Sensitive Nanomaterials Detection and Analysis in Solution

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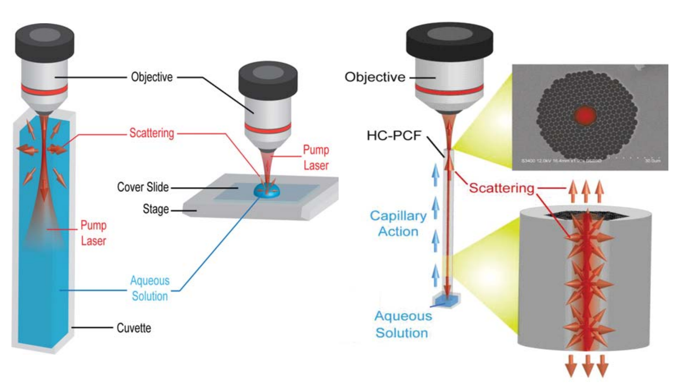
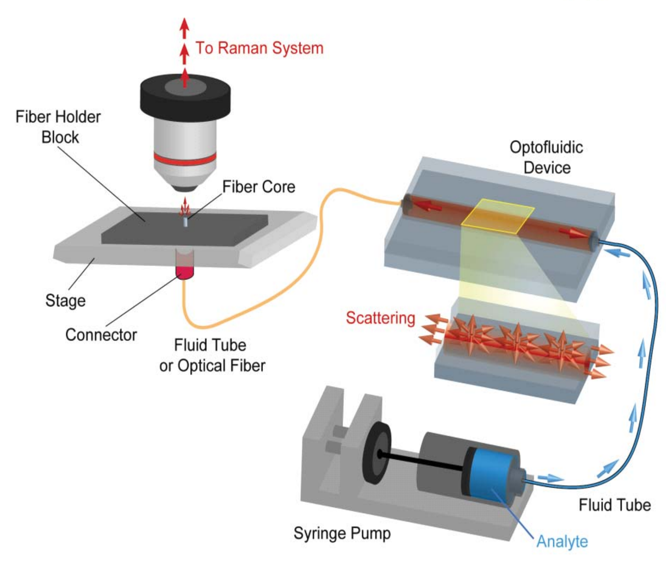
Motivation

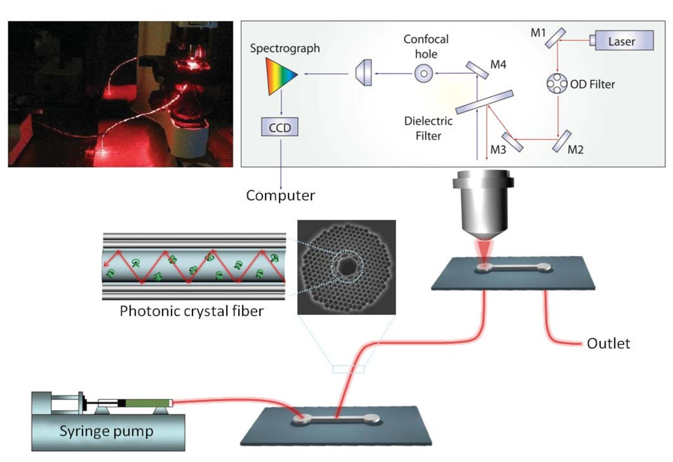
- Wafers are often exposed to aqueous solutions or liquid chemicals at various stages of the semiconductor manufacturing process. For example, of any metal contaminants in process liquids.
- Any contamination of these liquids reduces process yields.
- As defined by the ITRS, the maximum tolerable contaminant particle size scales roughly as the half-pitch dimension of a given technology node
- Early detection of contamination in the process liquids, rather than on the wafer after processing, allows for better yield.
- Particle detection in solution with chemical specificity is a key to improve yield.
- Most reported solutions are not readily adaptable to monitor process liquid quality at the distribution end-point (i.e. at the process tools).
- No sensitive means to identify nanomaterials in liquids at present:
- Laser based particle counting requires the nanomaterials size and type/nature to be known apriori. It cannot detect dissolved chemical contaminants.
- Optical spectroscopy techniques can be optimal candidates to monitor and quantify nanomaterials in water when their sensitivity is enhanced.

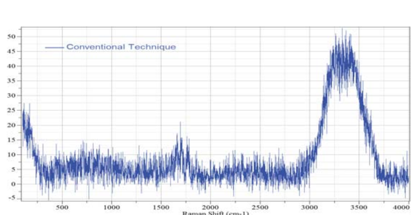
Background

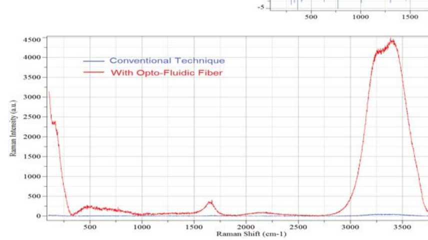
- Raman Spectroscopy probes vibrational modes of a molecular system.
- By noting the intensities of frequency shifted photons, we can use this as a unique fingerprint of that molecule.
- When comared to the cross section of variety of optical processes, Raman is the weakest.
- Using standard measurement approaches. Raman threshold sensitivities are near 0.1 mol/L.











- Various compounds will now be tested using this technique after they diluted in ultra purte water (UPW).
- The Raman spectrum of UPW will be obtained to serve as a reference.

Idenitfying Nanomaterials in Ultra Pure Water

Ultra Pure Water:

- Peaks from the vibrational modes of water are very evident in the 3000 cm-1 region.
- Silica peaks dominant in the 400 cm-1 region.
- Standard spectrum of water clearly observed.

Aluminium Oxide Samples:

- According to the literature Alumina modes are located at: 184.88, 252.81, 381.87, 419.23, 484.90, 538.11, 578.87, 646.80, 675.10, 710.20, 753.22, 815.49 and 852.85 cm-1
- Peak fitting with modes at 161.28 & 372.69 cm-1 accurately matches the Alumina spectrum after the background is subtracted
- The modes after the 100-400 cm-1 region cannot be accurately analyzed due to the presence of strong silica modes which coincide with that of Alumina; those can be attributed the silica fibre

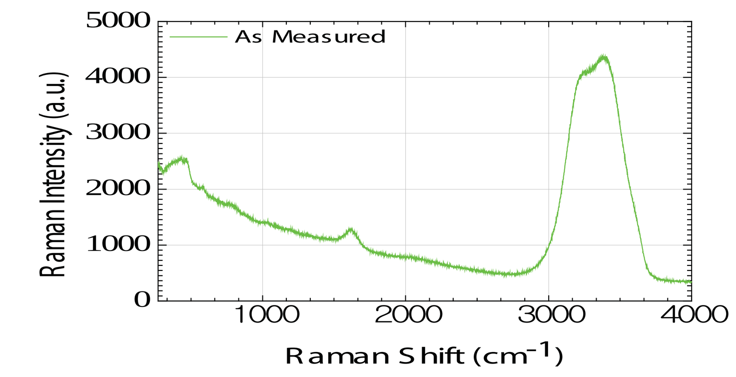
Copper Samples:

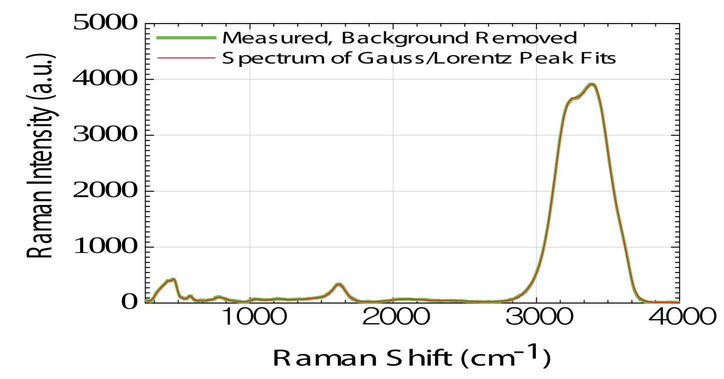
- Cu modes are located at: 192.64, 208.32, and 575.5 cm-1 as reported in the literature.
- The obtained spectra includes modes from both the Cu and the silica from which the fiber is made.
- Only one peak that is native to Cu is detected at 586.2 cm-1. The majority of the peaks belong to silica or UPW.

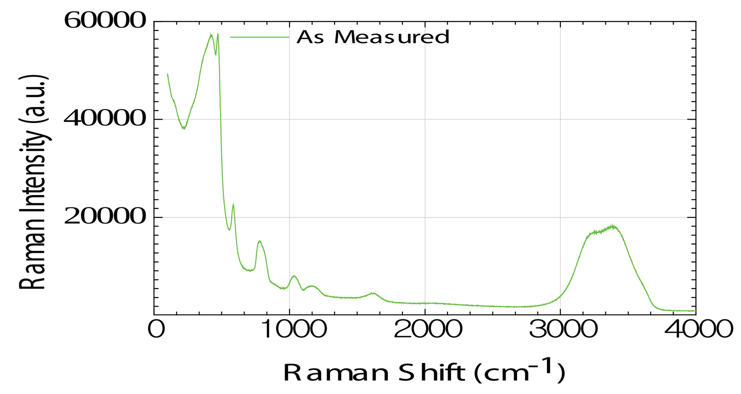
Aluminium Oxide - Different Structures

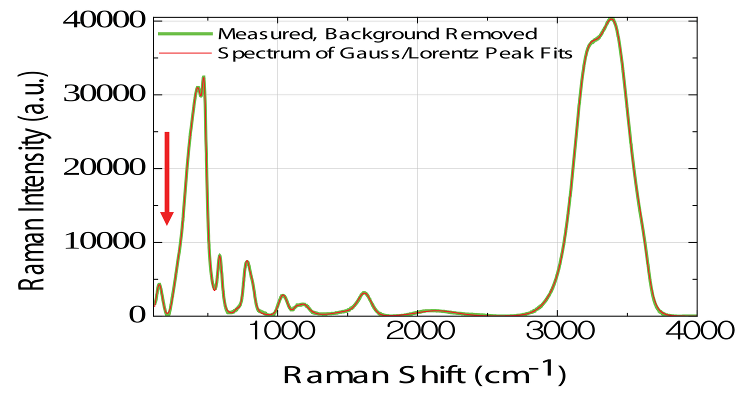
- Another aim of this work is to discern whether changes in nanoparticle structure (Alumina) will be evident and detectable through the Raman Spectra.
- From the information presented in the table and spectrum, one can conclude that while keeping concentration and particle size constant; the orientation of the Alumina nanoparticle has a significant impact on the Raman Spectra. Therefore the difference in structur can easily be discerned from the distinct modes of both samples.
- The Full Width Half Maximum (FWHM) is significantly broader in the gamma samples relative to its alpha sample.

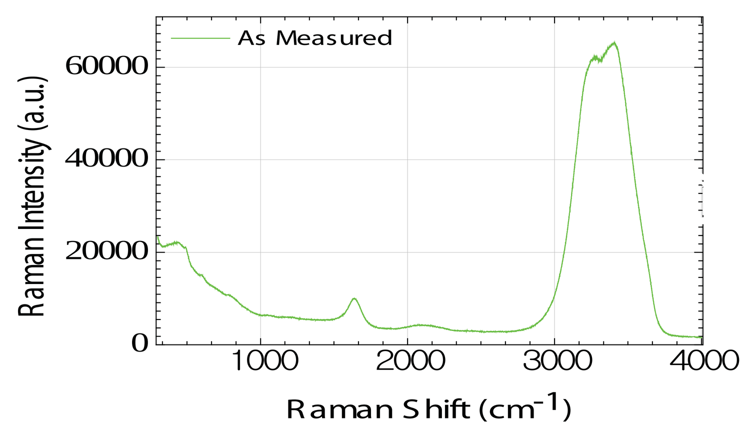
Al_2O_3 -30nm-alpha cm-1	Al_2O_3 -30nm-gamma cm-1
378.492	344.009
417.039	362.146
430.986	416.012
487.434	445.473
538.268	475.797
633.602	495.795
	601.085
	676.156
	716.258
	726.830
	783.825

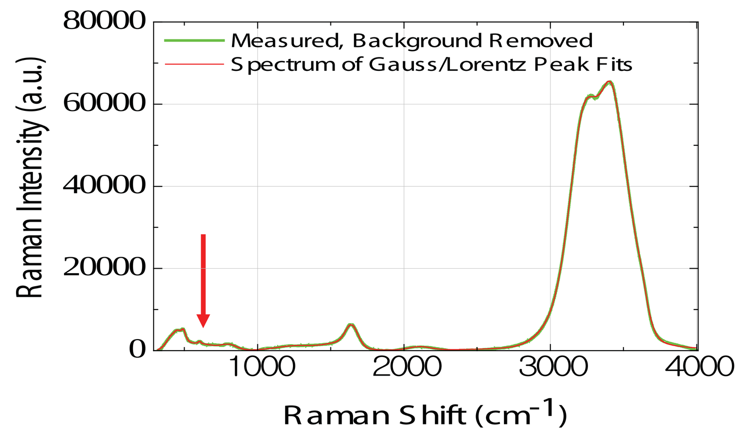


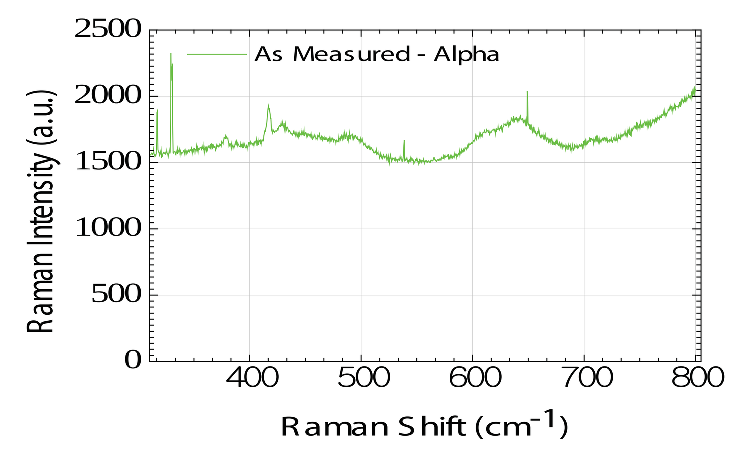


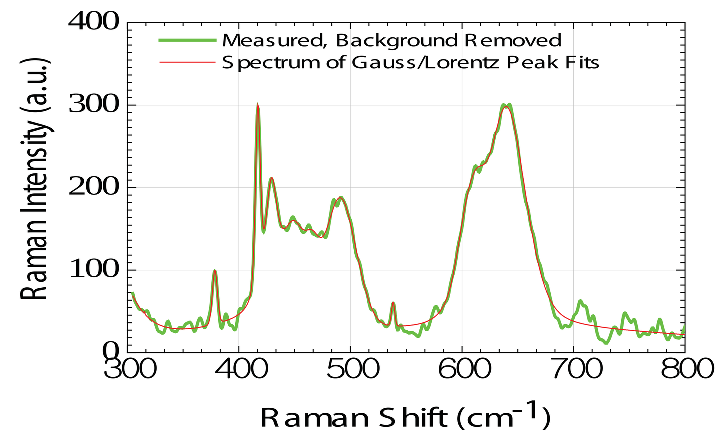


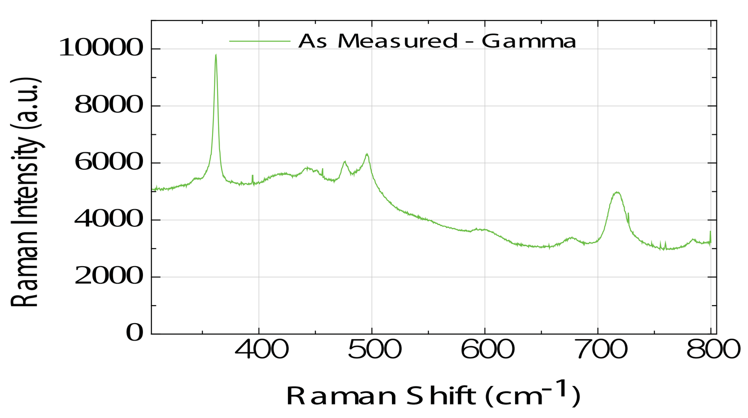


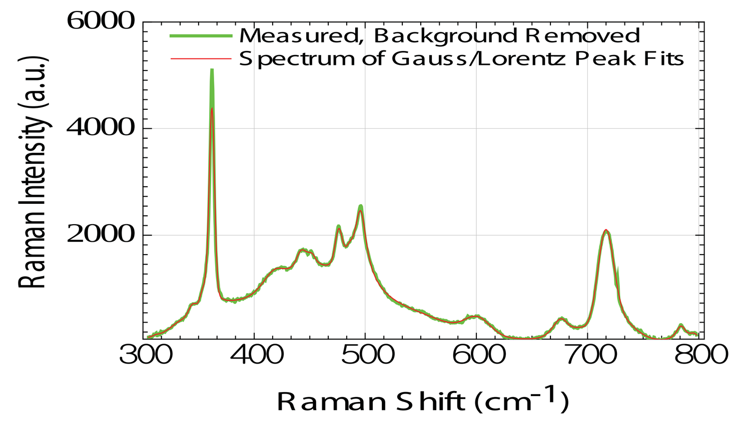












Nanoparticle Size Identification

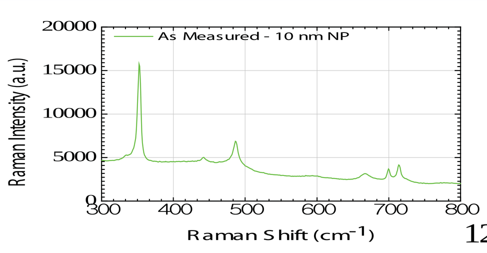
Similar phase but diferent size:

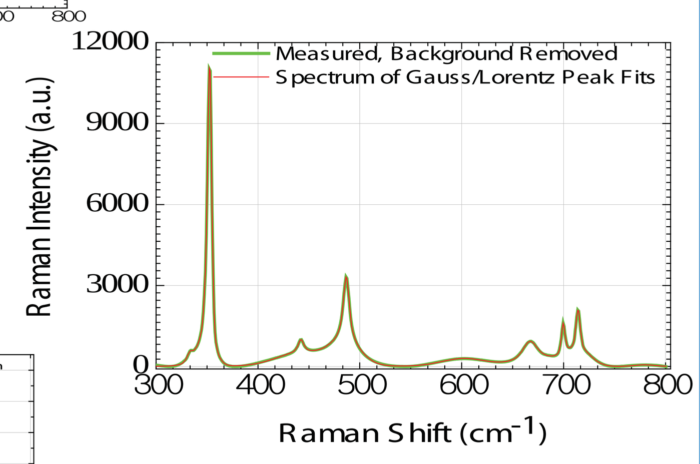
- Another aim of this work is to discern whether changes in nanoparticle size (Alumina) will be edetectable.
- For a similar concentration and crystal orientation, the size of the Alumina nanoparticle has a significant impact on the Raman spectra.
- Therefore the difference in size definitely impacts the Raman spectra in two ways:

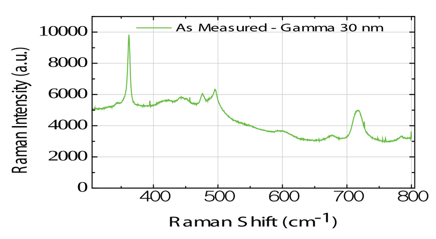
1.) The similar vibrational modes present in both samples are shifted relative to one another.

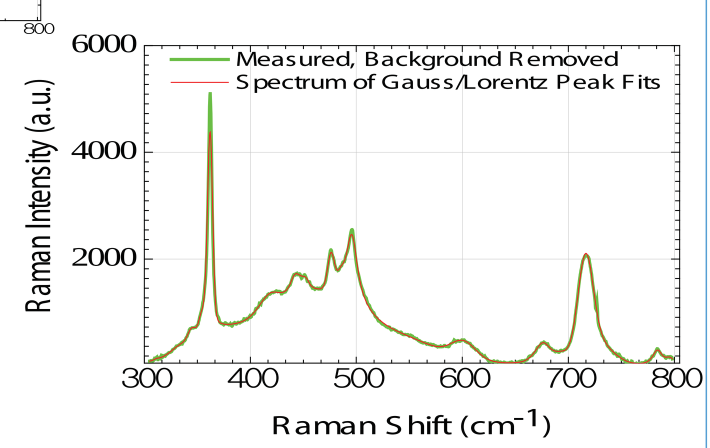
2.) There are vibrational modes that are unique and only present in one of the two samples but not common to both.

Al_2O_3 -30nm-gamma cm-1	Al_2O_3 -10nm-gamma cm-1	Shift Difference in cm-1 (Absolute Value)
344.009	334.133	9.876
362.146	352.215	9.931
416.012	Not Present	----
445.473	442.199	3.274
475.797	Not Present	----
495.795	486.502	9.293
601.085	596.302	4.783
676.156	667.096	9.06
716.258	Not Present	----
726.830	Not Present	----
783.825	Not Present	----
Not Present	699.6	----
Not Present	714.2	----









Summary

- Raman in optofluidics is a promising technique to serve as an alternative to nanoparticle detection and monitoring in UPW.
- The technique has been used to investigate the Raman modes of various contaminates in UPW. Contaminates such as Cu and Alumina have been investigated, where the Raman analysis has provided information about their chemical nature. Their respective Raman modes were detected along with those from UPW.
- The chemical septicity offered by this technique provides it with an edge when compared to scattering based particle detection (widely used in the industry at present)
- The technique has been used to investigate the Raman modes of Alumina nanoparticles with various crystalline phases. Clear distinctions in the Raman modes can be identified in both structures Gamma and Alpha
- The technique has also been used to investigate the Raman modes of Alumina nanoparticles with various sizes. Raman peaks of the various nanoparticles sizes are not identical:
- With sufficient calibration, this technique can help ascertain the size of the nanoparticles.
- The sensitivity of this technique offers the capability to distinguish contaminates at 100s of micro-molar. However the route to enhancing this sensitivity is readily available and is being pursued to obtain nano-molar sensitivity levels

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