http://engineering.larc.nasa.gov/

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

Gugu N. Rutherford*[a] and Elaine Seasly[a]

Brandon A. Walker[b], Bo Xiao[b] and Messaoud Bahoura[b]

[a]NASA Langley Research Center, 21 Langley Blvd, Hampton, VA USA 23681-2199

[b]Norfolk State University, 700 Park Avenue Norfolk, VA 23504, USA

Outline

- 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

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

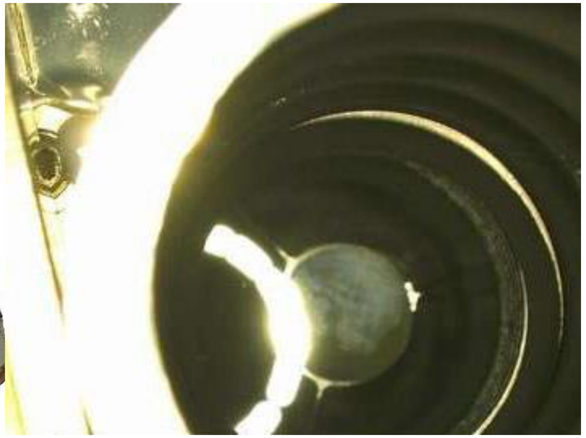
These methods are used intermittently through out the life cycle. Often contamination concerns can be further in the lifecycle before it is identified as a risk.

In Situ Raman Spectroscopy for Detection of Contaminants on Spacecraft

- Recently, in situ detection of a contaminant has occurred on spacecraft.

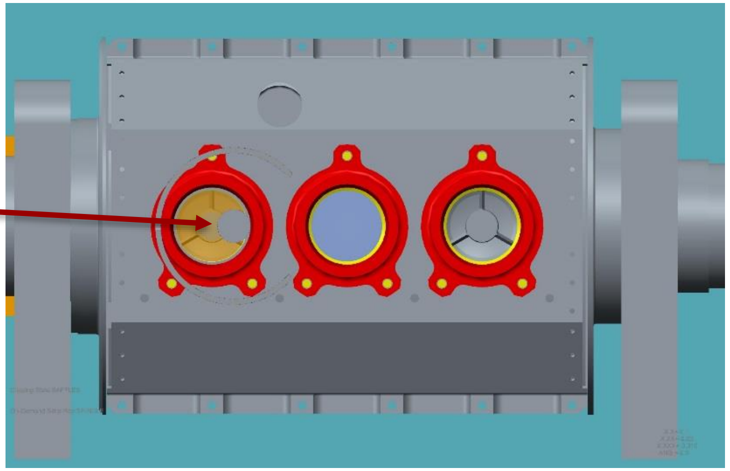
https://fpd.larc.nasa.gov/ceres-fm6-iraman-photos.html

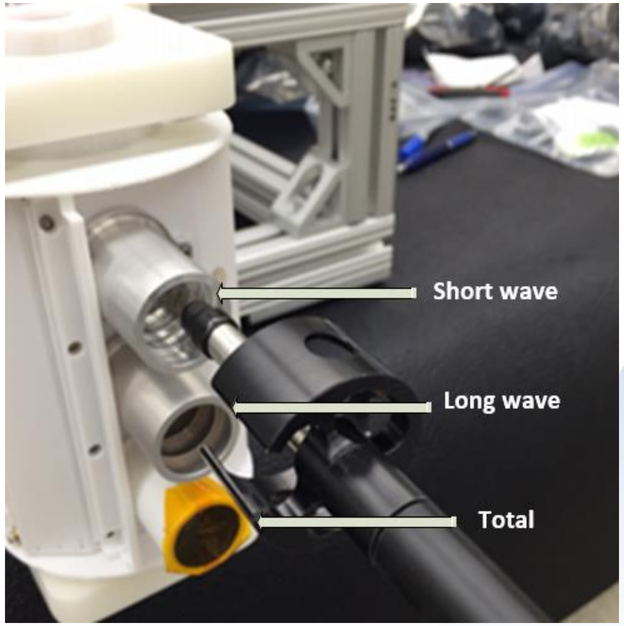
CERES FM 6



Credit: B&W Tek, http://bwtek.com/raman-technology/portable/

Location of Molecular Contaminant on The CERES FM6 Short Wave Filter





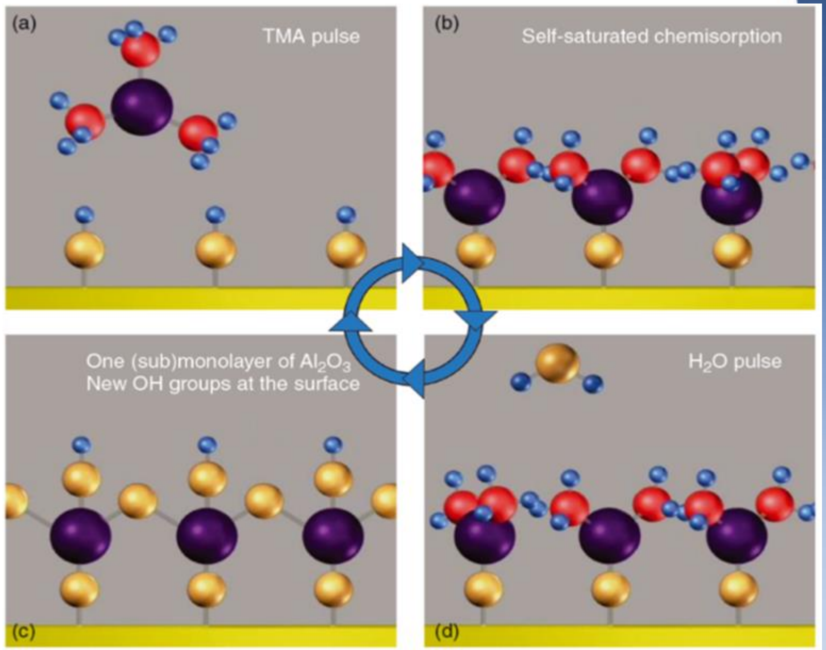
Solution to In Situ Raman Detection

- **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

Evaluation of Various Materials

- **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

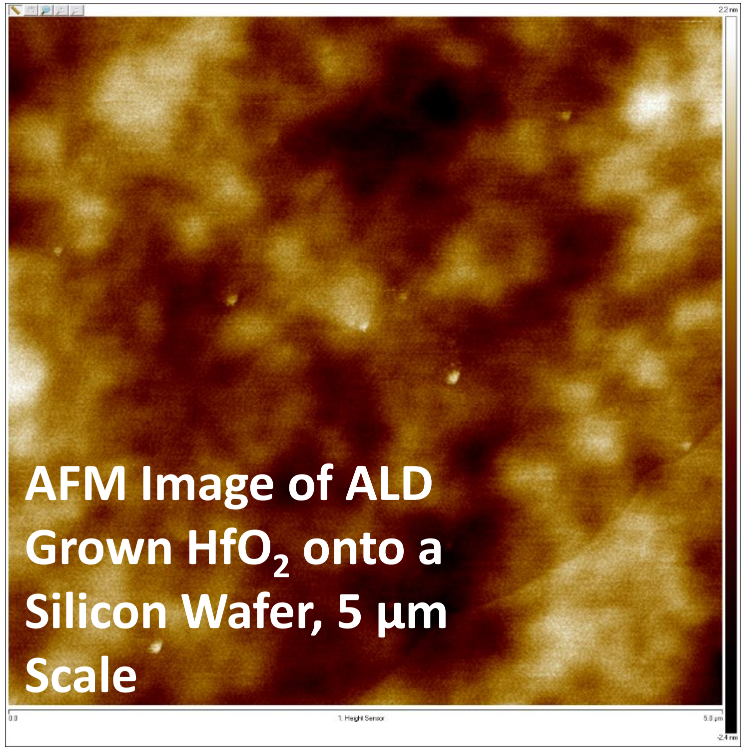


- **Recent research indicates thin precious metal films, precious metal nanostructures, metal oxide thin films, and self assembled monolayer films can be coupled with a Raman spectrometer to provide enhanced analyte detection.**
  - SERS (Surface Enhanced Raman Spectroscopy) and SPR (Surface Plasmon Resonance) devices has enabled non-invasive enhanced detection of an analyte.

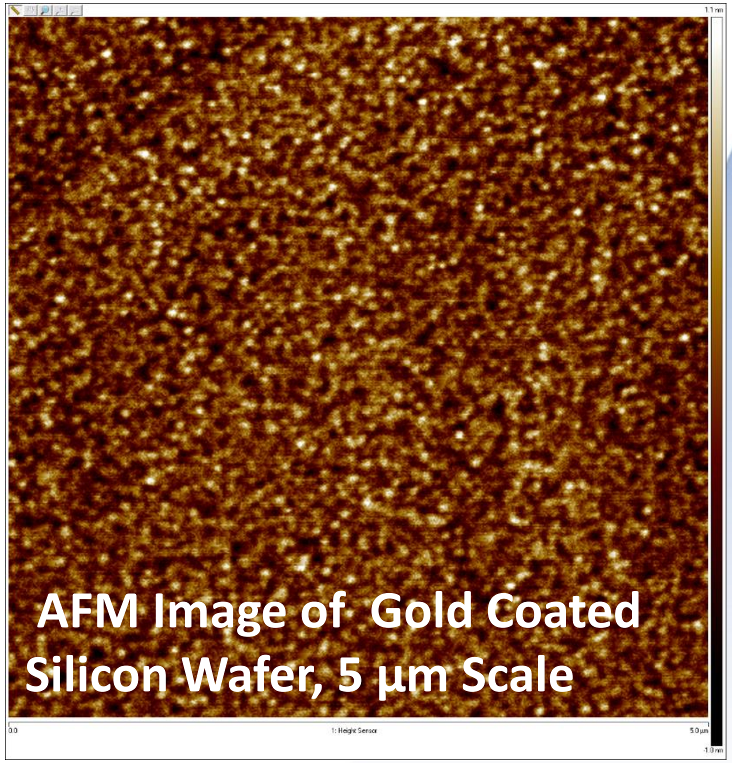
Surface Roughness Characterization

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

Sample ID	Mean Roughness (Ra) Value
Aluminum Foil	1093.3 µm
Gold Film Deposited onto Silicon Wafer	0.243 nm
ALD Grown HfO_2 onto Silicon Wafer	0.547 nm
Un doped Silicon Wafer	0.210 nm



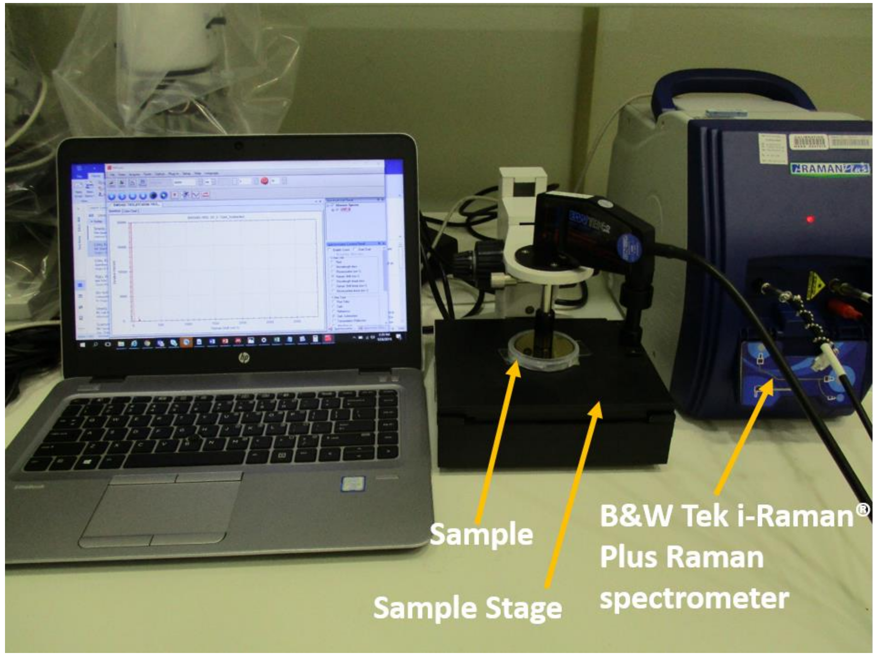
AFM Image of ALD Grown HfO_2 onto a Silicon Wafer, 5 µm Scale



AFM Image of Gold Coated Silicon Wafer, 5 µm Scale

Determination of Silicone Contamination with the Portable Raman Spectrometer

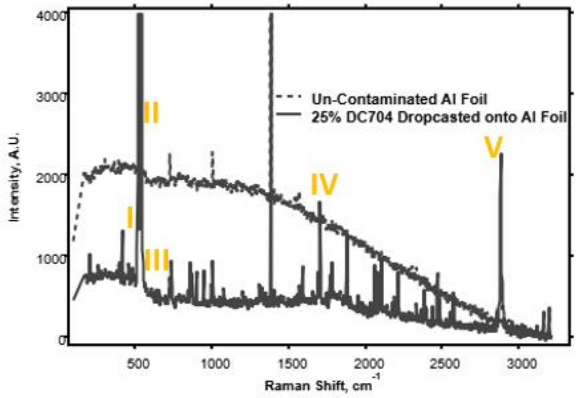
- A 25 % solution of Down Corning® (DC) 704 silicone oil in a 50/50 hexane/ isopropyl alcohol solution is drop casted onto each sample
- Once the samples are dry, each sample is characterized with the portable B&W Tek i-Raman® Plus Raman spectrometer over an average of three scans during a 10 second acquisition with 20% laser power.

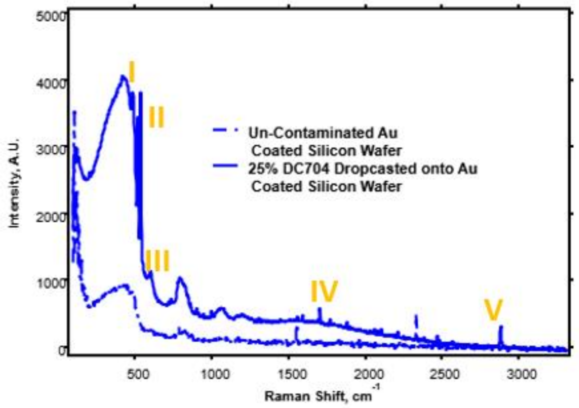


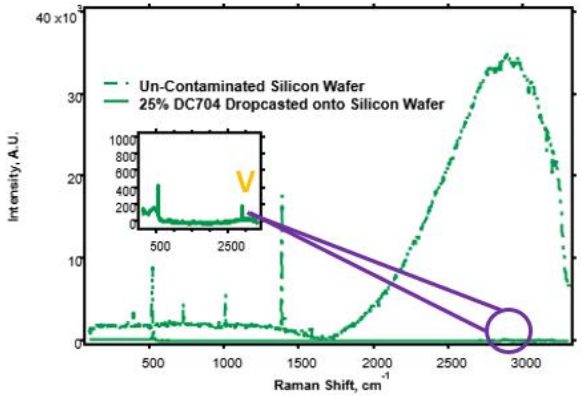
Raman Spectroscopy Witness Monitoring Program

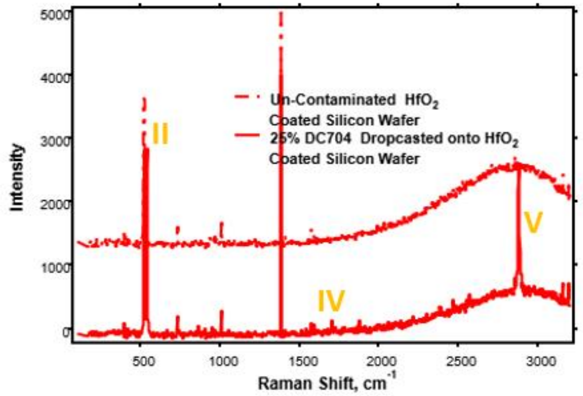
- **Raman bands unique to DC-704 are observed on the aluminum foil and the gold coated silicon wafer witness plates at peak locations I, II, III, IV, and V.**
- **Al foil and the gold coated silicon wafer witness plates enable the most conclusive detection of the silicone contaminant of DC-704**
  - Highest Intensity of these peaks

Raman Band Location	Functional Group
487 cm^{-1}	Si-O-C
520 cm^{-1}, 548 cm^{-1}	Si-O-Si
605 cm^{-1}	Si-O-Si
1702 cm^{-1}	Si-O-Si
2876 cm^{-1}	Si-O-Si









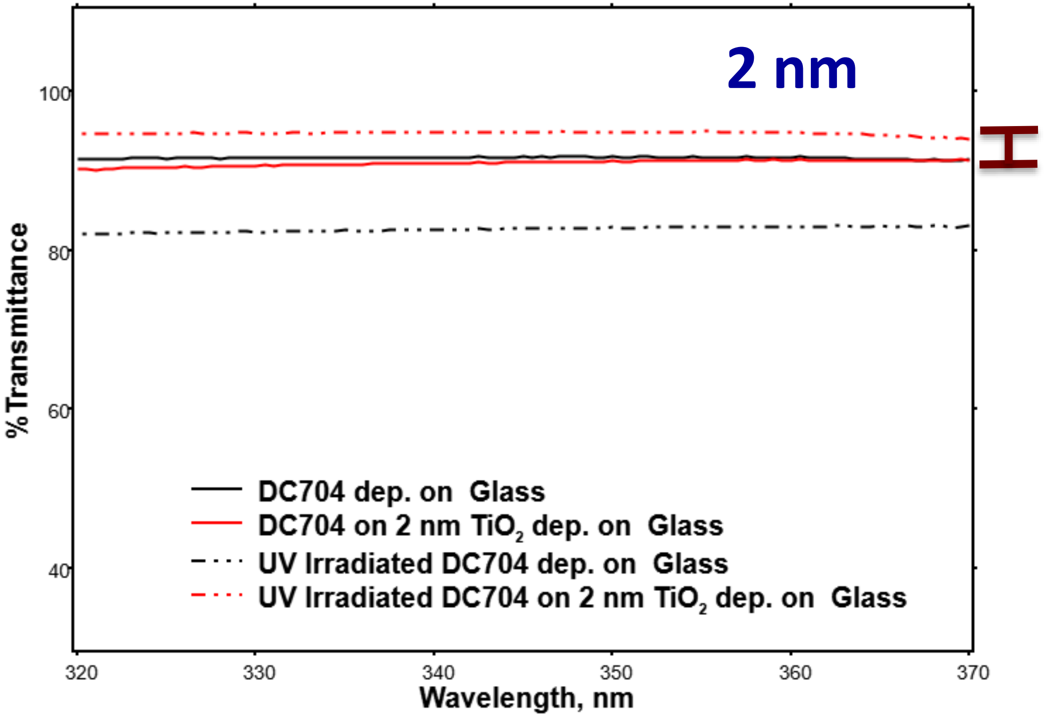
ALD Grown TiO_2 for Contamination Tolerant Optics

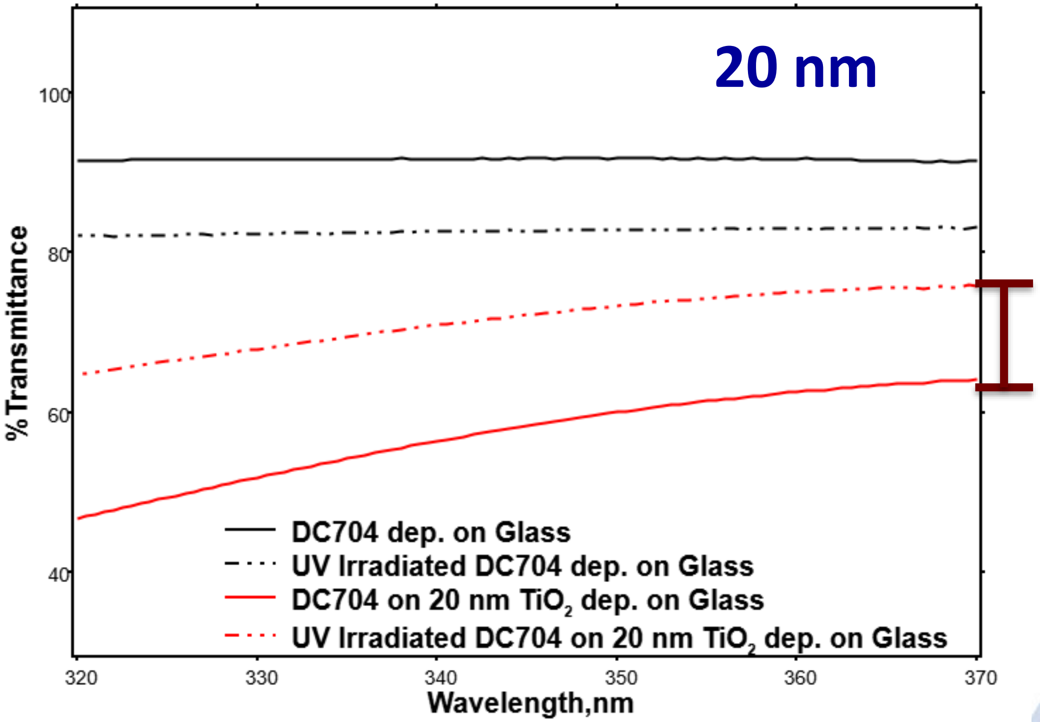
- **Existing self cleaning technology established TiO_2 is ideal for cleaning organic contamination**
  - Construction Industry
  - Water Treatment
  - Patent US6290180B1, Browall and Wei with Lockheed Martin Corporation, "Photocatalytic coatings on optical solar reflectors to decompose organic contaminants"
- **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 $\pm$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 TiO_2 vs 20 nm TiO_2

Δ + 0.95% Above 90% Transmittance

Δ + 15.1% Below 90% Transmittance





30 minutes of UV Irradiation

- 1. Is TiO_2 able to remove the contaminant? ☑
- 2. What is the optimal performance after UV irradiation? ☑
- 3. Which surface properties in TiO_2 can control the self-cleaning effect? ☑

Summary of Ra Value of TiO_2 and Self-Cleaning Effect

Sample	Electro Magnetic Range	Observed Self-Cleaning after UV Irradiation?	Percent Increase in Transmission	Transmission Above 90% After UV Irradiation?	Crystalline Phase
2 nm TiO_2 on Corning Glass	320 nm to 370 nm	☑	0.95%	☑	Brookite
2 nm TiO_2 on Corning Glass	400 nm to 800 nm	☑	1.07%	☑	Brookite
2 nm TiO_2 on Corning Glass	880 nm to 2300 nm	☑	0.88%	☑	Brookite
20 nm TiO_2 on Corning Glass	320 nm to 370 nm	☑	15.1%	☒	Amorphous
20 nm TiO_2 on Corning Glass	400 nm to 800 nm	☑	5.2%	☒	Amorphous
20 nm TiO_2 on Corning Glass	880 nm to 2300 nm	☒	-2.89%	☒	Amorphous

Conclusion and Path Forward

- **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

- 1. Tribble, A. C. *et al. Contamination Control Engineering Design Guidelines for the Aerospace Community*. (1996).
- 2. Rutherford, Gugu; Seasly, Elaine; O'Connell, Joseph; Thornblom, Mark; Xiao, Bo; Bahoura, Messaoud; *ALD-Grown Metal Oxide Films for the Detection of Molecular 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; Egges, 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).
- 4. Kuzma, A., Chovan, J., Uherek, F. & Weis, M. Surface Plasmon Resonance of Gold and Silver Nanoparticle Monolayers: Effect of Coupling and Surface Oxides. *Proc. SPIE* 8915, 1–6 (2013).
- 5. Cui, L., Butler, H. J., Martin-Hirsch, P. L. & Martin, F. L. Aluminium foil as a potential substrate for ATR-FTIR, transflection FTIR or Raman spectrochemical analysis of biological specimens. *Anal. Methods* 8, 481–487 (2016).
- 6. Knight, M. W. *et al.* Aluminium for plasmonics. *ACS Nano* 8, 834–840 (2014).
- 7. Yang, Z., Liu, C., Gao, Y., Wang, J. & Yang, W. Influence of surface roughness on surface plasmon resonance phenomenon of gold film. *Chinese Opt. Lett. Vol. 14, Issue 4, pp. 042401-*14, 042401 (2016).
- 8. Christesen, S. D., Iii, A. W. F., Emmons, E. D. & Guicheteau, J. A. Raman Detection of Explosives. in *Laser-Based Optical Detection of Explosives* 99–117 (2015).
- 9. Lambert, Joseph B.; Shurvell, Herbert F.; Lightner, David A.; Cooks, G. R. *Introduction to Organic Spectroscopy*. (Macmillan Publishing Company, 1987).
- 10. Jung, J. & Pedersen, T. G. Polarizability of nanowires at surfaces: exact solution for general geometry. *Opt. Express* 20, 3663–3674 (2012).
- 11. Campuzaon, R.G.; Mendoza, D. Plasmonic resonances in ordered and disordered aluminum nanocavities arrays. *J. Phys. Conf. Ser.* 792, 3–10 (2017).
- 12. Wang, X.-Y. *et al.* Lasing Enhanced Surface Plasmon Resonance Sensing. *Nanophotonics* 6, 472–478 (2017).
- 13. Reiner, A. T., Fossati, S. & Dostalek, J. Biosensor platform for parallel surface plasmon-enhanced epifluorescence and surface plasmon resonance detection. *Sensors Actuators, B Chem.* 257, 594–601 (2018).
- 14. Ritala, M. & Leskela, M. Chapter 2 - Atomic Layer Deposition. *Hand Book on Thin Film Materials* 103–159 (2002). doi:http://dx.doi.org/10.1016/B978-012512908-4/50005-9
- 15. Hao, Q. *et al.* Aluminum plasmonic photocatalysis. *Sci. Rep.* 5, 1–7 (2015).