STRUCTURAL AND OPTICAL PROPERTIES OF SILICON CARBONITRIDE THIN FILMS DEPOSITED BY REACTIVE DC MAGNETRON SPUTTERING

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Outline:

- Purpose of the Study
- Properties and Applications of SiCN Thin Films
- Coating Methods
- Experimental
- Characterization
- Results and Discussion
Purpose:

- Changing the composition of the coatings by modifying the reactive gas flow ratios,
- Investigating the effects of the composition change on structural and optical properties.
- SiCN films are mainly studied on their optical transmittance.
- This study is unique in terms of target material, reactive gas types, flow rates and application of Tauc rule.
Coating Methods:

SiCN films can be deposited by a variety of techniques,

- High temperature CVD,
- Radio frequency plasma enhanced CVD,
- Pyrolysis of polymer precursors,
- Electron cyclotron resonance PECVD,
- Pulsed laser deposition,
- Ion beam sputtering
- Reactive magnetron sputtering.

- From the various possible choices, magnetron sputtering appears to be very attractive, due to its relative simplicity, low depositing temperature, high attainable deposition rates and wide acceptance by industry.
Experimental:

- Substrates

- Vacuum and etching

- Coating
Substrates:

- **Corning glasses** for optical studies  
  (LT1001740, 26 mm x 76 mm x 1 mm)

- **M2 high speed steels** for other studies  
  (% 0.9 C, % 4.1 Cr, % 5 Mo, % 1.9 V, % 6.4 W)
Top Down Schematic View of TSD 350 PCVD Coating Chamber:

1. Vacuum Chamber
2. CMP-150 Magnetron cathode
3. Plasma Generator
4. Substrate Holder
5. Target Material
Vacuum and Etching:

- Base pressure of $1 \times 10^{-5}$ Pa
  (Rotary and turbomolecular pump combination)
- 99.999% purity argon gas for generating plasma
- 0.2 Pa working pressure
- Plasma booster for etching
- Bias etching 50 V - 250 V
Coating:

- Target Material: 150 mm radius, 7 mm thickness 99.999% purity single crystal Si
- Reactive gases: CH₄ & N₂
- Ar, CH₄ & N₂ total gas flow of 20 cm³/min
- CH₄ & N₂ gas flow rates 1-10 cm³/min
### Deposition Parameters:

<table>
<thead>
<tr>
<th></th>
<th>SiCN 1</th>
<th>SiCN 2</th>
<th>SiCN 3</th>
<th>SiCN 4</th>
<th>SiCN 5</th>
<th>SiCN 6</th>
<th>SiCN 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar Gas Flow [cm³/min]</td>
<td>13</td>
<td>10</td>
<td>8</td>
<td>5</td>
<td>13</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>CH₄ Gas Flow [cm³/min]</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>N₂ Gas Flow [cm³/min]</td>
<td>2</td>
<td>5</td>
<td>7</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

- **Base Pressure**: 1×10⁻⁵ Pa
- **Cathode Voltage**: 600±50 V
- **Working Pressure**: 0.2 Pa
- **Cathode Current**: 0.9±0.1 A
- **Deposition Temp.**: 50±10 °C
- **Bias Voltage**: 50 V
- **Target Power**: 500 W
- **Coating Duration**: 60 min.
Specimens (Group 1):

- SiCN 1: %25 CH₄, %10 N₂
- SiCN 2: %25 CH₄, %25 N₂
- SiCN 3: %25 CH₄, %35 N₂
- SiCN 4: %25 CH₄, %50 N₂
Specimens (Group 2):

SiCN 5: %10 CH₄, %25 N₂
SiCN 2: %25 CH₄, %25 N₂
SiCN 6: %35 CH₄, %25 N₂
SiCN 7: %50 CH₄, %25 N₂
Characterization:

- **Thickness**: Profilometer / Dektak 150 (Veeco, USA)
- **Microstructure**: SEM / JEOL JSM 7000F SEM
- **Chemical composition**: SIMS / Cameca IMS6F
- **Optical Properties**: Spectrophotometer / NKD 7000 (Aquila, UK) Pro-Optix software
- **Band Gap Calculations**: Tauc Rule
Film Thicknesses:

<table>
<thead>
<tr>
<th>Profilometer:</th>
<th>SiCN 1</th>
<th>SiCN 2</th>
<th>SiCN 3</th>
<th>SiCN 4</th>
<th>SiCN 5</th>
<th>SiCN 6</th>
<th>SiCN 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film Thickness [nm]</td>
<td>1380</td>
<td>1420</td>
<td>1390</td>
<td>1370</td>
<td>1370</td>
<td>1320</td>
<td>1280</td>
</tr>
</tbody>
</table>

All the thicknesses are in the standard deviation range of 1350±70nm.

Device used: Dektak 150 model profilometer (Veeco, USA)
SEM - SiCN 4 (%25 CH₄, %50 N₂)
SEM - SiCN 7 (%50 CH₄, %25 N₂)
SIMS - SiCN 7 (%50 CH₄, %25 N₂)
SiCN (%25 CH₄) (Group 1)
Transmittance and Reflectance

T-R (%) vs. Wavelength (nm)

- Glass
- SiCN 1 (%25 CH₄, %10 N₂)
- SiCN 2 (%25 CH₄, %25 N₂)
- SiCN 3 (%25 CH₄, %35 N₂)
- SiCN 4 (%25 CH₄, %50 N₂)
SiCN (%25 N₂) (Group 2)
Transmittance and Reflectance

T-R (%)

Wavelength (nm)

Glass
SiCN 5 (%10 CH₄, %25 N₂)
SiCN 2 (%25 CH₄, %25 N₂)
SiCN 6 (%35 CH₄, %25 N₂)
SiCN 7 (%50 CH₄, %25 N₂)
Calculation of Band Gap

\[ E = \frac{hc}{\lambda} \]

\[ \tilde{n} = n - ik \]

\[ n = \text{Real index of refraction} \]

\[ k = \text{Extinction coefficient} \]

\[ \sqrt{\alpha(hv)hv} = C_{Tauc}(hv - E_g^{Tauc}) \]

\[ (\alpha hv)^{1/2} - (hv) \text{ graph} \]
Band Gap Calculation 1-4:

SiCN 1

SiCN 2

SiCN 3

SiCN 4

\( a(hv)^{1/2} \times 10^{-12} \) cm\(^{-1/2}\) eV\(^{1/2}\)

\( h(v) \) (eV)

\( X = 3.23024055 \)

\( X = 2.83101375 \)

\( X = 2.35395189 \)

\( X = 2.35395189 \)
Band Gap Calculation 5-7:

**SiCN 5**

\[(\alpha h\nu)^{1/2} \text{ vs. } h\nu (eV)\]

\[X = 3.27641753\]

**SiCN 6**

\[(\alpha h\nu)^{1/2} \text{ vs. } h\nu (eV)\]

\[X = 2.69222509\]

**SiCN 7**

\[(\alpha h\nu)^{1/2} \text{ vs. } h\nu (eV)\]

\[X = 2.58483677\]
## Indirect Band Gaps

<table>
<thead>
<tr>
<th>Specimen</th>
<th>CH$_4$</th>
<th>N$_2$</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Set 1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiCN 1</td>
<td>5</td>
<td>2</td>
<td>3.23</td>
</tr>
<tr>
<td>SiCN 2</td>
<td>5</td>
<td>5</td>
<td>2.63</td>
</tr>
<tr>
<td>SiCN 3</td>
<td>5</td>
<td>7</td>
<td>2.35</td>
</tr>
<tr>
<td>SiCN 4</td>
<td>5</td>
<td>10</td>
<td>2.35</td>
</tr>
<tr>
<td><strong>Set 2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiCN 5</td>
<td>2</td>
<td>5</td>
<td>3.27</td>
</tr>
<tr>
<td>SiCN 2</td>
<td>5</td>
<td>5</td>
<td>2.63</td>
</tr>
<tr>
<td>SiCN 6</td>
<td>7</td>
<td>5</td>
<td>2.69</td>
</tr>
<tr>
<td>SiCN 7</td>
<td>10</td>
<td>5</td>
<td>2.58</td>
</tr>
</tbody>
</table>
SiCN (%25 CH₄)

Band Gap vs. Gas Flow

Band Gap (eV)

% N₂ (%25 CH₄)
SiCN (%25 N₂)

Band Gap vs. Gas Flow
Results:

- **Homogeneous, dense** and well-adherent silicon carbonitride thin films with thicknesses of 1280-1420 nm with variable compositions were successfully deposited on glass substrates by reactive DC magnetron sputtering.

- A **spectrophotometer** with inline software capability was used for determining the **transmittance**, **reflectance** and **extinction coefficient** values of silicon carbide films. **Tauc rule** was used for determining the **optical band gap** values.

- Increase in **carbon** and **nitrogen** concentration resulted in both increase and decrease in **T-R values** for different wavelengths.

- The **increase** in C and N concentrations results in a **decrease in optical band gap values**. The optical gaps range from 2.35 to 3.27 eV.
Conclusions

Carbon and nitrogen concentration in SiCN thin films has significant influence on both optical constants and optical band gaps.

Transmittance and reflectance values of SiCN films could easily be tailored by modifying Si, C and N concentrations in the coating, for the same film thickness.
Thank You For Your Attention

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