SiN films: Characterization workflow and examples from analysis

work-in-progress report

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for the Virgo Coating R&D Collaboration
The scientific case

- **Silicon Nitride coatings**
  - Losses are about 3 times lower than present $\text{Ta}_2\text{O}_5$-$\text{TiO}_2$ coatings
  - Can be annealed up to 900 °C without crystallization
  - Optical absorption is relatively high and has to be reduced

Challenge: 
*increase n, decrease k*

<table>
<thead>
<tr>
<th>Refractive Index</th>
<th>Extinction</th>
<th>Scattering</th>
<th>Internal friction</th>
<th>Coated diameter</th>
<th>Thickness uniformity</th>
<th>Surface roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_H &gt; 2.09$</td>
<td>$n_L &lt; 1.45$</td>
<td>$10^{-7} &lt; k &lt; 10^{-6}$</td>
<td>$\phi_s &lt; 10^{-4}$ at 100 Hz</td>
<td>$d \geq 35$ cm</td>
<td>$\Delta t \leq 0.1%$</td>
<td>$\leq 0.1$ nm rms</td>
</tr>
</tbody>
</table>

Origin of absorption

• Factors affecting the optical absorption & refractive index
  - Stoichiometry (S/N ratio)
  - Oxygen
  - Hydrogen
  - Contaminants
  - Coating (in)homogeneity
  - Density

Example: silicon-rich SiNx films have higher absorption [Paule et al., Vacuum 37:395, 1987]

• Characterization is required to track ALL the above factors, so that they can be optimized during the next fabrication campaign

Literature studies help (only up to a certain point...)
Tracking the factors affecting absorption

### Optical properties

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Technique</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>Spectrophotom. Ellipsometry</td>
<td>LMA Genova</td>
</tr>
<tr>
<td>k</td>
<td>Spectrophotom. Phototherm. defl. Ellipsometry</td>
<td>LMA Genova</td>
</tr>
<tr>
<td>gradient</td>
<td>Spectrophotom. Ellipsometry</td>
<td>LMA Genova</td>
</tr>
</tbody>
</table>

### Chemical/compositional properties

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Technique</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry, H content, O content, Contaminants</td>
<td>EDX XPS Raman LIBS FTIR RBS SIMS ERDA RBS</td>
<td>Perugia Roma1 Genova g-MAG g-MAG Padova SAFIR/Navier</td>
</tr>
</tbody>
</table>

### Morphological/structural properties

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Technique</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>Spectroph. Ellipsom.</td>
<td>LMA Genova</td>
</tr>
<tr>
<td>Surface analysis</td>
<td>SEM AFM</td>
<td>Perugia</td>
</tr>
<tr>
<td>Density, roughness</td>
<td>XRR</td>
<td>Padova</td>
</tr>
<tr>
<td>Cryst. content</td>
<td>GIXRD</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

The results from the characterization are evaluated and discussed by considering the theory describing the amorphous coatings (Navier)

**NOTE:** concerning the thermo-optic effect in SiNx coatings, see the poster by Matteo Bischi on 20 May
Workflow

Fabrication → Characterization

Requirements are satisfied?

Yes → Implement modifications

No → Find causes

So far: **4 batches of SiN films** have been produced by LMA and distributed to VCR&D for characterization. Other samples will be available soon.
Example of analysis (sample prod. date: dec2020-jan2021)

EDX data and analysis (Perugia)

<table>
<thead>
<tr>
<th>Element</th>
<th>series</th>
<th>[norm. wt.%]</th>
<th>[norm. at.%]</th>
<th>Error in wt.% (1 Sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>K-series</td>
<td>62.43918541</td>
<td>48.89649742</td>
<td>2.608289506</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>K-series</td>
<td>27.58287787</td>
<td>43.31181983</td>
<td>3.094118152</td>
</tr>
<tr>
<td>Aluminium</td>
<td>K-series</td>
<td>0.425638601</td>
<td>0.346958026</td>
<td>0.044989492</td>
</tr>
<tr>
<td>Carbon</td>
<td>K-series</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>4.548775018</td>
<td>6.253072217</td>
<td>0.581343653</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>L-series</td>
<td>3.105090425</td>
<td>0.711831517</td>
<td>0.134403896</td>
</tr>
<tr>
<td>Argon</td>
<td>K-series</td>
<td>0.359018787</td>
<td>0.197662736</td>
<td>0.037264495</td>
</tr>
<tr>
<td>Tantalum</td>
<td>L-series</td>
<td>LOD</td>
<td>LOD</td>
<td>LOD</td>
</tr>
<tr>
<td>Iron</td>
<td>K-series</td>
<td>0.349075697</td>
<td>0.137474594</td>
<td>0.037868634</td>
</tr>
</tbody>
</table>

Sum: 100 100

Si/N ratio: 1.129
Example of analysis (sample prod. date: dec2020-jan2021)

XPS data before and after sputtering (Roma1)

2° sputtering

1° sputtering

As-received

Note: O content decreases as depth is increased
Example of analysis (sample prod. date: dec2020-jan2021)

Compositional analysis across the coating with SIMS (Padova)

H content and vertical gradient measured with ERDA (SAFIR/Navier)

Michele Magnozzi  GWADW 2021  17/05/2021
Dominating band between 800 and 1200 cm⁻¹ is attributed to the group of Si-N and Si-O bonds.

The main peak position shifts to larger wavenumbers by increasing the O content as the predominant bond type passes from the Si-N stretching to the Si-O stretching.

Sample S21001 is richer in oxygen.

Presence of Oxygen evaluated by FTIR (Padova)
SiN composition measured with RBS (SAFIR/Navier)

Example of analysis (sample prod. date: dec2020-jan2021)

Michele Magnozzi
GWADW 2021
17/05/2021
SiN composition measured with RBS (Padova, previous batch)

After background subtraction:

\[
\begin{align*}
\text{Si} &= 1.40 \times 10^{17} \text{ atoms/cm}^2 \\
\text{O} &= 1.44 \times 10^{17} \text{ atoms/cm}^2 \\
\text{N} &= 1.20 \times 10^{17} \text{ atoms/cm}^2 \\
\end{align*}
\]

From these data one can obtain the corresponding atomic ratios:

\[
\begin{align*}
\text{N/Si} &= 0.86 \\
\text{O/Si} &= 1.03 \\
\end{align*}
\]
Presence of vertical gradient evaluated by ellipsometry (Genova)

Model without grading

Results from SE analysis:
- $n$ at 1064 nm: 1.90
- Thickness: 417 nm

Results from spectrophotometry:
- $n$ at 1064 nm: 1.94
- Thickness: 415 nm
Presence of vertical gradient evaluated by ellipsometry (Genova)

Results from SE analysis:

5.7% grading

Bottom to surface, n@1064nm: 1.85-1.96
Summary

• An **intensive, cooperative effort** is ongoing to provide a comprehensive characterization of the **optical, chemical, morphological/structural properties** of the SiN films produced by LMA

• 4 SiN batches produced and characterized so far; the “performances” of the films have been continuously improved thanks to optimizations in the fabrication process and feedback provided by characterization. Examples of negative factors that have been significantly reduced:
  - water content
  - vertical inhomogeneity

• New samples will be ready soon; the collaboration is ready to characterize them

• Best results so far on SiNx films and perspectives: **see next talk by Massimo Granata**