Early Contamination Detection Methods and Contamination Tolerant Surfaces utilizing ALD Grown Metal Oxide Films

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Review of Contamination Control Methods and In situ Raman Detection of Contamination

Lessons Learned from In Situ Raman Detection of Contamination

Development of Raman Spectroscopy Witness Monitoring Program

Development of Contamination Tolerant Optics

Conclusion and Path Forward
Contamination Control Methods for Monitoring Molecular Contaminants

<table>
<thead>
<tr>
<th>Type of Monitoring</th>
<th>Pros</th>
<th>Cons</th>
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</thead>
<tbody>
<tr>
<td>TQCM (Temperature Quartz Crystal Microbalances)</td>
<td>Quantitative data for determining in situ mass change within the $10^{-4}$ Torr to $10^{-8}$ Torr pressure range</td>
<td>Not Qualitative</td>
</tr>
<tr>
<td>Visual Inspection</td>
<td>Time effective, Low Cost</td>
<td>Not Qualitative and Not Quantitative</td>
</tr>
<tr>
<td>NVR Analysis with ATR-FTIR, XPS, TOF-SIMS, Witness Plate Program, and GC-MS</td>
<td>-Able to determine Quantitative and Qualitative information</td>
<td>-Time consuming, at least a week for results</td>
</tr>
<tr>
<td></td>
<td>-Determination of complex chemical content</td>
<td>-Additional sample preparation</td>
</tr>
<tr>
<td></td>
<td>-Low limits of detection for XPS, TOF-SIMS, and GC-MS</td>
<td>-High cost instruments that are bench top only usage</td>
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</table>

These methods are used intermittently throughout the life cycle. Often contamination concerns can be further in the lifecycle before it is identified as a risk.
Recently, in situ detection of a contaminant has occurred on spacecraft.

https://fpd.larc.nasa.gov/ceres-fm6-iraman-photos.html
Initial field work with the in situ Raman analysis identified that surface matters
- Scattering on surfaces is dependent on the light interactions with the material

Opportunity exist to engineer a witness monitoring program to pair with portable Raman spectroscopy
- Highly Reproducible
- Reduces impact to schedule
- Early detection within the AI&T phases
Existing witness plate materials were compared to conformal coated silicon wafers

- Gold Coated Silicon Wafers
- Un-doped Silicon Wafers
- Ultra High Vacuum Aluminum Foils (aka Non-Volatile Residue “NVR” Foils)
- Atomic Layer Deposition (ALD) Grown Metal Oxide Coatings on Silicon Wafers
  - ALD grown films are conformal and high quality films

Recent research indicates thin precious metal films, precious metal nanostructures, metal oxide thin films, and self assembled monolayer films can be coupled with a Raman spectrometer to provide enhanced analyte detection.

- SERS (Surface Enhanced Raman Spectroscopy) and SPR (Surface Plasmon Resonance) devices has enabled non-invasive enhanced detection of an analyte.
Surface Roughness Characterization

Using the Keyence® VHX-6000 Digital Microscope and the a VEECO® Atomic Force Microscope

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mean Roughness (Ra) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Foil</td>
<td>1093.3 μm</td>
</tr>
<tr>
<td>Gold Film Deposited onto Silicon Wafer</td>
<td>0.243 nm</td>
</tr>
<tr>
<td>ALD Grown HfO₂ onto Silicon Wafer</td>
<td>0.547 nm</td>
</tr>
<tr>
<td>Undoped Silicon Wafer</td>
<td>0.210 nm</td>
</tr>
</tbody>
</table>

AFM Image of ALD Grown HfO₂ onto a Silicon Wafer, 5 µm Scale

AFM Image of Gold Coated Silicon Wafer, 5 µm Scale
A 25% solution of Down Corning® (DC) 704 silicone oil in a 50/50 hexane/isopropyl alcohol solution is drop casted onto each sample.

Once the samples are dry, each sample is characterized with the portable B&W Tek i-Raman® Plus Raman spectrometer over an average of three scans during a 10 second acquisition with 20% laser power.
Raman bands unique to DC-704 are observed on the aluminum foil and the gold coated silicon wafer witness plates at peak locations I, II, III, IV, and V.

Al foil and the gold coated silicon wafer witness plates enable the most conclusive detection of the silicone contaminant of DC-704

- Highest Intensity of these peaks

<table>
<thead>
<tr>
<th>Raman Band Location</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>487 cm(^{-1})</td>
<td>Si-O-C</td>
</tr>
<tr>
<td>520 cm(^{-1}), 548 cm(^{-1})</td>
<td>Si-O-Si</td>
</tr>
<tr>
<td>605 cm(^{-1})</td>
<td>Si-O-Si</td>
</tr>
<tr>
<td>1702 cm(^{-1})</td>
<td>Si-O-Si</td>
</tr>
<tr>
<td>2876 cm(^{-1})</td>
<td>Si-O-Si</td>
</tr>
</tbody>
</table>
Existing self cleaning technology established TiO$_2$ is ideal for cleaning organic contamination

- Construction Industry
- Water Treatment
- Patent US6290180B1, Browall and Wei with Lockheed Martin Corporation, “Photocatalytic coatings on optical solar reflectors to decompose organic contaminants”

Proof of Concept Experiment with Silicone contaminated ALD grown TiO$_2$ thin films on Corning 2947 glass slides

- 50 cycles (est. 2nm)
- 75 cycles (est. 3 nm)
- 300 cycles (13.96 nm +/-0.03 nm)
- 500 cycles (21.08 nm ±0.020 nm)

To determine transmission, a Perkin Elmer Lambda 950 UV Visible spectrophotometer characterizes each sample

- Before contamination
- After contamination
- After UV irradiation

Each sample is then exposed to a 325 nm He-Cd Laser for 30 minutes
Transmission Characterization of 2 nm TiO₂ vs 20 nm TiO₂

Δ + 0.95% Above
90% Transmittance

Δ + 15.1% Below
90% Transmittance

• 1. Is TiO₂ able to remove the contaminant? ✓
• 2. What is the optimal performance after UV irradiation? ✓
• 3. Which surface properties in TiO₂ can control the self-cleaning effect? ✓

30 minutes of UV Irradiation
# Summary of Ra Value of TiO$_2$ and Self-Cleaning Effect

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electro Magnetic Range</th>
<th>Observed Self-Cleaning after UV Irradiation?</th>
<th>Percent Increase in Transmission</th>
<th>Transmission Above 90% After UV Irradiation?</th>
<th>Crystalline Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 nm TiO$_2$ on Corning Glass</td>
<td>320 nm to 370 nm</td>
<td>✓</td>
<td>0.95%</td>
<td>✓</td>
<td>Brookite</td>
</tr>
<tr>
<td>2 nm TiO$_2$ on Corning Glass</td>
<td>400 nm to 800 nm</td>
<td>✓</td>
<td>1.07%</td>
<td>✓</td>
<td>Brookite</td>
</tr>
<tr>
<td>2 nm TiO$_2$ on Corning Glass</td>
<td>880 nm to 2300 nm</td>
<td>✓</td>
<td>0.88%</td>
<td>✓</td>
<td>Brookite</td>
</tr>
<tr>
<td>20 nm TiO$_2$ on Corning Glass</td>
<td>320 nm to 370 nm</td>
<td>✓</td>
<td>15.1%</td>
<td>X</td>
<td>Amorphous</td>
</tr>
<tr>
<td>20 nm TiO$_2$ on Corning Glass</td>
<td>400 nm to 800 nm</td>
<td>✓</td>
<td>5.2%</td>
<td>X</td>
<td>Amorphous</td>
</tr>
<tr>
<td>20 nm TiO$_2$ on Corning Glass</td>
<td>880 nm to 2300 nm</td>
<td>X</td>
<td>-2.89%</td>
<td>X</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>
Surface roughness can increase the resonance angle
  • Impacting coupling between the Raman laser and the analyte adsorbed to the surface of the witness plate
  • Multiple studies link higher Ra values to enhanced Raman detection of analytes

The HfO$_2$ coated silicon wafer has a highest mean roughness values that is higher than the gold coated silicon wafer. HfO$_2$ coated silicon wafer was not able to detect all the Raman bands common to the silicone contaminant.
  • Gold has a surface plasmon that is in the visible range.
  • Al has a surface plasmon that is in the UV range
  • The natural surface plasmon of the gold could be coupling with the Raman laser wavelength of 785 nm which would amplify the signal detection capabilities

This study indicates that surface does matter for Raman spectroscopy.

Preliminary work identified the potential of ultra thin ALD grown TiO$_2$ coatings to create contamination tolerant optics

Future work will be to test the ALD grown coatings within a vacuum environment as witness plates and contamination tolerant optics
Questions?
References


2. Rutherford, Gugu; Sealsly, Elaine; O’Connell, Joseph; Thornblom, Mark; Xiao, Bo; Bahoura, Messaoud; ALD-Grown Metal Oxide Films for the Detection of Contaminants on Spacecraft. (Journal of IEST, in submission).

3. Wooldridge, Eve M; Henderson-Nelson, Kelly; Woronowicz, Michael; Novo-Gradac, Kevin; Perry, Radford L.; Macias, Matthew; Arenberg, Jon; Eggles, J. Contamination control requirements implementation for the James Webb Space Telescope (JWST), Part 1: Optics, instruments and thermal vacuum testing. SPIE 9196, 1–9 (2014).


