different compositions were deposited by varying the ratios of argon and nitrogen gas in the sputtering ambient. Investigation of the oxidation kinetics of these materials was performed to study high temperature compatibility of the material. Surface characterization of the deposited films was performed using X-ray photoelectron spectroscopy and optical profilometry. Studies
reveal that the chemical state of the films is highly sensitive to nitrogen flow ratios during sputtering. Surface analysis shows that smooth and uniform SiCBN films can be produced using this technique. Carbon and nitrogen content in the films seem to be sensitive to annealing temperatures. However depth profile studies reveal certain stoichiometric compositions to be stable after high temperature anneal up to 900°C. Electrical and optical characteristics are also investigated with interesting results. Finally a metal semiconductor metal structure based optoelectronic device is demonstrated with excellent performance improvement over standard silicon based devices under higher temperature conditions.
I wish to dedicate this work to my parents for their continued love and support.
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LIST OF ABBREVIATIONS

BE - Binding Energy
MEMS – Micro Electro Mechanical Systems
MSM - Metal Semiconductor Metal
PD – Photodetector
PDCR – Photodetector Current Ratio
PL – Photoluminescence
SIMS – Secondary Ion Mass Spectroscopy
XPS – X-ray photoelectron spectroscopy
XRD - X-ray diffraction
CHAPTER 1: INTRODUCTION

Over the last few decades there has been an increasing growth of performance enhancing electronics on a wide variety of automotive, aerospace, deep-well drilling, and other industrial systems. The increased demand on the performance levels and expectations of industrial systems is very prominent in the current high tech era.

1.1. Overview

Harsh environment devices can be characterized by the placement of integrated electronics. They can be placed closer to the ultimate point of use (often in high temperature environments) to reduce weight, decrease connection complexity and improve reliability. They might be needed in chemically corrosive or erosive environments to improve sensing capabilities and/or improve control (in chemical process plant or in marine environments). Additionally they can be placed in extremely low (cryogenic) temperatures (in superconducting systems or space environments) or in high radiation fields in space or for sensing and control functions in nuclear systems.

Presence of high temperatures, way beyond the limits of conventional electronics, is essential to the operation of many of these systems. High temperature electronic materials will allow increased accuracy, control, efficiency and reliability in safety-critical systems operating in harsh environments in many applications (see Figure 1.1). Current electronic monitoring systems require additional cooling sub-systems. However these thermal management approaches introduce added complexity leading to additional overhead costs. Hence it is essential to come up with new materials and designs that can meet and surpass current harsh environment electronics performance levels.
Furthermore, thin film based sensors are being considered as potential candidates for such applications, as they provide many advantages over conventional sensors as they are generally few micrometers thick and much thinner than the commonly used sensor wires. They have fast response times and add negligible mass to the surface thus creating minimal disturbance to the system operation [1]. Hence micro-fabricated thin film sensors have minimal impact on the thermal, heat load, strain and vibration patterns providing a minimally intrusive means of accurate measurements. Furthermore, they can be directly fabricated onto the test surface where measurements are needed, batch fabricated, diced and then packaged into multiple devices.

1.2. Motivation

Electrical, chemical and mechanical stability are critical factors in determining the materials used for implementing thin film harsh environment sensors. Silicon (Si) has traditionally been the choice of material for current electronic devices. However, performance of silicon based devices starts deteriorating after 125ºC. Hence it is increasingly recognized that
semiconductor materials that can function at ambient temperatures higher than 150ºC without external cooling could greatly benefit a variety of important applications.

Silicon Carbide (SiC) is proposed as an excellent candidate for these applications due to its intrinsic properties, which provides significant advantages over silicon [2, 3]. Conversion of electronic control and sensor systems from Si to SiC based devices will not only increase efficiency and safety through enabling instrumentation but also reduce the overall weight of an aircraft by eliminating the packaging, wiring and connectors necessary to link sensor systems with control electronics. This reduction would directly translate to increased range and lower fuel costs. But SiC is believed to become inadequate at extremely high temperatures (>600ºC)[4, 5]. Especially in situations where the material is required in the form of thin films for surface measurements, such as on protective hard coatings, micro or nano-scale non intrusive sensors. Thus, the development of new materials that can outperform currently available materials (i.e. Si and SiC) is the primary motivation for this project.

The four elements consisting of Si, C, B, and N can be used to form binary, ternary and quaternary compounds like carbides, nitrides, which are chemically and thermally stable with extreme hardness, thermal conductivity and can be doped n- and p-type. In this context the alloys formed are interesting materials ranging from the band gap of SiC (2.2 eV) to insulating film of Si₃N₄ (5.0 eV). Furthermore silicon carbide is a widebandgap semiconductor material known to have significant potential and boron nitride (BN) is another material known for its hardness and chemical inertness. Hence it is expected that a combination of these components in a single material can provide a material with enhanced properties such as tunable bandgap, dopability, hardness, oxidation resistance and chemical inertness, which enable application of this material in extreme temperature conditions.
1.3. Objective and outline

Therefore the focus of this work was to look into the synthesis of the quaternary silicon boron carbon nitride (SiCBN) alloy through sputtering and investigating the various physical, chemical and electrical properties of the novel material to assess its application potential under harsh conditions.

Chapter 2 is intended to provide the reader with a comprehensive background on the current state of research in Si, C, B and N based alloy efforts. A historical perspective on both the different methods of synthesis as well as the significant properties of the materials that makes them useful is presented.

Chapter 3 describes the actual experimental process, equipment, and techniques used to synthesize and characterize the SiCBN thin films and the fabricated electronic devices. This section focuses on the materials processing and characterization, and relates the methods conditions and various tools used to determine relationship between deposition process and film properties.

Chapter 4 forms the core of this dissertation and includes results and discussions. Initial focus is on SiCBN film deposition and characterization of various deposition process parameters. Later we proceed to discuss the significant properties of the different films obtained to identify the optimal deposition parameters. Properties of the material such as chemical structure, optical properties and electrical properties are also discussed in detail with correlation between important parameters affecting each observation. Finally a optoelectronic device is demonstrated with better performance levels than conventional silicon based devices at higher temperatures.

Chapter 5 summarizes the present work with overall concluding remarks drawn from the various observed characteristics of the SiCBN thin film material. Another section is included to
discuss other possible material combinations for high temperature applications as well as suggested experimental work on SiCBN films that could provide possible insights into other properties of the material that could be exploited for high temperature applications.
CHAPTER 2: LITERATURE REVIEW

Materials that allow operation at high temperature are essential in many industries from material producing and processing to transportation and power generation. The basic functionality of these materials, is, the ability to withstand as well as provide protection for other components from the harsh conditions. However with technological advances in the industry, functional requirements have grown. Development of materials that can not only withstand the harsh conditions but also provide useful operational feed back functions such as sensors has become the new challenge. In this section we review the evolutionary path that lead to the current status of high temperature electronic materials.

2.1. High temperature materials

High temperature materials provide the basis for a wide variety of technology areas, including energy, electronic, photonic, and chemical applications. Defining “high temperature” can be quite a challenge. A commonly used definition in the field of materials science and technology is that it is a temperature equal to, or greater than, about two-thirds of the melting point of a solid. A more general form of the definition, attributed to Leo Brewer (widely regarded as the founder of modern high-temperature chemistry), is that high temperatures are those at which extrapolations of a material’s properties, kinetics, and chemical behavior from near ambient temperatures are no longer valid [6]. Chemical reactions that are unfavorable at room temperature could become prominent at higher temperatures. Vaporization processes and species become increasingly important at high temperatures. Unusual compounds and vapor species, which do not conform to the familiar oxidation states of the elements, may form. For example, in the vaporization of \( \text{Al}_2\text{O}_3(s) \), common high temperature gas species can include...
Al$_2$O, AlO, and AlO$_2$[6]. Increasing temperatures could cause, ordered defect structures to become disordered. For example, stoichiometric solids such as MgAl$_2$O$_4$ may develop significant composition ranges at high temperatures[6]. Hence physical properties of materials that correlate with the high temperature chemical behavior can be unpredictable through extrapolations of their low temperature properties.

High temperature materials are found in various forms from advanced alloys, to oxide and non-oxide ceramics and various types of composite materials. In addition to the chemical and physical properties that make a material important for technology, the ability to synthesize the material in physical forms ranging from powders to thin films to bulk pieces of various sizes and shapes is crucial to their application. While some applications involve the use of these materials at high temperatures, others require them as materials processed at high temperatures for room temperature application. Silicon-based ceramics such as SiC, Si$_3$N$_4$, and SiAlONs (formed when silicon nitride (Si$_3$N$_4$), aluminium oxide (Al$_2$O$_3$) and aluminium nitride (AlN) are reacted together) along with other borides, carbides, nitrides, silicides, and diamond and diamond-like materials are now common high temperature materials of scientific and technological interest in both bulk and coating configurations[7-9]. SiC and Si$_3$N$_4$ have properties of value for advanced microelectronic applications as well as for use as lightweight structural components at high temperatures. Single crystal SiC can be used as a high temperature semiconductor, while Si$_3$N$_4$ and its oxy-nitride Si$_2$N$_2$O provide excellent insulating coatings in device production. In their bulk form, both these materials are lightweight and can be used for structural applications at higher temperatures in place of metal alloy systems. Furthermore, SiC particles, fibers, and weaves have been used extensively in composite materials developed for lightweight, high temperature structural applications[10].
2.2. Electronic materials for high temperature applications

Interest in high temperature electronics has been longstanding dating from at least as early as the 1950s as a topic of government aerospace development[11]. Active components in most electronic circuits during the period were predominantly comprised of vacuum tubes. The vacuum tube has been known to be more tolerant to higher temperatures than currently known semiconductor devices. Another major venture undertaken during the same era was the use of silicon carbide as a semiconductor for high temperature devices. Various companies such as Westinghouse and General Electric had come out with SiC based thermistors, rectifiers and photodiodes with operational range above 500ºC[12]. However significantly low demand for these products during that time prompted the manufacturers to discontinue SiC based products. Furthermore the boom in the integrated circuit industry and the discovery of silicon as a ideal material for semiconductor devices diverted attention from SiC based devices.

Since 1990 the interest in high temperature electronics has revived and is advancing in new directions. Apart from some early work with vacuum tubes nearly all practical high temperature electronics has been based on silicon devices and circuits. Recently the development of silicon-on-insulator (SOI) technology has boosted silicon based high temperature applications[13-16]. Silicon is an excellent semiconductor for ambient and little higher than ambient operating conditions. However, for practical purposes they tend to become useless at high temperatures around 250º-300ºC. The high operational devices were mostly demonstrated on SOI based substrates. However bulk silicon performs poorly above 100ºC temperatures. At temperatures exceeding 300ºC electrical performance of Si devices declines rapidly[11]. Hence circuits that must operate at such temperatures must be based on materials with larger energy
bandgap than Si (1.12eV at room temperature) or on a completely different non-semiconductor electronic technology.

![Graph showing the relationship between maximum usable temperatures versus bandgap energy $E_g$ for various semiconductor materials.]

Figure 2.1: Maximum useful temperature range for different semiconductor materials [11]

Exotic large-bandgap semiconductor materials such as SiC, GaN and diamond (C) are receiving more attention[17]. Materials such as GaN have also shown significant promise in optoelectronic applications[18-20]. However progress in SiC based electronics has overshadowed all other materials. A chart showing relationship between maximum usable temperatures versus bandgap energy $E_g$ for various candidate materials plotted based on theoretical results reported by various researchers is shown in Figure 2.1. Another significant issue with these widebandgap materials is the availability of good quality substrates[21]. Processing issues will also have to be overcome before they can be successful commercially[22]. The outlines of some of the better known high-temperature electronics application areas, that,
widebandgap semiconductors might play a significant role in the future, once they have become sufficiently developed. is shown in Table 2.1 [23]

Table 2.1: Semiconductor technologies for selected high temperature applications.[23]

<table>
<thead>
<tr>
<th>High Temperature Electronics Application</th>
<th>Peak Ambient</th>
<th>Chip Power</th>
<th>Current Technology</th>
<th>Future Technology</th>
</tr>
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<td>Automotive</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Engine Control Electronics</td>
<td>150 °C</td>
<td>&lt; 1 kW</td>
<td>BS &amp; SOI</td>
<td>BS &amp; SOI</td>
</tr>
<tr>
<td>On-cylinder &amp; Exhaust Pipe</td>
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<td>&lt; 1 kW</td>
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<td>&gt; 10 kW</td>
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<td>Electric/Hybrid Vehicle PMAD</td>
<td>150 °C</td>
<td>&gt; 10 kW</td>
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<td>Turbine Engine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensors, Telemetry, Control</td>
<td>300 °C</td>
<td>&lt; 1 kW</td>
<td>BS &amp; SOI</td>
<td>SOI &amp; WBG</td>
</tr>
<tr>
<td></td>
<td>600 °C</td>
<td>&lt; 1 kW</td>
<td>NA</td>
<td>WBG</td>
</tr>
<tr>
<td>Electric Actuation</td>
<td>150 °C</td>
<td>&gt; 10 kW</td>
<td>BS &amp; SOI</td>
<td>WBG</td>
</tr>
<tr>
<td></td>
<td>600 °C</td>
<td>&gt; 10 kW</td>
<td>NA</td>
<td>WBG</td>
</tr>
<tr>
<td>Spacecraft</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power Management</td>
<td>150 °C</td>
<td>&gt; 1 kW</td>
<td>BS &amp; SOI</td>
<td>WBG</td>
</tr>
<tr>
<td></td>
<td>300 °C</td>
<td>&gt; 10 kW</td>
<td>NA</td>
<td>WBG</td>
</tr>
<tr>
<td>Venus &amp; Mercury Exploration</td>
<td>550 °C</td>
<td>~ 1 kW</td>
<td>NA</td>
<td>WBG</td>
</tr>
<tr>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High Temperature Processing</td>
<td>300 °C</td>
<td>&lt; 1 kW</td>
<td>SOI</td>
<td>SOI</td>
</tr>
<tr>
<td></td>
<td>600 °C</td>
<td>&lt; 1 kW</td>
<td>NA</td>
<td>WBG</td>
</tr>
<tr>
<td>Deep-Well Drilling Telemetry</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil and Gas</td>
<td>300 °C</td>
<td>&lt; 1 kW</td>
<td>SOI</td>
<td>SOI &amp; WBG</td>
</tr>
<tr>
<td>Geothermal</td>
<td>600 °C</td>
<td>&lt; 1 kW</td>
<td>NA</td>
<td>WBG</td>
</tr>
</tbody>
</table>

BS = bulk silicon, SOI = SOI, NA = not presently available, WBG = wide bandgap.

With increasing improvements in electronic performance at high temperatures other demands could also be placed on high temperature materials. Some applications could require the material to be super hard, chemically inert to corrosive agents and possess high thermal stability. In addition to these requirements these materials need to possess semiconducting properties so that they can be exploited as electronic devices. Table 2.2 shows the comparison between different widebandgap candidates for high temperature electronics and their significant properties.
# Table 2.2: Comparison of various semiconductors and their properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Silicon</th>
<th>GaAs</th>
<th>3C-SiC</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
<th>GaN</th>
<th>Diamond</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å) (RT)</td>
<td>5.430</td>
<td>5.65</td>
<td>4.3596</td>
<td>3.073</td>
<td>10.053</td>
<td>3.0806</td>
<td>3.567</td>
<td>3.11 a₀</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.98 c₀</td>
</tr>
<tr>
<td>Thermal expansion (x 10⁻⁵) °C</td>
<td>2.6</td>
<td>5.9</td>
<td>4.7</td>
<td>—</td>
<td>4.2 a₀</td>
<td>5.6</td>
<td>0.08</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.328</td>
<td>5.52</td>
<td>3.210</td>
<td>—</td>
<td>3.211</td>
<td>—</td>
<td>3.515</td>
<td>3.255</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1420</td>
<td>1238</td>
<td>2830*a</td>
<td>2830*a</td>
<td>2830*a</td>
<td>—</td>
<td>4000</td>
<td>3000</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>1.1</td>
<td>1.43</td>
<td>2.39</td>
<td>3.26</td>
<td>3.02</td>
<td>3.45</td>
<td>5.45</td>
<td>6.2</td>
</tr>
<tr>
<td>Saturated electron velocity (x 10⁷ cm/s)</td>
<td>1.0</td>
<td>1.0</td>
<td>2.2</td>
<td>2.0</td>
<td>2.0</td>
<td>2.2</td>
<td>2.7</td>
<td>—</td>
</tr>
<tr>
<td>Carrier mobility (cm²/V·s)</td>
<td>1,500</td>
<td>8,500</td>
<td>1,000</td>
<td>1,000</td>
<td>370</td>
<td>1,250</td>
<td>2,200</td>
<td>14</td>
</tr>
<tr>
<td>Electron</td>
<td>600</td>
<td>400</td>
<td>50</td>
<td>50</td>
<td>90</td>
<td>250</td>
<td>1,600</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Hole</td>
<td>6</td>
<td>6</td>
<td>20</td>
<td>30</td>
<td>32</td>
<td>&gt;50</td>
<td>100</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Breakdown (x 10⁶ V/cm)</td>
<td>11.8</td>
<td>12.5</td>
<td>9.7</td>
<td>—</td>
<td>9.6-10</td>
<td>11</td>
<td>5.5</td>
<td>10</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>10³</td>
<td>10⁸</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>10⁸</td>
<td>10⁸</td>
<td>10⁸</td>
</tr>
<tr>
<td>Resistivity (Ω·cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity (W/cm·K)</td>
<td>1.5</td>
<td>0.46</td>
<td>5</td>
<td>4.9</td>
<td>4.9</td>
<td>1.3</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td>Absorption edge (µm)</td>
<td>1.4</td>
<td>0.85</td>
<td>0.50</td>
<td>0.37</td>
<td>0.40</td>
<td>0.36</td>
<td>0.22</td>
<td>0.12</td>
</tr>
<tr>
<td>Refractive index</td>
<td>3.5</td>
<td>3.4</td>
<td>2.7</td>
<td>2.712</td>
<td>2.7</td>
<td>—</td>
<td>2.42</td>
<td>3.32</td>
</tr>
<tr>
<td>Hardness (kg/mm²)</td>
<td>1,000</td>
<td>600</td>
<td>3,980</td>
<td>2,130 a₀</td>
<td>—</td>
<td>—</td>
<td>10,000</td>
<td>1,200</td>
</tr>
</tbody>
</table>
The set of binary ternary and quaternary alloys consisting of silicon boron carbon and nitrogen are believed to be good candidates for such applications [24]. To understand their usefulness we look into a few of the alloys with respect to their properties and processing techniques.

2.3. Boron Nitride

Boron nitride can be used to make crystals that are extremely hard, near diamonds, and the similarity of this compound to diamond extends to other applications. Like diamond, boron nitride acts as an electrical insulator but is an excellent conductor of heat. Boron nitride (BN) material is not found naturally. BN is mostly found in cubic (c-BN or β-BN) and hexagonal (h-BN) phases. The hBN is found to be a soft material that's insulating in nature with a band gap of 5 eV. In contrast c-BN shows properties similar to that of diamond and is known to be the second hardest material next to diamond. However, unlike diamond it is chemically inert to ferrous materials at high temperature. Furthermore for electronic applications it can be made with either n- or p-type conductivity [25, 26].

2.3.1. Cubic boron nitride

The allotrope of boron nitride very similar to diamond, is known as cubic boron nitride, c-BN, β-BN, or z-BN (after zinc blende crystalline structure, see Figure 2.2), is widely used as an abrasive for industrial tools[27]. Its usefulness is derived from the fact that boron nitride is insoluble in iron, nickel and related alloys at high temperatures. Similar to diamond, BN has good thermal conductivity primarily caused by phonons; unlike metals, where the mediators are electrons. When contacted with oxygen at high temperatures, BN forms a passivation layer of boron oxide.
Cubic BN is prepared in forms of powders from a submicron size up to small crystals with a size 0.8 mm by a high pressure–high temperature (HPHT) method [28, 29]. Such granular c-BN materials are industrially exploited in tooling industry with the aid of sintering. Cubic BN films have also been prepared by a variety of physical vapor deposition (PVD) techniques and plasma enhanced chemical vapor deposition (PECVD) methods [30-33]. Both direct current (dc) and radio frequency (rf) sputter magnetron depositions have been used for synthesis of c-BN films employing conductive or non-conductive targets (h-BN, boron, B₄C composite) and substrate bias[34, 35]. However the c-BN films prepared still suffer from low quality of crystallinity, presence of interfacial softer layers, low phase purity, high internal stress and poor...
adhesion to the substrates limiting the film thickness. Limitations in film thickness have been a serious obstacle in c-BN applications. The thickest c-BN films have been produced using dc plasma jet and electron cyclotron resonance ECR deposition using complex gas mixtures [36]. However these techniques involving complex precursor mixture chemistry can be expensive and inadaptable into a production flow. This major drawback prevents the use of these films in practice.

2.3.2. Hexagonal boron nitride

Hexagonal boron nitride, h-BN, α-BN (see ), or g-BN (graphitic BN), and sometimes called white graphite, is useful as both a very low temperature and high-temperature lubricant (up to 900 °C in oxidizing atmosphere) and in situations where the electrical conductivity or chemical reactivity of graphite would be problematic [37]. As the lubricity mechanism does not involve water molecules trapped between the layers, boron nitride lubricants can be used even in vacuum, e.g. for space applications. Due to higher electronegativity of the nitrogen atoms, the electrons that in graphite form a delocalized system, are concentrated around nitrogen atoms, sequestered outside the conductivity band, therefore not playing role in conductivity nor absorbing visible light.

h-BN can be included in ceramics, alloys, resins, plastics, rubbers and other materials, giving them self-lubricating properties. Such materials are suitable for construction of e.g. bearings. Plastics filled with BN have decreased thermal expansion, increased thermal conductivity, increased electrical insulation properties, and cause reduced wear to adjacent parts.

Hexagonal boron nitride is stable in temperatures up to 1000 °C in air, 1400 °C in vacuum, and 2800 °C in inert gas. It has one of the best thermal conductivities of all electric
insulators. It is fairly chemically inert and is not wetted by many melted materials (e.g. aluminium, copper, zinc, iron and steels, germanium, silicon, boron, cryolite, glass and halide salts) [38]. h-BN parts can be made by hot-pressing with subsequent machining; due to the mechanical hardness similar to graphite, the machining cost is low. The parts are made from boron nitride powders, using boron oxide as a sintering agent.

![h-BN, hexagonal](image)

**Figure 2.3:** 3-D structural reconstruction of hexagonal BN.

Due to its excellent dielectric and insulating properties, BN is used in electronics e.g. as a substrate for semiconductors, microwave-transparent windows, structural material for seals, electrodes and catalyst carriers in fuel cells and batteries. Fine-grained h-BN is used in some cosmetics, paints, dental cements, pencil leads, etc.

Hexagonal boron nitride is produced by the nitridation or ammonolysis of boron trioxide. Thin films of boron nitride can be obtained by chemical vapor deposition from boron trichloride.
and nitrogen precursors. Industrial production is based on two reactions: melted boric acid with ammonia, and boric acid or alkaline borates with urea, guanidine, melamin, or other suitable organic nitrogen compounds in nitrogen atmosphere. Combustion of boron powder in nitrogen plasma at 5500 °C is used for production of ultrafine boron nitride for lubricants and toners.

Addition of boron nitride to silicon nitride ceramics improves the thermal shock resistance of the resulting material[39]. For the same purpose, BN is added also to silicon nitride-alumina and titanium nitride-alumina ceramics. Other materials being reinforced with BN are e.g. alumina and zirconia, borosilicate glasses, glass ceramics, enamels, and composite ceramics with titanium boride-boron nitride and titanium boride-aluminium nitride-boron nitride and silicon carbide-boron nitride composition.

2.4. Silicon Carbide

The mature state of silicon micromachining in the semiconductor industry has enabled the implementation of electronic devices and micro-electro-mechanical (MEMS) structures with silicon as the primary building block. However, the properties of silicon which make it useful for MEMS and device applications are suitable only for operations at temperatures lower than 200 °C. Harsh environment applications demand good performance under high temperatures (>150 °C), corrosive environments and physically stressful environments. Hence silicon based devices become inadequate for harsh environments. Silicon Carbide is proposed as an excellent candidate for these applications due to its intrinsic properties, which provides significant advantages over silicon for such harsh environments. Applications in high temperature areas such as power electronics, peizoresistive sensors, gas sensors and flame detectors are increasingly using SiC as material.
2.4.1. Properties and advantages

Silicon carbide is a stable binary alloy formed by the combination of silicon and carbon. The crystalline structure of SiC consists of close packed stacking of double layers of Si and C atoms. The bonding between Si and C atoms is 88% covalent and 12% ionic with an atomic distance being around 1.89 Å. All polytypes have a hexagonal frame with a carbon atom situated above the center of a triangle of Si atoms and underneath a Si atom belonging to the next layer (Figure 2.4). The distance, a, between neighboring silicon or carbon atoms is approximately 3.08 Å for all polytypes [40]. Different stacking schemes have revealed multiple polytypes of SiC. Cubic form of SiC (β-SiC), with 3C-SiC being the most commonly found. Hexagonal and rhombohedral types are referred to as α-SiC with 6H-SiC the most common occurrence. Other hexagonal phases commonly found are 2H-SiC and 4H-SiC [41].

Figure 2.4: Tegragonal bonding structure of SiC. Each carbon atom is attached to 4 of nearest silicon atoms. Atomic distances \( a = 3.08 \) Å and Si –C = 1.89 Å respectively.
SiC has long been recognized as a semiconductor with outstanding physical and chemical characteristics, especially when compared to Si. In terms of electronic properties, SiC exhibits a wide range of larger bandgap values (2.3-3.4 eV) depending on the phase of the material, a higher breakdown field ($30 \times 10^5$ V/cm), higher thermal conductivity (3.2-4.9 W/cm K), and a high saturation velocity ($2 \times 10^7$ cm/s) than Si. Silicon Carbide is recognized for its excellent mechanical properties, particularly its hardness and wear resistance. In terms of hardness, SiC has a Knoop hardness of 2480 kg/mm$^2$, which compares favorably with values for other hard materials such as diamond (7000 kg/mm$^2$) and Al$_2$O$_3$ (2100 kg/mm$^2$), and greatly exceeds that of Si (850 kg/mm$^2$)[42]. SiC has a wear resistance value of 9.15, as compared with 10 for diamond and 9 for Al$_2$O$_3$. In addition, SiC has a high Young's modulus (700 GPa), which is about 3.5 times greater than the Young's modulus of Si (190 GPa). SiC is not etched by most acids. It can, however, be etched by alkaline hydroxide bases (i.e. KOH) but only at molten temperatures (>600 °C). SiC does not melt, but sublimes above 1800 °C (Si melts at 1410 °C). The surface of SiC can be passivated by the formation of a thermal SiO$_2$ layer, but the oxidation rate is very slow when compared with Si [4].

2.4.2. Synthesis and applications

Crystalline nature of the material plays a significant role in determining its electronic properties. While bulk 4H-SiC is the material of choice for power and high frequency devices, other types of materials can be useful for sensors development and especially low stress 3C-SiC on Si, bulk 6H-SiC, porous SiC and low temperature deposited SiC coatings.

There are several techniques that can be used to grow single crystal SiC. Several breakthroughs have been reported in the past decade that lead to the availability of n- and p-type
single crystal SiC wafers. However, conventional micromachining of these wafers is not yet matured hence making them unsuitable for MEMS applications. Mono-crystalline layers have been successfully grown on silicon substrates by using Metalorganic Chemical Vapor Deposition (MOCVD), gas source Molecular Beam Epitaxy (MBE), electron cyclotron resonance (ECR) plasma and liquid phase epitaxy [43, 44]. These substrates are more attractive for MEMS applications when combined with silicon substrates, due to the well developed and widely used silicon micromachining techniques. Fleischman et al. reported the growth of 3C-SiC polycrystalline films in a APCVD system at 1000ºC, using poly-silicon as seed layer [45]. Hot wall LPCVD at temperatures between 900-1050 ºC for poly-SiC films on 3 and 4 inch silicon wafers with controllable mechanical stress has been used by Yamaguchi et al. [46]. Reactive sputtering process at temperatures of 650-750 ºC was used by Onuma et al. to produce silicon carbide films rich in β-phase, which are suitable for high temperature thermistors and pressure sensors [47]. Epitaxial 3C-SiC films were obtained on (111) silicon substrates by Wahab et al. by reactive magnetron sputtering at 850 ºC [48]. However, IC compatible processing would require lower deposition temperatures. It is believed that the thermal mechanical and chemical inertness of SiC can improve device performance significantly. Amorphous SiC deposition has been demonstrated by low temperature deposition techniques. Plasma enhanced techniques have been used by several groups to obtain SiC films[49, 50]. Boily et al. demonstrated the use of laser ablation deposition (LAD) in which a high purity SiC target was ablated using KrF pulsed excimer laser to obtain a-SiC films[51]. Magnetron sputtering was applied to produce stoichiometric silicon carbide films on silicon substrates by Lei et al. Further analysis of these films showed the formation of columnar nanometer sized crystallites [52]. In recent years several research groups have successfully reported deposition of a-SiC films by reactive magnetron
sputtering. Extensive characterization and study of deposition parameters have been reported. It is believed that different stoichoimetric films can be produced by this method with varying properties that can be useful for various applications [53-55].

Amorphous silicon carbide (a-Si$_{1-x}$C$_x$) is an attractive material from a technological point of view. Its electronic and optical properties make it potentially useful as a solar selective coating. In addition, because of its high temperature resistance, wide band gap and high electron saturation velocity, a-Si$_{1-x}$C$_x$ alloy is a good candidate for stable high-T semiconductor and high power devices. One principal focus area for SiC MEMS has been SiC sensor systems for gas turbine engines [56]. To meet the efficiency, emissions, cost, and safety goals set by military and commercial customers, the next generation of gas turbine design requires instrumentation in or near the hot-gas flow path, which must operate above 350 °C. Sensors are needed for turbine development testing and in-flight service in order to measure combustor liner temperature, rotor and stator metal temperatures, internal cooling temperatures, steady-state and transient cooling flow and temperature, pressure and rate of change of pressure, hot gas path leakage, and coolant leakage. Conversion of electronic control and sensor systems from Si to SiC-based devices will not only increase efficiency and safety through enabling instrumentation but also reduce the overall weight of an aircraft by eliminating the packaging, wiring and connectors necessary to link sensor systems with control electronics [4]. This reduction would directly translate to increased range and lower fuel costs.

2.5. Silicon Carbonitride

Liu and Cohen made the theoretical prediction, that β-C$_3$N$_4$ which is isomorphic with β-Si$_3$N$_4$ can possess a bulk modulus which can surpass that of diamond.[57-59] This has inspired a
lot of research work in the development of $C_3N_4$ over the past two decades[54]. In addition to hardness the C-N material is expected to possess wide bandgap, high thermal conductivity, high strength, high decomposition temperature, and excellent resistance to corrosion and wear. More recently binary, ternary and quaternary carbonitride materials such as $CN_x$, BCN, SiCN, SiBCN and AlBCN have been investigated and found to be of significant interest to industry owing to their light weight and multi-functional properties[24].

2.5.1. Properties and synthesis

Gomez et al. suggested that if $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ have the same structure, it might be expected that both should be miscible giving rise to SiCN alloys[60]. Miyagawa et al. have demonstrated that nitrogen-ion implantation in silicon carbide produces a surface layer with an intermediate state $SiC_xN_y$ or into $Si_3N_4$ under appropriate conditions[61]. Further studies on such films have revealed them to be thermally stable to certain temperatures and at higher temperatures it was observed that, nitrogen present in interstitial states is lost[62]. Bendeddouche et al. stated that the properties of this new material could be an interesting combination of silicon carbide, a semiconductor, and silicon nitride, a dielectric[63]. In other words, it might be a hard material with a wide band gap having interesting optical and electronic properties.

Considerable efforts have been made to synthesize SiCN films by different techniques like electron cyclotron resonance (ECR) and plasma enhanced chemical vapor deposition (PECVD) [60, 64]. More recently Cheng et al studied the morphology and bonding structure of SiCN films deposited using microwave plasma CVD by varying film composition through the $N_2$ flow rate and temperature. They report that, higher substrate temperatures facilitate crystallization and larger crystalline size [65]. Other techniques used to synthesize CN alloys are
reactive sputtering and ion assisted dynamic mixing [66-68]. Lehmann et. al. deposited amorphous SiC$_x$N$_y$ films with various compositions by ion beam sputtering and observed the decrease in Youngs modulus with increase in carbon content [69]. The hardness and effective modulus of hydrogen-containing and hydrogen-free amorphous C$_{Si_x}N_y$ films, deposited by electron cyclotron resonance plasma chemical vapor deposition (ECR-CVD) and hydrogen free ion-beam sputtering deposition (IBSD), respectively, were studied through nano-indentation by Lo et al. [70]. Yamamoto et al. formed amorphous SiCN films on Si (100) substrate by nitrogen ion-assisted pulsed-laser ablation of an SiC target and the dependence of the formed chemical bonds in the films on nitrogen ion energy and substrate temperature were investigated by XPS [71]. In a more recent publication Bruns et al. report the deposition of thin SiCN films using rf sputtering combined with ion implantation [72]. They claim that it is an effective technique to produce nitrogen rich high purity SiCN films. However it was found that the region of attainable stoichiometries is narrowed by formation of Si-C-N phases and N$_2$, respectively.

According to Lutz et al, for the reproducible production of SiCN thin films with tailored stoichiometries and high-purity, r. f. (radio frequency) magnetron sputtering and ion implantation are very promising techniques [73]. Also magnetron sputtering is the most versatile technique when it comes to deposition of a wide range of materials with practically no restrictions on the type of substrate to be used. Wei at al., used dc magnetron sputtering with rf biasing to deposit SiCN films from silicon and graphite planar targets under a N$_2$- Ar ambient. It was found that the N$_2$ fraction in the gas mixture has a major influence on the deposition rate and composition of the films: a high N$_2$ fraction results in increased deposition rate and N/(C+Si) and C/(N+Si) ratios [74]. They found that the SiCN films deposited were amorphous with chemical analysis showing the existence of Si – N, C – N single, C = N double and C ≡ N triple bonds.
Almost no Si – C bonding was found in the films. Analysis of bonding structures in chemical vapor deposited SiCN films, performed by Bendeddouche et al. indicate the presence of Si – C bonds in addition to Si – N, C – C and C – N bonds[63]. This shows that there could be a difference in structure between films due to different deposition methods.

RF magnetron sputter deposition technique was applied by Sundaram et al. [28] where a powder pressed SiC target was used under N$_2$+Ar ambience, instead of the two target method used by Wei et al [75]. They studied the optical absorption characteristics of the SiCN films. It was found that the band gap of the films increased with increase in N$_2$/Ar ratios and the percentage of optical transmission also increased with the N$_2$/Ar ratio. Amorphous silicon carbonitride (a-SiCN) films synthesized by ion enhanced radio-frequency (rf) magnetron sputtering from a SiC target using a mixture of Ar and N$_2$ gases [76, 77]. The oxidation resistance of the films was investigated in an oxygen atmosphere over the temperature range of 0–1000 °C. X-ray photoelectron spectroscopy showed that the SiCN films exhibited a well-defined Si–C–N bonding structure. The composition, density, hardness, and stress were uniquely characterized with respect to the average energy per deposited atom. It was demonstrated that under optimum deposition conditions a-SiCN films can be prepared to exhibit high density (>2.6 g cm$^{-3}$), high hardness (>25 GPa), and enhanced oxidization resistance at temperatures up to 800 °C.

Wu et al. obtained SiCN films by rf sputtering with a highly pure polycrystalline silicon target and a gaseous ambient comprising of Ar, N$_2$, H$_2$ and CH$_4$ [78]. Their studies on the electrical conductivity of the films indicate a decrease in conductivity with increase in N$_2$ flow ratio. They also found their films to be thermally stable at high temperatures and attribute this to the coexistence of carbon and nitrogen in the films. Xie et al. studied varying substrate
temperature characteristics of SiCN films during deposition by rf sputtering from a SiC target in \( \text{N}_2 + \text{Ar} \) gas ambient [79]. It was observed that the growth rate of SiCN films increases with growth temperature. Analysis of the films suggested a variation in chemical bonding states of the SiCN films with deposition temperature. The carbon content in the SiCN film was observed to increase while that of nitride decreased with the increasing substrate temperature. Hence, they conclude that high substrate temperature is not favorable for nitrogen incorporation into SiCN films.

### 2.5.2. Applications

SiCN has a wide range of applications due to its properties. One of the earliest applications, proposed by Misaki at al. [80] used SiCN as protective films for magneto-optical media. SiCN is finding increasing application in the semiconductor device industry as a candidate for high voltage SiCN/Si hetero-junction diodes for high temperature applications [81]. Crystalline thin films of SiCN grown by PECVD show optical properties indicating the potential for blue and UV optoelectronic applications[82]. Another interesting and promising area is in the fabrication of microelectromechanical systems for harsh environments where SiCN could prove as a good candidate. A simple SiCN MEMS thermal actuator was demonstrated by Liew et al [83-86].

### 2.6. Silicon Boron Carbon Nitride

The quaternary compound of SiCBN has been realized primarily using polymer precursor derived chemistry. Riedel et al. first reported studies on silicoboron carbonitride ceramic stable to 2000°C. The ceramic was observed to convert to a polycrystalline composite of silicon nitride and carbide (with some non-crystalline boron nitride) at 1700 °C [87]. Studies on the structure
and electronic transport properties of Si-B-C-N ceramics were reported by Hermann et al. They report on Silicoboron-carbonitride ceramics as obtainable by boron doping precursor derived ceramic SiCN material [88]. The structural make up of the material was believed to be comprised of basic building blocks of Si tetrahedral with B, C and N at the corners. Furthermore they report that the boron doping leads to enhanced p-type conductivity. Ramakrishnan et al conclude that the high conductivity combined with excellent high temperature stability makes these classes of ceramics potential candidates for variety of high temperature electrical applications such as high temperature filaments and conducting coatings [89]. Several other groups have published results that helped establish that the material thus produced possessed better conductivity than the SiCN ceramic and also had outstanding thermal and chemical stability [90-92]. Cerver et al reported on the formation of SiBCN by high-dose N⁺⁺C⁺⁺BF₂⁺ ion implantation of Si (100) substrates at 600ºC [93]. They suggest that the sequential doping of these gases produces SiCBN mainly formed by a SiC network with a significant content of B and N. Not much work has been done on studying SiCBN films produced by sputtering. Sputtering provides the advantage of low temperature deposition as well as freedom to choose substrate. Furthermore since the method eliminates the need for hydrogen containing precursors, the resulting films are low in hydrogen content.

Vlcek et al were the first to report deposition of S-B-C-N films using magnetron sputtering[94]. A composite C-Si-B target was used in a nitrogen-argon mixed gas ambient to produce films of varying stoichiometry. They report that the films produced show high hardness up to 47 GPa and extremely high oxidation resistance in air at elevated temperatures up to 1350 ºC. Ab initio simulation of of nitrogen evolution in quenched SiBCN amorphous materials was performed by Houska et al [95]. It was found that higher material density and shorter cooling
times lead to reduced N₂ formation and thus higher nitrogen incorporation into the structure. The same group has reported on the effect of negative substrate bias voltage on structure and properties of SiBCN films prepared by reactive magnetron sputtering was reported [96]. Electrical conductivity of the SiBCN films with high carbon content was successfully controlled by gas mixture composition and the bias voltage values. More recently Houska and co workers have reported on the bonding statistics and electronic structure of SiBCN material based on ab initio molecular dynamic simulations and experimental verification[97]. Effect of Si/C ratio on bonding statistics, photoconductivity and band gap were studied. The authors report that both higher Si/C ratio and addition of hydrogen increases band gap of the material. However there are several unanswered questions when we consider the high temperature application of this material. Hence it is proposed to do a detailed study of the SiCBN films produced through reactive sputtering and ascertain their applicability to harsh environment sensors. Therefore, the focus of this research is to make a detailed study of the characteristics of SiCBN thin films deposited by reactive rf sputtering and provide a broader understanding about the properties of these films. Surface analysis of the films was carried out using, optical profilometry and X-ray Photoelectron Spectroscopy (XPS). Electrical and optical properties were studied to demonstrate the potential for applications as harsh environment sensors.
CHAPTER 3: METHODOLOGY

In this chapter the experimental procedures and techniques used to fabricate and characterize the SiCBN based thin films and devices are reported. This chapter also outlines various materials and electrical characterization techniques used to study the thin film samples. The chapter is broadly divided into four main sub-sections; one explaining the actual film processing method and then moving on to the various characterization methods and the specific analytical techniques that were applied in each case.

3.1. Thin film deposition

Sputter deposition technique was used to obtain thin film samples. Sputter deposition is a physical vapor deposition PVD method of depositing thin films by eroding, material from a source, which then deposits onto a substrate. One advantage of sputtering as a deposition technique is that the deposited films have the same composition as the source material. The similarity of the film and target stoichiometry is due to the fact that the sputter yield depends on the atomic weight of the atoms in the target. Magnetron sputtering was used to utilize strong electric and magnetic fields to trap electrons close to the surface of the target. Insulating targets can cause charge build up hence varied biasing of the anode and cathode was obtained with a radio frequency (rf) power source. Sputter deposition sources (also called sputter “guns”) creates low pressure plasma by the excitation of an inert gas (typically argon) contained at 1 to 30 millitorr in a vacuum chamber. This process extracts energetic ions which accelerate toward the cathode target, striking it with kinetic energy up to several hundred electron volts. Energy transfer then ejects material from the target with approximately 90% leaving as neutral atoms and 10% as ions. Gas phase collisions between target atoms and argon atoms scatter the ejected
material into a distributed cloud. As the cloud migrates towards the substrate, the random approach angles result in deposition of a uniform film, even on surfaces that have micron-sized vertical structures.

![Figure 3.1: Sputtering process cartoon representation](image)

Thin films of SiCBN were deposited by reactive RF magnetron sputtering in a UHV system. Two inch, powder pressed, SiC and BN targets with a purity of 99.5% were used. The system base pressure was approximately $1 \times 10^{-8}$ Torr and the purity of the process gas was maintained by a hot reactive metal getter. Process gas contamination in the deposition chamber at the typical deposition pressure of 4 mTorr was confirmed to be less than 10 ppm (the instrumental sensitivity limit) by closed ion source quadrupole mass spectrometry. Reactive sputtering was used where the deposited film is formed by chemical reaction between the target material and a gas which is introduced into the vacuum chamber. Oxide and nitride films are fabricated using this technique. The composition of the film is controlled by changing relative flow of inert and reactive gases. In this case nitrogen was used as the reactive gas and, the $N_2$ to Ar ratio was varied from 0 to 1, in steps of 0.25 by changing the individual gas flow rate, while the total gas flow was kept constant at 20 sccm and a constant deposition pressure of 4 mTorr.

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3.2. Material Characterization

Material characterization is an essential part of thin film analysis. Several characterization techniques are involved that can give us information ranging from surface morphology and roughness of the sample to chemical nature and bonding structure of the material. Appropriate tools used in correlation with observed properties can help correlate properties in turn explaining some uniquely observed phenomena in the material.

High temperature oxidation kinetics of the SiCBN films was investigated. The films were oxidized in a programmable box furnace from room temperature to 900 °C. Oxygen as well as air was used to study effect of oxidation ambient on film characteristics. Analysis of the films before and after anneal can reveal more information about the high temperature behavior of the SiCBN material.

3.2.1. Surface Morphology

Surface roughness of the thin films is an important factor in determining their reliability. Degradation in film properties occurs when the thickness is reduced to the point that the surface roughness of the film becomes comparable the film thickness. When the root mean square (RMS) roughness of the film exceeds 20% relative to the film thickness then thin spots in the film can start to dominate the thin film properties. The surface profile of the deposited films was measured using a VEECO NT3300 Optical profilometer. The NT3300 is a non-contact surface profiler which was used to measure the thickness and surface roughness of the sputtered dielectric and metal films. This profilometer uses two different technologies to measure a wide variety of surface heights. Phase shifting interferometry (PSI) is reliable for smooth surfaces and small steps in which the height change between two adjacent points is not more than 160 nm.
The vertical resolution for PSI mode is 3Å for a single measurement and 1Å for multiple averaged measurements. Vertical scanning interferometry (VSI) allows measurement of rough surface profiles and steps up to few millimeters high. The vertical resolution is 3nm for a single measurement and <1nm for averaged multiple measurements.

The average roughness and peak to valley roughness was measured for oxygen annealed SiCBN thin films. Average roughness ($R_a$) represents the two dimensional roughness averages, the arithmetic mean of the absolute values of the surface departures from the mean plane.

$$R_a = \frac{1}{MN} \sum_{j=1}^{M} \sum_{i=1}^{N} |Z_{ji}|$$

where $M$ and $N$ are the number of data points in the X and Y direction, respectively of the array, and $Z$ is the surface height relative to the surface reference mean plane.

### 3.2.2. X-ray Photoelectron Spectroscopy

In X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA). X-rays excite photoelectrons, and the emitted electron signal is plotted as a spectrum of binding energies. Differing chemical states resulting from compound formation are reflected in the photoelectron peak positions and shapes. Spectral information is collected from a depth of 2-20 atomic layers, depending on the material studied (Schroeder, 1998)[98]. The energy of the photoelectrons leaving the sample is determined using a chemical analyzer (Concentric hemispherical analyzer-CHA) and this gives a spectrum with a series of photoelectron peaks. The binding energy of the peaks is characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of the materials surface. The shape of each peak and the binding energy can be slightly altered by the
chemical state of the emitting atom. Hence XPS can provide chemical bonding information as well.

Figure 3.2: Cartoon illustrating the basic components of an XPS system.

XPS was performed using a PHI 5400 ESCA system. The base pressure during analysis was $10^{-9}$ Torr and Mg K-α X-ray source ($h\nu = 1253.6$ eV) at a power of 350 watts was used for the analysis, samples were transferred in a sealed petri-dish to the XPS analysis chamber. Although care was taken to minimize the exposure time in air, the atmospheric exposure could not be completely avoided.

Both the survey and the high-resolution narrow spectra were recorded with electron pass energy of 44.75 eV and 35.75 eV, respectively, to achieve the maximum spectral resolution. Any charging shift produced by the samples was carefully removed by using a B.E. scale referred to C(1s) B.E. of the hydrocarbon part of the adventitious carbon line at 284.6 eV [99]. Non-linear least square curve fitting was performed using a Gaussian/Lorentzian peak shape after the background removal.
3.2.3. Secondary Ion Mass Spectroscopy

Secondary ion mass spectroscopy (SIMS) is a technique for the characterization of solid surfaces and thin films. It uses the process of ion formation by bombarding the surface to be tested with a highly collimated beam of primary ions. The surface then emits material through a sputtering process - only a fraction of these emitted particles is ionized. These secondary ions are measured with a mass spectrometer to determine the quantitative elemental, isotopic or molecular composition of the surface.

The SIMS technique requires high vacuum to ensure undisturbed movement of secondary ions to the detector. The primary ion beam used (often Cs+, O2-, Ga+ or Bi clusters like Bi32-) determines the detection limits of the instrument. Two surface analysis modes are static and dynamic. Static SIMS is the process involved in surface atomic monolayer analysis, usually with a pulsed ion beam and a time of flight mass spectrometer, while Dynamic SIMS is the process involved in bulk analysis, closely related to the sputtering process, using a DC primary ion beam and a magnetic sector or quadrupole mass spectrometer.

SIMS analysis was performed using a PHI Adept 1010 Dynamic quadrupole SIMS system capable of depth resolution up to 1nm. A cesium (Cs+) ion source operated at 3 kV and 25nA was used so that oxygen detection can be possible. For depth profile the depth scale was quantified by measuring the analysis craters with a stylus profilometer.

3.2.4. X Ray Diffraction Analysis

X-ray diffraction is a non-destructive analytical technique which reveals information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. The technique is based on observing the scattered intensity of an x-ray beam
hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. Thin film diffraction and grazing incidence x-ray diffraction may be used to characterize the crystallographic structure and preferred orientation of substrate-anchored thin films.

XRD measurements were carried out using a Rigaku D-Max powder diffractometer with a thin film attachment, and subsequent analysis was performed using Jade version 7.5. Since the microstructure of the thin film was of interest, the penetration depth of the incident x-ray beam was limited, thereby preventing substrate artifact from dominating the signal. A depth profile was performed by fixing the sample tilt ($\omega$) relative to the incident beam, and scanning the detector ($2\Theta$). The desired sample tilts were determined by plotting the attenuation length as a function of sample tilt.

3.3. Electrical Measurements

Sheet resistance measurement of the film was used to characterize the high temperature electronic properties of the film. Platinum wires were attached to the sample and taken out of the furnace with thermal insulation to ensure high temperature measurement capability. A high temperature conducting epoxy (Pyroduct®) was used to ensure wire contact with sample. A programmable box furnace was used to produce the high temperature testing environment (Figure 3.3). Process gases ($O_2$ or Ar) were flown through continuously to ensure purged gas ambient. A four probe test setup was used to measure the current by sourcing voltage. Current was sourced through a Keithley source meter (Model 2400) and a nano-voltmeter (Model 2181A) was used to measure the voltage between two closely placed probes. Generation of thermal e.m.f. and additional thermal noise in the platinum wires due to the significant difference between temperature at the measured point and that at the measuring instrument cannot be
avoided. However measurements were carried out by switching polarity of the probes. Hence measured values can be used to generate an average that in general would cancel out the common factor which is the thermal e.m.f. and noise.

![Diagram of high temperature electrical measurement setup](image)

Figure 3.3 Block schematic describing the high temperature electrical measurement setup

It is important to note that this measurement does not project an accurate value of the materials sheet resistance. However it is assumed that these values do exhibit a trend which is extendable to the predicted trend in actual values (which would require sophisticated instrumentation to accomplish).

### 3.4 Optical Characterization

Optical properties of thin films can be very informative about the application prospects as electronic devices. Wavelengths from ultra violet (UV) through the visible and infrared to the millimeter range have enormous power to examine all aspects of solids, especially...
semiconductors such as; crystal lattice, the electronic band structure and bang gap. Characteristics such as optical transmission, absorption, reflectance and band gap studies are considered. Samples for optical transmission were deposited on quartz substrates.

3.4.1. Photoluminescence

Photoluminescence is a process in which a chemical compound absorbs photons (electromagnetic radiation), thus jumping to a higher electronic energy state, and then radiates photons back out, returning to a lower energy state. Here, photoluminescence is excited by illumination of the device with light which has photon energy above the bandgap of the material. Photoluminescence then occurs for wavelengths near the bandgap wavelength. The spectrum of photoluminescence (PL spectrum) and the dependence of its intensity on the irradiation intensity and device temperature can deliver important information for device characterization. In particular, PL spectra and their intensity dependencies can allow the determination of the bandgap energy. It can also be used to determine the composition of ternary or quarternary layers and impurity levels[100].

Photoluminescence measurements were performed using a PTI spectrofluorometer with a xenon arc lamp as UV excitation source. Excitation wavelength for the SiCBN thin film samples was chosen as 340nm. It is notable that the measurements use a lamp source instead of a laser which is more prominently used to study photoluminescence properties. The xenon lamp produces luminescence results of a lower resolution, however this is deemed to be sufficient to give us a good idea about the optical properties of the SiCBN films. The general hypothesis obtained about the bandgap emissions of the material was useful in determining and identifying the optical device application discussed later.
3.4.2. UV-Visible Spectroscopy

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (Io). The ratio I / Io is called the transmittance, (see Figure 3.4) and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

\[ A = - \log(\%T) \]

The basic parts of a spectrophotometer are a light source (often an incandescent bulb for the visible wavelengths, or a deuterium arc lamp in the ultraviolet), a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collects light of different wavelengths on different pixels.

![Figure 3.4: Schematic of Transmission measurement through UV-VIS spectroscopy.](image-url)
A Cary 5E high resolution spectrophotometer was used to study the optical characteristics of the thin film samples. This is a double beam instrument controlled by a microprocessor and has a measurement range of 3150 - 185 nm. The ratio of transmitted light to that of incident light ($%T$) and absorption data were collected and base line correction (obtained using blank substrate) was applied prior to collection of spectral data.
CHAPTER 4: RESULTS AND DISCUSSIONS

4.1. Characteristics of sputtered SiCBN thin films

The quaternary compound of SiCBN has been realized primarily using polymer precursor derived chemistry. Ramakrishnan et al reported on Silicoboron-carbonitride ceramics as obtainable by boron doping of precursor derived ceramic SiCN material[89]. Room temperature dc conductivity in the range of $10^{-10} \ \Omega^{-1} \ \text{cm}^{-1}$ has been reported earlier for SiCN ceramics. The incorporation of boron into the structure leads to p-type conductivity, dramatically increasing room temperature conductivity to $10^{-1} \ \Omega^{-1} \ \text{cm}^{-1}$. Hence the material thus produced possessed better conductivity than the SiCN ceramic and also had outstanding thermal and chemical stability. Cerver et al reported on the formation of SiBCN by high-dose $N^+ + C^+ + BF_2^+$ ion implantation of Si (100) substrates at 600 °C [93]. They suggest that the sequential doping of these gases produces SiCBN mainly formed by a SiC network with a significant content of B and N. Not much work has been done on studying SiCBN films produced by sputtering. The work reported by Vlcek et. al, recently, focused on deposition of Si-B-C-N thin films through dc magnetron sputtering from a single C-Si-B target under varying nitrogen gas mixtures [94]. They were able to produce SiBCN films with excellent hardness (up to 47 GPa) and oxidation resistance in air up to 1350 °C. Sputtering technique provides certain advantages over other techniques such as freedom to choose substrate material, uniform deposition over relatively larger area and furthermore it is possible to control the deposition parameters to prepare SiCBN films of various compositions. A more detailed analysis of the complex bonding structure in the films obtained by sputtering is thus necessary to understand and improve the technique further. In this section we study the deposition characteristics of SiCBN thin films deposited by reactive
radio frequency (RF) magnetron sputtering. The films were deposited by co-sputtering from a silicon carbide (SiC) target and a boron nitride (BN) target under varying nitrogen ambient. The induced chemical modifications of the films were studied as a function of various nitrogen compositions.

Initial deposition studies were focused on determining the film quality and composition based on the rf power applied to the SiC and BN targets. Table 4.1 shows the sample deposition matrix with varying power and gas flow ratios with sample labels.

Table 4.1: Sputtering parameter matrix showing sample labeling and optimum power ratio after analysis of resultant films through XPS surface scans.

<table>
<thead>
<tr>
<th>N₂/Ar Gas Flow Ratio</th>
<th>RF Power Ratio (SiC:BN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200/200</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0.25</td>
<td>6</td>
</tr>
<tr>
<td>0.5</td>
<td>11</td>
</tr>
<tr>
<td>0.75</td>
<td>16</td>
</tr>
<tr>
<td>1</td>
<td>21</td>
</tr>
</tbody>
</table>

Analysis of chemical composition was needed to determine the most optimum power level to obtain boron rich films. Rutherford backscattering (RBS) analysis was attempted for this purpose. However the detection of lighter elements such as boron becomes difficult, hence this method was not very helpful in the analysis. As an alternative, XPS was tried and resulted in
decent detection of lighter elements. Hence analysis of sputtering power was based on atomic concentration values obtained from XPS. Surface scans were analyzed and relative atomic concentrations for the different elements were calculated. The results for N$_2$/Ar ratios of 0, 0.5 and 1.0 are shown for SiC/BN power of (a) 200/200, (b) 100/200 and (c) 200/100 in Figure 4.1.

Figure 4.1: Atomic Concentration versus power ratio at different N$_2$/Ar deposition pressures.

(a) Boron, (b) Carbon, (c) Nitrogen and (d) Silicon

The high carbon concentrations in all the films show extensive carbon bonding in the films. Nitrogen content in the film is high up to intermediate N$_2$/Ar gas flow ratios and then seems to decrease at high flow rates. Boron concentration in film (Figure 4.1 (a)) is dependent on
BN target power as well as gas flow rates. Highest boron concentrations were observed in films produced at 200W power and lower N\textsubscript{2} flow rates. However, higher SiC power does seem to slightly reduce boron content. This is most likely due to the increased sputtering and subsequent incorporation of Si and C atoms in the film. Hence based on the results especially with boron the power ratio was fixed as 0.5 (SiC – 100W over BN – 200W) for most optimal boron incorporation into film. This is further corroborated through surface chemical analysis described in more detail later in this chapter.

4.1.1. Surface Morphology

Figure 4.2 shows a plot of the average roughness of the sputtered samples at different N\textsubscript{2}/Ar gas ratios and for different SiC/BN power levels. The overall roughness for all the samples is less than 10nm which falls within the acceptable range of roughness for fabrication of devices.

The varying nitrogen concentration produces small changes in the roughness of the sputtered samples. It can be observed that the samples deposited at lower SiC power of 50W and 100W produce much higher roughness which increases with N\textsubscript{2}/Ar ratio. The same cannot be said for BN power levels since the change of BN power between 200W, 150W and 100W does not produce any change in the average roughness. Hence it can be inferred that the roughness of the samples is influenced by the applied SiC power and the N\textsubscript{2}/Ar ratio.

The average roughness values for all the samples produced by sputtering were less than 9 nm. Furthermore it can be noted that samples generated at no N\textsubscript{2} flow rates shows minimum roughness irrespective of the rf power applied to the individual targets. Excepting the case of 0.5 power ratio this holds good for all other power ratios. Interestingly this happens to be the most
optimum power settings to produce boron rich films. Hence it is important to consider the compositional changes to understand the effect of surface morphology in these films.

![Average Roughness plot for different N₂/Ar ratios and varying power levels. The power level is represented as SiC/BN power in Watts.](image)

Figure 4.2: Average Roughness plot for different N₂/Ar ratios and varying power levels. The power level is represented as SiC/BN power in Watts.

### 4.1.2. Chemical composition

XPS was used to analyze the chemical composition of the sputtered films. Surface scans were analyzed and it was seen that boron peaks were very small. Hence high resolution scan was used for Boron to determine the trends in boron composition with respect to sputtering parameters. The results for different N₂/Ar ratios of 0, 0.5 and 1.0 are shown in Figure 4.3. It can be observed that the boron peak diminishes progressively as the nitrogen gas flow rate is...
increased during sputtering. This could imply that the amount of boron incorporated into the film during sputtering decreases significantly with increased N₂ flow. This could be possible due to a decrease in sputtering yield of BN target at higher N₂ flow rates. Additional nitrogen present in the ambient could replenish nitrogen at surface of target. Furthermore, the chemical composition of the films formed at higher N₂ flow rates could be different.

Figure 4.3: XPS high resolution scans for Boron peak at different N₂/Ar gas flow rates.

High resolution scans were obtained to analyze the chemical nature of the films obtained at as a function of N₂/Ar flow ratios. Figure 4.3 shows the deconvolved high resolution spectral data for carbon (C 1s). The broad envelope of the peaks clearly indicates the presence of different C 1s states. The peak at 284.6 eV is attributed to carbon 1s binding energy for
adventitious carbon [77]. The peak at lower binding energy of 283.5 eV is due to Si-C covalent bonding [101]. The peaks located at 285.6-286.3 eV are attributed to the presence of C-N bonds.
The peaks located at 287.5 eV-289.4 eV are primarily due to the presence of C-O contamination bonds [103]. The intensity of C-N bonding is prominent at low N\textsubscript{2}/Ar flow rates and decreases with increasing N\textsubscript{2} in the sputtering ambient. The SiC bonding is present in all cases and does not show any decrease in intensity with increase in N\textsubscript{2} flow ratios. This could imply that the increase in N\textsubscript{2} flow rates primarily affects the C-N bonding which could possibly be part of the SiCBN structure. The SiCBN structure can be envisioned as Si tetrahedral with B, C and N at the corners [89]. Any formation of Si\textsubscript{3}N\textsubscript{4} would not be evident from the C 1s results and hence N 1s XPS scans were analyzed.

The N 1s spectra for films deposited at various N\textsubscript{2}/Ar ratios are shown in Figure 4.5. The deconvolution of N 1s peak at low N\textsubscript{2} flow (Fig. 4.5 (a)) shows a single distinct peak that characterizes the bulk of the nitrogen in the film. This peak at 398.2 eV is primarily attributed to the presence of B-N bonding. The other small peak at 400.3 eV could be due to N-O contamination bonds. In comparison, deconvolution of the N 1s peaks for higher N\textsubscript{2} flow ratios (Fig. 4.5 (b) and (c)), reveals a different compositional nature of the films formed. The larger peak at 398.8 eV is due to C-N bonding [104]. The peak at 397.2 eV is attributed to Si-N bonds in the films [105]. The lack of a distinct BN peak and the increase in intensity of the Si-N peak at higher N\textsubscript{2} flow rates show that higher concentration of N\textsubscript{2} in sputtering ambient is unfavorable for boron incorporation into the films.

Deconvolution of the high resolution scan for the silicon (Si 2p) is shown in Figure 4.6. The broad spectra obtained for film deposited at low N\textsubscript{2} flow (Figure 4.6 (a)) shows the presence of the oxides of silicon SiO\textsubscript{2} and SiO at 103.6 eV and 102.7 eV respectively [106, 107]. The peak at 101.5 eV can be attributed to Si-C bonding [108]. The larger peak located at 100.9 eV is found to be due to SiCBN bonding [101]. The presence of such a large peak for SiCBN clearly
indicates that the sputtering technique is effective in producing thin films with quaternary SiCBN bonding structure. Figure 4.6 (b) and (c) show the deconvolved spectra at higher nitrogen flow ratios and the large distinct peak observed here at 101.5-101.9 eV is attributed to Si$_3$N$_4$. The smaller peak at 100.4 eV is due to the presence of SiCBN bonding. It can be observed that the SiCBN peaks are significantly lower at larger N$_2$ flow rates. This strengthens the earlier assumption that the higher N$_2$ flow ratio during sputtering is unfavorable for boron incorporation into the films.

The de-convolved peak for Boron (Figure 4.7) shows multiple peaks combining to form the observed intensity. The peak at 188.3 eV can be due to a small amount of B$_4$Si and the peak at 188.8 eV can be attributed to SiCB bonding structure [109]. The peak at 191.2 eV is a clear indication of the presence of BN in the film [110]. The major portion of the deconvoluted area which is at a peak of 189.92 eV can be due to the formation of some intermediate chemical state between BN and SiC/B. Hence there is a clear possibility that this is due to the quaternary SiCBN in the film. This peak is observed to decrease in intensity as the N$_2$ flow rate is increased (Figure 4.7 (b)). This observation confirms the earlier hypothesis and can be used to summarize that the incorporation of Boron to form SiBCN thin films by sputtering is highly dependent on the reactive ambient created by the N$_2$/Ar flow ratio during sputtering. Furthermore, higher boron concentration leading to SiBCN stoichiometry is favorably obtained at lower N$_2$ flow during deposition.
Figure 4.5: XPS N 1s spectra for sputtered SiCBN thin films as a function of N$_2$/Ar gas flow ratio: (a) 0, (b) 0.5 and (c) 1.0. Possible peak identification: (1) BN; (2) C-N; (3) Si-N; (4) N-O.

Dots represent experimental data and solid lines represent curve fitting lines.
Figure 4.6: XPS Si 2p spectra for reactively sputtered SiCBN films as a function of N₂/Ar gas flow ratio: (a) 0, (b) 0.5 and (c) 1.0. Possible peak identification: (1) SiCBN; (2) Si-N; (3) SiO; (4) SiO₂. Dots represent experimental data and solid lines represent curve fitting lines.
Figure 4.7: XPS B 1s spectra for sputtered Si-C-B-N films as a function of N₂/Ar gas flow ratio:

(a) 0, (b) 0.5. Possible peak identification: (1) SiCBN; (2) SiC-B; (3) B₄Si; (4) BN. Dots represent experimental data and solid lines represent curve fitting lines.

Figure 4.8 shows a plot of the average roughness of the sputtered samples at different N₂/Ar gas ratios. The roughness of the films increases with N₂ flow ratio during sputtering clearly indicating that the N₂ concentration in the ambient also affects the surface morphology of the deposited film. Surface morphology of the films also shows that the films deposited at lower N₂ rates have fewer voids than the ones deposited at higher N₂ rates. Since the films are formed by a reactive sputter process higher concentration of N₂ in the sputtering ambient could cause
additional ion bombardment of the films surface during deposition and lead to increased surface roughness.

![Graph of Avg. Roughness vs. N2/Ar ratio](image)

**Figure 4.8:** Variation of average surface roughness as a function of N2/Ar flow ratios for the sputter deposited SiCBN films.

### 4.2. High temperature oxidation studies

Initial analysis of the sputtered films has revealed that nitrogen flow rate change in the sputtering chamber also affects the film surface characteristics. Roughness of the films increases with higher N2 flow rates and could be due to increased ion activity in the chamber at these flow rates. Characterization of the sputtered films under high temperature conditions is also essential to understand potential for applications under such conditions. We now consider annealing the thin film samples at various incremental temperatures under oxygen ambient to accelerate the
degradation (oxidation) of the film. Table 2.1 shows the samples studied and temperatures as well as labeling convention used.

Table 2.1: Samples studied and temperatures as well as labeling convention used.

Table 4.2: Sample labeling and temperature annealing matrix.

<table>
<thead>
<tr>
<th>N₂/Ar Gas Flow Ratio</th>
<th>Annealing Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>room</td>
</tr>
<tr>
<td>0</td>
<td>3.00</td>
</tr>
<tr>
<td>0.25</td>
<td>8.00</td>
</tr>
<tr>
<td>0.5</td>
<td>13.00</td>
</tr>
<tr>
<td>0.75</td>
<td>18.00</td>
</tr>
<tr>
<td>1</td>
<td>23.00</td>
</tr>
</tbody>
</table>

4.2.1. Chemical analysis through XPS

Surface atomic composition was obtained from XPS scans and the normalized atomic concentrations of the individual elements detected are shown in Figure 4.9 and Figure 4.10. It was observed that the boron content in the films decreases as the nitrogen gas flow rate is increased during sputtering. Lower sputtering yields of BN target at higher N₂ flow rates as well as, variations in the chemical composition of the films formed at higher N₂ flow rates could cause this effect. Figure 4.9 shows the change in atomic concentrations of C, N and O in the films with increasing annealing temperatures. It can be observed that the carbon concentration decreases steadily with increasing temperatures with almost a linear trend. The nitrogen concentration also follows a similar trend but at a more rapid rate and almost no nitrogen was -
Figure 4.9: Surface atomic concentration calculated from XPS peaks of (a) C, (b) N and (c) O for various N<sub>2</sub>/Ar deposition ratios and annealing temperatures.
detected in the films beyond 700°C anneal. The presence of oxygen in the as deposited films is primarily due to surface oxide formation and increase in oxygen concentration after annealing can be directly attributed to the increased oxygen interaction at these temperatures. Figure 4.10 shows the atomic concentration of B and Si calculated from XPS peak heights. The boron concentration does not change significantly whereas the percentage silicon concentration shows slight increase with temperature and could be a direct consequence of the loss of nitrogen and carbon in the films.

![Graph](image)

**Figure 4.10:** Surface atomic concentration of (a) Boron and (b) Silicon calculated from XPS peaks as a function of anneal temperatures and varying reactive gas ambient.
C 1s spectra - High resolution scans were obtained to analyze the chemical nature of the films as a function of annealing temperature. Figure 4.11 shows the deconvolved high resolution carbon (C 1s) spectral data for the films deposited at 0 N\textsubscript{2} flow. The broad envelope of the peaks clearly indicates the presence of different C 1s states. The peak at 284.6 eV is attributed to C 1s binding energy for adventitious carbon [99]. The peak at lower binding energy of 282.9 eV and 283.5-283.8 eV are due to Si-C covalent bonding [101, 111, 112]. The peaks located at 285.6-286.3 eV are attributed to the presence of C-N bonds [102]. The peaks located at 287.5eV-289.4 eV are primarily due to the presence of C-O contamination bonds [103]. The C-N peaks noticeably decrease in intensity as the annealing temperature increases. This could be due to the loss of carbon in the films as the C-N bonds are broken, nitrogen is free to escape as gas and the carbon could combine with oxygen to form CO or CO\textsubscript{2} and escape as gas during annealing [77].

A more quantitative analysis of the C-N and Si-C bonding in the films is presented in the normalized percentage plot in Figure 4.12. The intensity of C-N bonding is prominent in the as deposited samples at all three flow rates and decreases with increasing annealing temperature. The Si-C bonding is present in all cases and does not show any decrease in intensity with anneal temperature. This could imply that the carbon loss in the film is primarily due to the breaking of C-N bond which could possibly be part of the Si-B-C-N network. Structure of the SiCBN material is presumed to be in the form of a Si tetrahedral with B, C and N attached to the corners [89]. Any formation of oxy-nitrides (such as Si-O-N) would not be evident from the C1s results and hence N 1s XPS scans were analyzed.
Figure 4.11: XPS C 1s spectra for Si-C-B-N films deposited at 0 N₂/Ar at different anneal
temperatures: (a) un-annealed, (b) 500°C and (c) 900°C. Possible peak identification: (1) CH; (2)
Si-C; (3) C-N; (4) C-O. Dots represent experimental data and solid lines represent curve fitting
lines
Figure 4.12: Normalized (a) C-N and (b) Si-C bonding percentages with respect to Carbon in the films deposited at 0, 0.25 and 1.0 N$_2$/Ar as a function of anneal temperature.

N 1s spectra – Figure 4.13 shows the deconvolved nitrogen spectra for film deposited at 0 N$_2$/Ar ratio as deposited and after anneal at 500 °C. The N 1s peak for un-annealed sample (Figure 4.13 (a)) shows a single distinct peak that characterizes the bulk of the nitrogen in the film. This peak at 398.2 eV is primarily attributed to the presence of B-N bonding [110]. The smaller peak at 400.3 eV could be due to N-O contamination bonds. Deconvolution of the N 1s
peak after 500 °C anneal (Figure 4.13 (b)), reveals the change in film composition due to oxygen interaction at higher temperatures. Other than the original peaks there is now a significantly large peak at 397.7 eV, this is due to formation of oxy-nitride (Si-O-N) [113]. The lower intensity of the B-N peak shows the loss of nitrogen in the film and increase in oxy-nitride component most likely shows the favorable formation of surface oxides.

Figure 4.13: Deconvolution of N 1s high resolution scans for film deposited at 0 N₂/Ar at (a) unannealed and (b) 500°C. Possible peak identification: (1) BN; (2) Si-N; (3) N-O. Dots represent experimental data and solid lines represent curve fitting lines.
B 1s spectra - The de-convolved peaks for Boron show multiple peaks combining to form the observed intensity. For the un-annealed sample (Figure 4.14), the peak at 188.3 eV is due to a small amount of B₄Si and the peak at 188.8 eV can be attributed to SiC/B bonding [109]. The peak at 191.2 eV is a clear indication of B-N content in the film [101]. The major portion of the deconvoluted area which is at a peak of 189.92 eV can be due to the formation of Si-C/B-N bonding network. Figure 4.14(b) and (c) shows the deconvolved boron peaks for the sample annealed in oxygen ambient at 500°C and 900°C respectively. The new peak developed at 189.5 eV is attributed to the presence of BNₓO₁₋ₓ and the peak at 193.3-193.6 eV is due to B₂O₃ [101].

The boron peaks clearly show the transition of the B-N in the film to B-N-O and finally at 900°C with almost no nitrogen content in the film, the boron present gets completely oxidized to B₂O₃. Figure 4.15 presents a quantitative analysis of the chemical species in the boron peaks at different temperatures and for films deposited at 0, 0.25 and 1.0 N₂/Ar gas flow. Si-C/B-N bonding intensity decreases with increasing temperatures and almost no SiC/BN is observed in the films annealed at 900°C. Similarly the un-annealed film shows no B-O content which increases in intensity with annealing temperature and at temperatures beyond 700°C the boron interaction with oxygen is maximum and the film predominantly consists of B₂O₃.
Figure 4.14: XPS B 1s spectra for Si-C-B-N films deposited at 0 N₂/Ar gas flow at different annealing temperatures: (a) un-annealed, (b) 500 °C and (c) 900 °C. Possible peak identification: (1) BN; (2) SiC/B; (3) B₄Si; (4) SiC/BN; (5) B₂O₃; (6) B-N-O. Dots represent experimental data and solid lines represent curve fitting lines.
Figure 4.15: Normalized (a) SiCBN and (b) B-O bonding percentage with respect to Boron in the films deposited at 0, 0.25 and 1.0 N$_2$/Ar as a function of annealing temperature.

Si 2p3 spectra - Deconvolution of the high resolution scans for silicon (Si 2p3) is shown in Figure 4.16. The broad spectra obtained for film as deposited (Figure 4.16 (a)) shows the presence of the small quantities of surface oxides of silicon SiO$_2$ and SiO at 103.6eV and 102.7eV respectively [106, 107]. This could be due to some minimal exposure of film to atmosphere during transfer into the XPS chamber. The large distinct peak observed at 101.5-101.9 eV is attributed to Si$_3$N$_4$ [114, 115]. The larger peak located at 100.9 eV is found to be due to SiC/BN+SiC bonding [103]. Figure 4.16 (b) and (c) show the deconvolved spectra for samples annealed at 500 °C and 900 °C respectively. The leftward shift in the silicon peak
clearly indicates the transition between chemical states in silicon. Figure 4.17 shows the normalized Si-O concentration with respect to silicon in the annealed films. It can be clearly seen that the Si-O interaction is favored at higher temperatures and the silicon in the film after losing most of the nitrogen, completely gets converted to SiO$_2$.

![Figure 4.16: Deconvolution of Si 2p3 spectra for 0 N$_2$/Ar ratio Si-C-B-N films at different annealing temperatures: (a) un-annealed, (b) 500 °C and (c) 900 °C. Possible peak identification: (1) SiC/BN+SiC; (2) Si-N; (3) SiO; (4) SiO$_2$. Dots represent experimental data and solid lines represent curve fitting lines.](image)
Figure 4.17: Normalized Si-O bonding percentage with respect to Silicon in the films deposited at 0, 0.25 and 1.0 N\textsubscript{2}/Ar

Although the SiCBN films show extensive formation of oxide species on the surface after 700 °C anneal in oxygen ambient, there is a possibility that this effect does not extend into bulk of the film. Furthermore thermogravimetric analysis of SiCBN films annealed in air by Vlcek et al has revealed stable films up to 1350 °C, and they speculated that a surface passivation layer forms that protects the film from further oxidation [94]. This effect cannot be ruled out for oxygen annealed films. However, thermogravimetric analysis is based on recording of mass changes of the material, as a function of temperature and does not provide any information about the changes in structure and chemical nature of the material. Hence extensive depth profiling studies of the films could be useful in confirming this effect. Further spectroscopic studies were carried out using secondary ion mass spectroscopy (SIMS) to investigate and clarify this effect.
4.3. In-situ high temperature electrical measurements

The amorphous SiCBN films produced by sputtering were reported to have complex chemical bonding structure and atomic local order due to the variations in composition, preparation, and treatment conditions. However there is a lack of information on the electrical properties of sputtered SiCBN thin films. Houska et al, very recently reported that electrical conductivity of semiconducting SiBCN thin films can be controlled over a wide range by varying N$_2$/Ar gas flow rates and through substrate biasing [96]. The present research reports for the first time on the electrical properties of reactively sputtered SiCBN thin films under high temperature conditions. In-situ current-voltage electrical characterization was performed under varying temperature conditions ranging from room temperature to 900 ºC. Chemistry of the material clearly plays a major role in determining electrical properties under these conditions. Hence, the induced surface chemical modifications of the films were studied using x-ray photoelectron spectroscopy (XPS) and the depth profile was analyzed using SIMS.

Figure 4.18 shows the SIMS scans for the SiCBN thin films deposited under different N$_2$ gas flow ambient. The SIMS analysis clearly distinguishes three regions of SiCBN samples. First region is the actual SiCBN films on the surface and then the thermally grown SiO$_2$ oxide layer and finally the bulk silicon region. It can also be clearly observed that all three films are very low on oxygen content. Furthermore, the variations in B, C, and N elemental percentages of the films indicate the stoichiometric differences due to the different deposition conditions. Figure 4.18 (a) and (b) show boron concentration to be significantly higher than that of N in the films but decreases in Figure 4.18 (c). This is primarily due to lower sputtering yield of the BN target at high N$_2$ gas flow rates. The N concentration in the film increases with inclusion of N$_2$ gas in the sputtering ambient, however this effect does not extend to higher N$_2$ flow rates. Moreover it has
Figure 4.18: SIMS depth profiles showing the elemental composition of the SiCBN films deposited under (a) 0 N<sub>2</sub>/Ar, (b) 0.25 N<sub>2</sub>/Ar and (c) 1.0 N<sub>2</sub>/Ar gas flow ratios. Regions specified as I, II and III represent SiCBN, thermally grown SiO<sub>2</sub> and Si substrate respectively.
been typically observed that increasing N<sub>2</sub> flow in the sputtering ambient beyond a certain saturation level actually lowers N incorporation in the films. De-convolution of high resolution XPS data for C and B indicate strong presence of Si-C and C-N and SiCBN bonding states in the films. Figure 4.19 shows the normalized percentages of the significant bonding states observed as a function of N<sub>2</sub>/Ar gas flow ratio. It can be observed that the CN and SiCBN content in the film decreases due to N<sub>2</sub> gas flow. The highest concentration of SiCBN was observed at 0 N<sub>2</sub>/Ar flow rate and hence it can be inferred that increasing N in the reactive ambient does not favor SiCBN formation. However the SiC and BN concentrations seem to follow the trend with respect to sputtering yield of the respective targets.

![Figure 4.19: Comparison of normalized C-N and Si-C bonding percentages with respect to Carbon in the films and normalized SiCBN and B-N bonding percentage with respect to Boron in the films deposited at 0, 0.25 and 1.0 N<sub>2</sub>/Ar gas flow ratios.](image-url)
Hence we restrict our electrical characterization and analysis to the films with highest SiCBN concentrations i.e. the 0 N₂/Ar films. This is due to the added reason that the observed resistance values are lower and well within instrument measurable range. Figure 4.20 shows the sheet resistance of the films measured as a function of increasing ambient temperature during annealing in air. It can be observed that the resistance decreases with increasing temperature. This could be due to the possible increase in charge carriers due to thermal generation. However, increased temperatures can also lead to change in chemical states in the films, which could influence the electrical characteristics. Earlier studies on SiCBN films have revealed that, as annealing temperatures increase there are structural changes occurring at the surface of the film. It was revealed that C-N bonds break leading to significant loss of nitrogen from the film surface. Furthermore, almost no N content was detected in the surface after 700 °C anneal. The increasing trend observed in the resistance values after 600 °C can be attributed to this effect. With the loss of nitrogen from the surface there is a possibility of oxygen incorporation at the surface due to the higher ambient temperatures. The increased formation of surface oxide content at higher temperature can be directly correlated with the higher resistance value observed. The in-situ measurement of resistance during cool down reveals more information about the nature of the films. It can be noted that there is a small increase in resistance as temperature decreases from 900 °C to 700 °C. This effect could be due to the oxide formation process at the surface of the film. However beyond this point at lower temperatures, the resistance values follow the same trend observed during the temperature ramp up. This is clear evidence that there are two phenomena that affect the conduction properties. For temperatures lower than 700 °C the resistance is controlled by change in thermally generated carriers in the bulk of the film. At
temperatures higher than 700 °C the effect of surface chemical changes due to increasing oxygen content seems to overshadow the thermal generation and increases resistance of the film.

Figure 4.20: In-situ measurement of sheet resistance with respect to ambient temperature during temperature ramp up and cool down.

Figure 4.21 plots the sheet resistance values as a function of dwell time (1 hour) at different temperatures. It can be clearly observed that the resistance is not affected by the duration of time the sample dwells at a certain temperature. This clearly shows the time dependent reliability of the resistance measurements. Furthermore, additional measurements were carried out to study the resistance behavior of the same films after multiple heating and
cooling cycles. Figure 4.22 shows the plots for the in situ measured resistance values with respect to temperature during the 2nd and 5th ramp up and cool down cycles. It can be observed that the change in resistance is very negligible after multiple cycles. Furthermore the increase in resistance at high temperatures is not as pronounced as that observed for the first heating cycle. This leads us to believe that there could be a thin stable oxide layer formed at the surface that prevents the film from getting further oxidized.

Figure 4.21: In-situ measurement of sheet resistance with respect to ambient temperature during temperature for multiple ramp up and cool down cycles.
Figure 4.22: Sheet resistance measurement at different temperatures of 300 °C, 600 °C and 700 °C for a soak period of 60 minutes.

XPS analysis of the annealed films was conducted to confirm oxide formation at the surface. Figure 4.23 shows the high resolution deconvolution of B and Si peaks of the sample after annealing at 900 °C. Both the curves indicate single distinct peaks representing the respective stable oxides of boron and silicon namely B₂O₃ (193.6 eV) [101] and SiO₂ (103.6 eV) [106]. Therefore the bulk of the films could possibly still be in original stoichiometric composition. Analysis of sputtered SiCBN films annealed in air using thermogravimetry has revealed stable films up to 1350 °C, and it was speculated that a surface passivation layer forms, that protects the film from further oxidation [94]. This effect can be confirmed through depth profiling of the film. SIMS was utilized to analyze the composition of the annealed films with respect to depth.
Figure 4.23: XPS deconvolution of high resolution data for silicon (Si 2p) and boron (B 1s) peaks indicating complete oxidation of the species to form oxides SiO₂ and B₂O₃ respectively at the surface of the film. Dots represent experimental data and solid represent curve fitting lines.

Figure 4.24 shows the depth profile for 0 N₂/Ar film after annealing at 900 °C. It can be observed that the surface has excess of oxygen up to a depth of approximately 5nm, beyond which the composition closely resembles that observed for the original as deposited film (see Figure 4.18 (a)). Furthermore it can be observed that N and C are considerably depleted from the surface and hence leading us to believe that remaining B and Si on the surface combine with oxygen to form surface oxides as indicated by XPS. This data confirms the earlier hypothesis that there is a stable surface film formed which prevents the bulk of the films from getting
further oxidized. Repeated annealing cycles failed to increase resistance of the films which imply that the surface layer prevents the film from getting further oxidized. Hence strongly indicating the thermal stability of the 0 N₂/Ar stoichiometric film. Similar resistance measurements on 0.25 and 1.0 N₂/Ar gas flow ratio films show no particular trend of interest. Furthermore, SIMS depth profile of the annealed 0.25 and 1.0 N₂/Ar samples revealed that the films get oxidized completely. It can be speculated that the presence of N₂ in the sputtering ambient somehow changes the structure of SiCBN formed. However, the reason for complete failure of the higher N₂ flow based films is not yet clear.

Figure 4.24: Multi-element SIMS depth profile for 0 N₂/Ar flow rate deposited SiCBN film stack after annealing at 900 ºC for 30 minutes. Regions specified as I, II, III and IV represent SiCBN, thermally grown SiO₂, Si substrate and the protective surface oxide respectively.
4.4. Optical Characteristics

In order to investigate the prospects of sputtered SiCBN thin films as the next generation of luminescent materials with wide band gap, it is necessary to explore and understand the relationship between the luminescent properties, composition and bond structure. In this section, we study SiCBN films by rf magnetron sputtering and observed the change of microstructure, chemical bonding type, and the luminescent properties before and after annealing treatment. Based on x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS) results, the cause for photoluminescence is analyzed. Furthermore, optical properties are studied with respect to compositional gas mixtures during film deposition. The effect of annealing on the optical characteristics is also reported in correlation with observed changes in chemical nature of the material.

4.4.1. Photoluminescence

Sputtered samples were analyzed for various significant bonding states. High resolution XPS peak for C1s was de-convolved to study the presence of Si-C and C-N and presented in Table 4.3: as percentages relative to total carbon peak area. The remaining area of the C1s peak is attributed to presence of C-H and C-O bonds. Similar analysis was performed on the XPS B1s peak to study BN and SiCBN bonding states in the films. Table 1 shows the normalized percentages of the significant bonding states observed as a function of N2/Ar gas flow ratio. The SiC and BN concentrations seem to follow the trend with respect to sputtering yield of the respective targets with lower yields observed for high N2 gas flow rates. However, it can be observed that the CN and SiCBN content in the film decreases due to N2 gas flow. The highest
Table 4.3: Representation of normalized C-N and Si-C bonding percentages with respect to C in the films and normalized SiCBN and B-N bonding percentage with respect to B in the films deposited at 0, 0.25 and 1.0 N₂/Ar gas flow ratios. (Also see Figure 4.19)

<table>
<thead>
<tr>
<th>N₂/Ar</th>
<th>Si-C</th>
<th>C-N</th>
<th>B-N</th>
<th>SiCBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>32.3</td>
<td>30</td>
<td>17</td>
<td>62</td>
</tr>
<tr>
<td>0.25</td>
<td>56.3</td>
<td>15</td>
<td>21</td>
<td>33</td>
</tr>
<tr>
<td>1.0</td>
<td>40.4</td>
<td>15</td>
<td>17.6</td>
<td>40</td>
</tr>
</tbody>
</table>

concentration of SiCBN was observed at 0 N₂/Ar flow rate hence suggesting that higher nitrogen flow in the reactive ambient is unfavorable for the formation of B rich SiCBN stoichiometry. Furthermore it is already clear that the SiCBN film obtained with 0 N₂/Ar flow shows good temperature stability performance. Hence we restrict our studies to the SiCBN films obtained with 0 N₂/Ar flow conditions.

The photoluminescence spectra of the 0 N₂/Ar SiCBN thin film samples are shown in Figure 4.25. For the as-deposited sample, a strong PL peak is observed at 465 nm and smaller satellite peaks can be seen at 483 nm and 497 nm. The observation of these peaks indicates the promising luminescent property of the SiCBN material. The strong peak in the visible blue region at 465 nm corresponds to energy of 2.67 eV. Photoluminescence effects are known to be predominantly influenced by the crystalline properties of materials. PL studies on amorphous SiC and SiCN films have been reported in the past , [116, 117]. One unique feature reported has been the change in PL peak position after annealing. This is primarily attributed to the increase in crystallization of the material due to high temperature annealing. Polycrystalline phase materials could exhibit different PL properties than their amorphous phase. However the
sputtered 0 N₂/Ar SiCBN films do not exhibit any shift in PL property after high temperature annealing. This clearly suggests that there is no clear change in crystallinity of the material. To confirm this, x-ray diffraction analysis was performed to study the microstructure of the thin films before and after annealing.

Figure 4.25: Photoluminescence measurement for rf sputtered SiCBN thin films at different annealing temperatures.

Figure 4.26 (a) and (b) show the XRD scans for the SiCBN samples as-deposited and after annealing at 900 °C respectively. Depth profiles were performed by fixing the angle between the sample and incident x-ray beam (ω), while scanning the detector (2Θ) from 10° to 80°; after which ω was increased and the 2Θ scan was repeated. Additionally, a bare silicon wafer was similarly analyzed to demonstrate the reproducibility of substrate artifacts, thus
further confirming that evidence of crystallinity is the result of x-ray interactions with the silicon substrate, and not from the SiCBN thin film. The background scans are overlaid in conjunction with corresponding thin film scans. Little difference was observed between the film and background.

Figure 4.26: XRD depth profile scans for the SiCBN samples (a) as-deposited and (b) after annealing at 900°C respectively.

Amorphous films are known to possess complex chemical nature. Hence x-ray photoelectron spectroscopy was used to study the chemical states in these films. High resolution scans were obtained to analyze the chemical nature of the films as a function of annealing.
temperature. Figure 4.27 shows the deconvolved high resolution carbon (C 1s) spectral data for the films. The broad envelope of the peaks clearly indicates the presence of different C 1s states. The peak at 284.6 eV is attributed to C 1s binding energy for adventitious carbon. The peak at lower binding energy of 282.9 eV and 283.5-283-8 eV are due to Si-C covalent bonding. The peaks located at 285.6-286.3 eV are attributed to the presence of C-N bonds. The peaks located at 287.5eV-289.4 eV are primarily due to the presence of C-O contamination bonds. However the decrease in PL peak intensity due to annealing could be an effect of minor chemical changes. Studying the changes in SiC chemical state could provide some insight into the possible causes. A more quantitative analysis of the Si-C bonding in the films is presented in the normalized plot in Figure 4.19. The intensity of Si-C bonding is prominent in the as-deposited samples and decreases with increasing annealing temperature. At higher temperatures carbon covalent bonds could break leading to the escape of carbon in the form of CO_{2} gas during annealing. This effect could also contribute to diminish the PL intensity of the films. Therefore a direct correlation can be drawn between the cause for luminescence and the presence of SiC states in the amorphous matrix of the film.

Crystalline silicon carbide (SiC) is a material recognized to exhibit weak blue photoluminescence. It was further established that crystalline SiC is a semiconductor material with a band gap in the range of 2.2-2.3 eV [118-120]. However SiC nano-crystals can be expected to possess band gaps larger than that of bulk material due to the quantum confinement effect. The same theory can be extended to amorphous SiC based alloys which could mean even larger bandgaps. Amorphous BN films have revealed a wide range of luminescence based on structural defects, composition and crystallinity from higher energy ultraviolet emissions centered at 326 nm (3.8 eV) to deep-blue photoluminescence around 413 nm (3 eV) [121, 122].
All the emissions observed for the SiCBN films (Figure 4.25) are in the visible range and at energies of 2.67 eV – 2.49 eV, which fall between the range of SiC and BN. Therefore these luminescence peaks could be an effect of alloying of SiC and BN forming the amorphous SiCBN films. An average approximation method has been used in the past to calculate the average bandgap of well mixed ternary compounds. This can be extended to the quarternary SiCBN alloy by assuming a linear increase in bandgap from that of SiC (2.2 eV) to that of BN (3.8 eV). Based on the specific SiC or BN percentage in the alloy the approximate bandgap can be identified from the linear curve in Figure 4.28. The BN content in the SiCBN alloy obtained with the 0 N₂/Ar flow rates is observed to be around 8-12 percent. This corresponds to a bandgap in the range of 2.4 eV clearly in good agreement with the bandgap energies obtained from the PL peaks.

![Figure 4.27: XPS C 1s spectra for the as-deposited SiCBN film. Possible peaks identified: (1) CH; (2) C-N; (3) Si-C; (4) C-O. Dots represent experimental data and solid lines represent curve fitting lines. (Re-printed for reference from Figure 4.4 (a))](image-url)
Additionally no appreciable change in the PL peak position was seen after annealing of the films at 500 °C and 900 °C. However, the intensity of the peaks showed significant decrease after annealing. The film annealed at highest temperature showing lowest peak intensity. This effect leads us to believe that there is no significant change occurring in the bulk properties of the amorphous matrix of the SiCBN alloy due to annealing at 900 °C. SIMS analysis of 0 N$_2$/Ar SiCBN films before and after annealing at 900 °C has been observed earlier. It was revealed that there is no significant change in the bulk of the films due to annealing. Our observation with the PL peak intensity is in agreement with this theory additionally confirming the high temperature stable nature of this particular composition of SiCBN films.
4.4.2. Band gap and absorption studies

Elemental compositions of the films were obtained from XPS scans and the relative atomic concentrations of the respective elements are shown in Table 4.4. Carbon content in the films seems to be steady with changing gas flow ratios. The boron and silicon content in the films decreases as the nitrogen gas flow rate is increased during sputtering. Detailed analysis of the effect of N$_2$/Ar gas mixture on the SiCBN films obtained and the effect of annealing on the chemical structure was investigated in earlier sections of this chapter. It was revealed that lower sputtering yields of the two targets at higher N$_2$ flow rates could cause this effect. Interestingly the nitrogen content in the film is highest for lower N$_2$ flow rates. This could be due to saturation of the gas ambient at certain intermediate N$_2$ flow level beyond which increased N$_2$ levels in the ambient could affect the nitrogen incorporation into the film. Hence we restrict our optical analysis to films obtained under zero N$_2$ flow condition and compare that with films obtained under low N$_2$ flow (0.25) and high N$_2$ (1.0) flow rate conditions. Furthermore, it is believed that the SiCBN films with relatively stable carbon content and varying boron, nitrogen and silicon concentrations could exhibit interesting optical properties.

Table 4.4: Relative atomic concentration of sputtered samples based on N$_2$/Ar flow ratios

<table>
<thead>
<tr>
<th>N$_2$/Ar</th>
<th>B 1s</th>
<th>C 1s</th>
<th>N 1s</th>
<th>Si 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.052</td>
<td>0.38</td>
<td>0.07</td>
<td>0.23</td>
</tr>
<tr>
<td>0.25</td>
<td>0.025</td>
<td>0.35</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>1.0</td>
<td>0.015</td>
<td>0.40</td>
<td>0.09</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Figure 4.29 shows the optical transmission scans of the films for the three gas flow ratios considered. Transmittance of the film increases with introduction of N\textsubscript{2} into the sputtering ambient. However further increase of N\textsubscript{2} flow rates does not produce any significant change in the transmittance properties of the film. This could imply that the incorporation of N\textsubscript{2} in gas ambient during sputtering produces compositional change in the film affecting its optical property. Furthermore this change does not seem to be dependent on the quantity of nitrogen in the gas ambient. Hence it is believed the change in nitrogen concentration does influence the optical properties but need not be the only cause for this effect.
Additional insights into the influence over optical properties can be gained by considering the annealed films. Figure 4.30 shows the transmission data for 0.25 N₂/Ar flow rate after for different annealing temperatures. It can be observed that annealing increases transmittance of the films and the film annealed at 900 °C is almost completely transparent. The shift in optical transmittance is very gradual initially from as deposited sample up to 500 °C annealing. This clearly indicates the temperature stability of the film with respect to optical characteristics. However annealing at temperatures higher than 500 °C produces large shift in transmission property. The high transmission properties of the films after 900 °C annealing indicate extensive oxide formation. Similar trends were observed in the samples prepared at 0 N₂/Ar and 1.0 N₂/Ar gas flow ratios.

Figure 4.30: Transmission (%T) curves of 0.25 N₂/Ar SiCBN films at different annealing temperatures
Figure 4.31: Absorption coefficient ($\alpha$) with respect to photon energy for (a) 0 N$_2$/Ar, (b) 0.25 N$_2$/Ar and (c) 1.0 N$_2$/Ar gas flow ratios.
Figure 4.32: Tauc Plot for 0.25 N₂/Ar SiCБN films. Dotted lines represent extrapolated straight line intercept indicating optical band gap for each curve.

Transmission (%T) data can be used to calculate optical density (OD) of the films and ultimately used to calculate absorption coefficient as shown in equation below.

\[
\alpha = 2.303 \times OD = \frac{-2.303}{t} \log_{10}(\%T)
\]

Where, \( \alpha \) is the absorption coefficient and ‘\( t \)’ is the thickness of the film.

Absorption coefficient values were calculated from the transmission spectra and plotted with respect to photon energy. Figure 4.31 shows the absorption coefficient values for all three gas flow ratios under various annealing conditions. It can be observed that there is no sharp or
distinct absorption edge especially after annealing at higher temperatures. The absorption
coefficient values were subsequently used to calculate the optical band gap \((E_{\text{opt}})\) of the
amorphous SiCBN films. This is realized from the Tauc plot given by the equation below[123].

\[
(\alpha h \nu)^{1/2} = B(h \nu - E_{\text{opt}})
\]

Where, B, is a constant factor and \(h \nu\) is the photon energy. Figure 4.32 shows a Tauc plot
for films deposited at 0.25 N₂/Ar flow rate subject to various annealing conditions. The
extrapolation of the linear region of the Tauc curve to intercept the x-axis leads to \(E_{\text{opt}}\) values
for the material and the slope of this line can be used to calculate B. It can be observed that the
optical band gap values for the as deposited SiCBN film is around 2.3 eV and increases after
annealing. This is in agreement with expected energy gap value of the material between that of
amorphous SiC (2.1 eV) [118, 124], and that of BN (3.6 eV - 6 eV) [125].

Figure 4.33 shows a plot of \(E_{\text{opt}}\) with respect to annealing conditions for all three
deposition gas flow rates. In all the three cases the optical band gap of the films increases with
annealing. This increase is more prominent at higher temperatures (above 500 °C). Furthermore
it can be noted that the band gap for 0.25 N₂/Ar flow ratio is greater than the other two flow
ratios and continues the trend after annealing. However after 900 °C anneal all the three cases
display almost identical band gap values (~ 4 eV). Compositional changes in the films due to
process conditions as well as annealing are believed to cause these variations in optical
properties. In order to investigate this further we consider the chemical analysis of the films
before and after annealing.
Figure 4.33: Optical band gap for 0 N\textsubscript{2}/Ar, 0.25 N\textsubscript{2}/Ar and 1.0 N\textsubscript{2}/Ar SiCBN films with respect to annealing conditions.

High resolution XPS scans were obtained to analyze the chemical nature of the SiCBN films. Figure 4.34 shows the deconvolved high resolution carbon (C 1s) spectral data for the films deposited at 0.25 N\textsubscript{2} flow for as deposited sample as well as after annealing at 500°C. The broad envelope of the peaks clearly indicates the presence of different C 1s states. The large peaks at lower binding energy of 283.5-283.8 eV are due to Si-C covalent bonding. The peak at 284.6 eV is attributed to C 1s binding energy for adventitious carbon. The peaks located at 285.6-286.3 eV are attributed to the presence of C-N bonds. The peaks located at 287.5 eV-287.9 eV are primarily due to the presence of C-O contamination bonds. It can be observed that the C-N peak intensity decreases after the annealing process. This implies that there is a loss of carbon
and nitrogen in the films. The C-N bonds break due to annealing, leaving nitrogen free to escape as gas and the carbon could combine with oxygen to form CO or CO₂ and escape as gas during annealing.

Figure 4.34: XPS C 1s spectra for SiCBN films deposited at 0.25 N₂/Ar for: un-annealed and 500 °C annealed sample. Possible peak identification: (1) CH; (2) Si-C; (3) C-N; (4) C-O. Dots represent experimental data and solid lines represent curve fitting lines

A more quantitative analysis of the percentage of C-N bonding in the films as well as the normalized carbon and nitrogen concentrations are presented in the plot in Figure 4.35. The intensity of C-N bonding is prominent in the as deposited samples at all three flow rates and decreases slightly after 500 °C anneal, however annealing at 900 °C drastically reduces the C-N
bonding in the films. Both carbon and nitrogen concentrations decrease in the films after annealing with almost no carbon or nitrogen present after 900 °C. Hence it is clear that other than nitrogen, carbon content also plays a significant role in determining the optical properties of the films. Our results are in agreement with similar studies on amorphous SiCN thin films by Chen et al.[126], where carbon content in the films was reported to play an important role in determining optical responses in the films.
Figure 4.35: Normalized percentages for various N$_2$/Ar deposition ratios and annealing temperatures; (a) C-N bonding with respect to Carbon in the films; (b) % C composition and (c) % N composition.
4.5. Simple Optoelectronic device

Electro-optic systems using light as a signal carrier are being applied increasingly in various types of sensors such as position, pressure and temperature sensors. Such systems are lighter, cost less and are least sensitive to electro-magnetic interference enabling efficient telemetry. Amorphous silicon (a-Si) based alloys offer quite a wide range of applications in the field of photosensitive devices due to their high photosensitivity in the visible light spectrum, low-cost of fabrication, ability of deposition at low temperature and to their homogeneity over large area substrates [127-129]. However, in many applications, various components in the system must operate at temperatures higher than 125°C. Silicon based devices are rendered inefficient under these conditions due to thermal carrier generation and significant shifts in optical properties causing deterioration in spectral response [130, 131].

4.5.1. Photodetector fabrication

Deposition was carried out in a multi-gun UHV sputtering system evacuated to a base pressure of $10^{-8}$ Torr. Sputtering power was maintained at 100 Watts and 200 Watts for the SiC and BN targets respectively and deposition pressure was kept constant at 4mTorr. The N$_2$ to Ar gas flow ratio was set to 0.25 with the total gas flow kept constant at 20 sccm. Films of 100nm thickness were deposited on oxidized silicon wafers which were subjected to standard cleaning procedures before deposition. Ring type structure was used to fabricate the PD’s and Aluminum was evaporated to form contact electrodes. Active area of the fabricated PD device was 1mm$^2$. A Keithley M6487 picoammeter/voltage source was then used to measure current–voltage (I–V) characteristics of the fabricated PD. A Signatone hot chuck was utilized for high temperature measurements.
4.5.2. MSM photodetector characteristics

Figure 4.36 shows the high resolution deconvolution for carbon and silicon peaks in the SiCBN films. The broad envelopes for both the peaks clearly indicate the presence of different carbon 1s and silicon 2p states. The C 1s peak at 284.6 eV is attributed to binding energy for adventitious carbon. The large peak at lower binding energy of 283.5 eV is due to Si-C covalent bonding. The remaining sub-peaks located at higher energy levels are identified to be primarily due to the presence of C-N and C-O contamination bonds. Similarly the Si 2p deconvolution shows the presence of large percentage of SiC in the film. The other peaks identified are attributed to SiC-BN interface and small amount of Si₃N₄. The detection of large amount of SiC in the films clearly indicates the presence of a SiC network with a considerable B and N presence.

The photoluminescence spectrum for the sample is shown in Figure 4.37. A strong PL peak is observed at 465nm (2.67eV) and smaller satellite peaks can be seen at 483nm and 497 nm. These PL peaks can be correlated to presence of major fraction of silicon carbide in the film. SiC is a wide band gap material that exhibits weak blue photoluminescence at low temperatures. The emissions are in the visible range and can be related to the crystal phase of SiC. Crystalline SiC is a well known semiconductor material with a band gap of 2.2 eV [118] or 2.3 eV [119]. However the band gap of SiC nanocrystals is larger than that of bulk material due to the quantum confinement effect. The same theory can be extended to amorphous phase of SiC, which suggests even larger bandgaps. Therefore these luminescence peaks at 2.67 eV and satellite peaks at 2.57 eV and 2.49 eV can be attributed to the presence of SiC phase in the amorphous matrix of the film.
Figure 4.36: XPS deconvolution of Carbon (C1s) and Silicon (Si2p) peaks of the SiCBN film. Possible peaks have been identified and marked for each case with numbers. Dots represent experimental data and solid lines represent curve fitting lines.
Figure 4.37: Photoluminescence (PL) measurement for rf sputtered SiCBN thin film.

The dark and photo I-V characteristic of the device is illustrated in Figure 4.38. Increased voltages apparently produce higher currents. This is possible due to the fact that higher electrical fields can boost the electron-hole pairs to penetrate film grain boundaries and effectively be collected at electrodes [132]. Results show that dark current values are pretty low even at higher electric field which is desired for a good PD. Improved performance of the PD is measured through the sensitivity factor called photodetector current ratio (PDCR) defined as follows [133].

$$PhotoDetectorCurrentRatio(PDCR) = \frac{I_p - I_d}{I_d}$$
Where \( I_d \) is the dark current and \( I_p \) (photo current) is the current produced under illumination. Figure 4.39 shows the PDCR value as a function of temperature. PDCR values were obtained at 5 V biasing. It can be seen that PDCR value obtained is greater than 5 at room temperature (22 °C) and above 3 at 100 °C. Further increase in temperature produce lower sensitivity factor however PDCR is appreciably greater than 2 even at 200 °C. This is believed to be primarily due to increase in dark current at higher temperatures. The thermal generation of carriers at higher temperatures cannot be completely eliminated. However the high temperature current sensitivity values obtained for SiC-BN are quite high and can be considered a significant improvement on conventional silicon based photodetector performance at higher temperatures. This is primarily due to the smaller levels of dark current at high temperatures and the thermal stability of the SiC-BN films. This clearly indicates that amorphous SiC-BN based PD’s are good candidates for sensing applications under harsh temperature conditions.

Figure 4.38: I-V curve showing photo generated current and dark current of the SiC-BN MSM photodetector at room temperature under various biasing voltages.
Figure 4.39: Photodetector current ratio (PDCR) of SiCBN MSM photodetector obtained under 5 V biasing with respect to temperature.
CHAPTER 5: CONCLUSIONS

5.1. Concluding remarks

Thin SiCBN films were successfully deposited by co-sputtering of SiC and BN targets. The formation of SiCBN is evident from XPS analysis. Film stoichiometry is strongly dependent on the N₂ flow ratio during deposition. Boron content in the film is observed to decrease at higher N₂ flow ratios. Si-C bond formation does not seem to be affected by the N₂ gas flow rates. Higher nitrogen concentrations during deposition also show increased probability of formation of SiNₓ in the deposited films. Nitrogen flow rate change in the sputtering chamber also affects the film surface characteristics. Roughness of the films increases with higher N₂ flow rates and could be due to increased ion activity in the chamber at these flow rates.

Oxidation studies on thin SiCBN films obtained by reactive sputtering were carried out. Surface chemical composition and state of the annealed films were studied using XPS. Carbon and Nitrogen content in the film decreased significantly at higher temperatures. No nitrogen can be seen in the films after 700 °C anneal. The effect is primarily due to the breaking of C-N bonding in the film and the loss of N₂ and CO/CO₂ as gases during anneal. Oxygen interaction with silicon and boron in the film seems to increase with annealing temperatures. Transition from nitrides to oxides occurs through the formation of oxy-nitrides at intermediate temperatures and after anneal at 900 °C the silicon and boron in the film are almost completely converted to their respective oxides.

The electrical properties of reactively sputtered SiCBN thin films have been investigated under high temperature conditions using in-situ sheet resistance measurements. The electrical properties are highly sensitive to variations in the chemical composition of the SiCBN films. The
film obtained with 0 N$_2$/Ar gas flow ratio shows good thermal stability with very interesting electrical characteristics. Whereas the samples obtained with 0.25 and 1.0 N$_2$/Ar gas flow ratios get completely oxidized at high temperatures. Stable and repeatable sheet resistance values were observed for the 0 N$_2$/Ar sample after multiple heating and cooling runs. XPS analysis shows oxide formation at the surface; however depth profile analysis through SIMS showed the oxide formed was restricted to a depth of 5nm-6nm from the surface of the film. The surface oxide forms a stable barrier against further oxygen incorporation into the film and hence clearly provides the film with good thermal stability. Furthermore the stable reproducible electrical properties indicate that this particular SiCBN film will have potential for high temperature applications.

Considering the results obtained, we summarize that SiCBN films deposited by rf sputtering technique show PL peaks in the visible region. Annealing at higher temperatures reveals no shift in PL peaks. Analysis of the film microstructure by x-ray diffraction analysis shows the amorphous nature of the films even after high temperature anneal. Surface characterization of the films by x-ray photoelectron spectroscopy reveals change in surface chemical composition at different annealing temperatures. Decreasing concentrations of SiC in the films at higher annealing temperatures corresponding to the lowering of PL peaks observed further substantiates this theory. The alloying of BN and SiC in the amorphous matrix of the films is identified as the possible source for luminescence. Band gap values in the range of 2.5 eV – 2.67 eV reveal a possible linear trend between that of SiC (2.2 eV) to BN (3.8 eV) for potential band gap engineering applications.

Optical properties of amorphous SiCBN thin films obtained by reactive sputtering were studied. Transmission property of the films improves with nitrogen incorporation during
deposition, however does not change significantly with increased N₂ gas flow rates. High temperature annealing also leads to considerable increase in transmittance. Optical energy gap is significantly influenced by annealing temperatures. Chemical analysis through XPS studies reveals C-N bonding in the films. C and N concentrations in the films are highly sensitive to temperature. Annealing at higher temperatures leads to broken C-N bonds which results in the loss of C and N in the films. This is believed to be the primary cause for variations in optical properties of the films.

Amorphous SiCBN based MSM photodetector was studied. The optoelectronic performance of the devices examined through photo current measurements indicate good room temperature sensitivity factor. Effect of temperature on sensitivity of the device was studied. Device showed good current ratio of greater than 2 even at high temperature of 200 °C. The improved performance of the device even at high temperature could open avenues for low cost and easy to fabricate high temperature photodetector applications.

5.2. Outlook for future efforts

Several avenues for exploring the potential applications for such materials is still open for investigation. Some are listed below

- Investigating extreme temperature performance (above 1000 °C)
- Exploring more into device application area (particularly optoelectronic device).

Implementing the PD with a better electrode design could result in much better performance levels. The most commonly used structure currently is the interwoven finger structure. This can be implemented through a lithography process with proper mask design to ensure maximum light pass through.
• Since the material has shown luminescence, it can be used as a host for doping highly luminescent rare earth dopants (such as Er\textsuperscript{3+} or Eu\textsuperscript{3+}) that can have potential applications in harsh environment sensors.

• Material has shown significant resistance to oxidation at high temperature conditions. Thus it would be worthwhile to investigate the diffusion barrier property. If successful it would open up a new application as diffusion barrier for Copper metal interconnects beyond the second metallization level in a multi level interconnect scenario.

Future efforts could also focus on other variants of the SiC alloy system. Other possible variations could involve the combination of SiC and AlN to form SiCAlN alloy.
LIST OF REFERENCES


