Applications of Raman Spectroscopy in Copper CMP

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Presenter

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Motivation

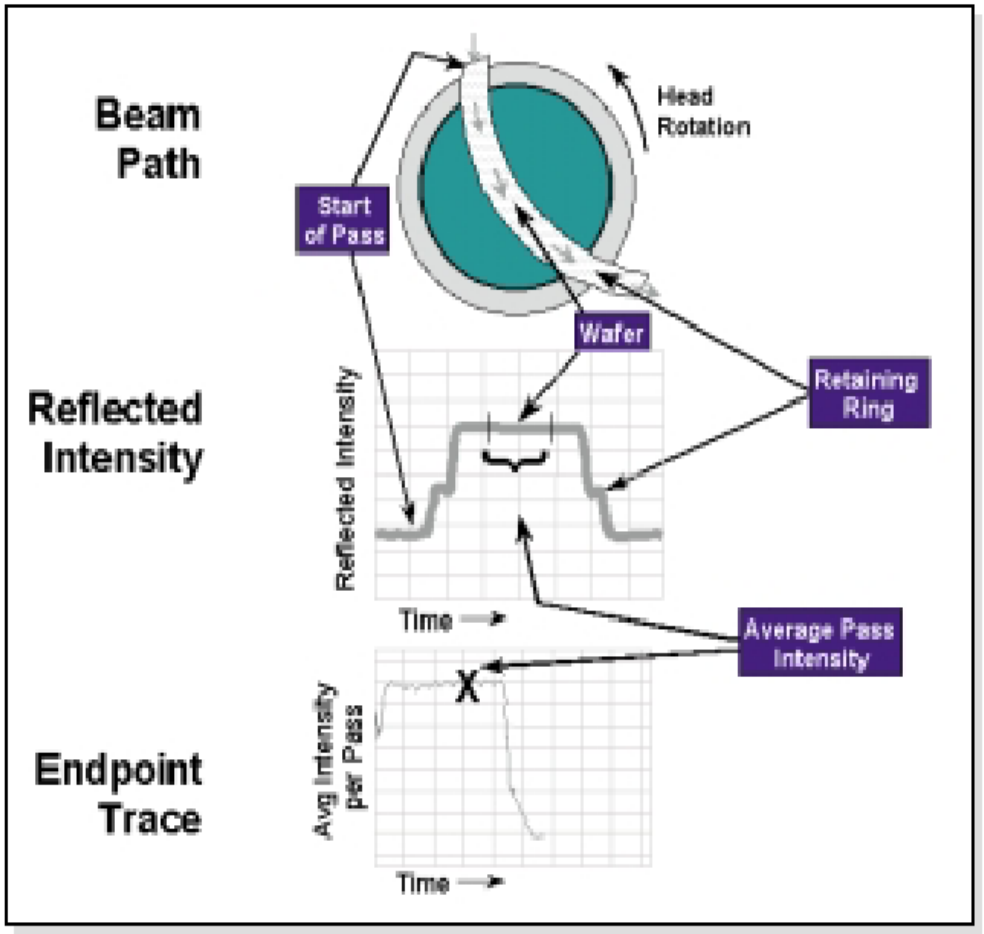
- In copper CMP, ***in-situ*** detection of barrier to dielectric layer transition is typically done using reflectivity measurements. Use of carbon containing low-k materials for dielectric layers have opened up the possibility of using spectroscopic techniques for detection of transition
- Information on chemical reactions between slurry and the wafer is usually obtained by analyzing the slurry waste collected from the pad; such a method may miss short lived intermediates. Slurry constituents and reaction products may have unique signatures that can be detected by spectroscopic techniques.
- Since CMP is carried out in aqueous media , infrared (IR) spectroscopic technique is not very desirable due to interference from strong water signal.

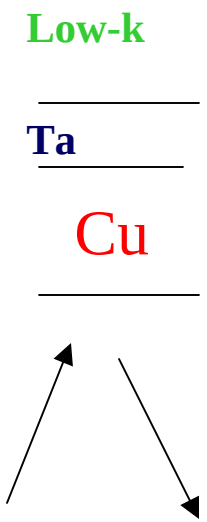
Objective of this work

To develop a Raman spectroscopy based technique to monitor metal CMP processes, *in-situ*.

End Point Detection System

(Applied Materials : ISRM)





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Outline

- Materials
- **Static mode Raman experiments**
  - Experimental set up
  - Spectra of low-k materials
  - Monitoring of low-k layer thickness
  - Barrier layer breakthrough
  - Raman vs. Reflectivity measurements
- **Dynamic mode Raman experiments**
  - Experimental setup
  - *In-situ* measurements (Si peak and CDO peak)
- **Chemistry**
- Conclusions and Acknowledgement

Materials

SiLK : 1500 Å SiLK on Si substrate
(highly crosslinked polyphenylene polymer)

CDO-I: 10,000 Å -thick carbon-doped oxide (CDO) film on Si substrate (source I).

CDO-II: 5,000 Å -thick CDO film on Si substrate (source II).

(Different alkyl siloxane precursors were used in the deposition of CDO-I and CDO-II)

Ta: 250 Å Ta on CDO-I & CDO-II

Raman Spectroscopy

Raman spectroscopy is a well-established technique that provides information on the vibrational frequencies of molecules from regions as small as 1 cubic micrometer.

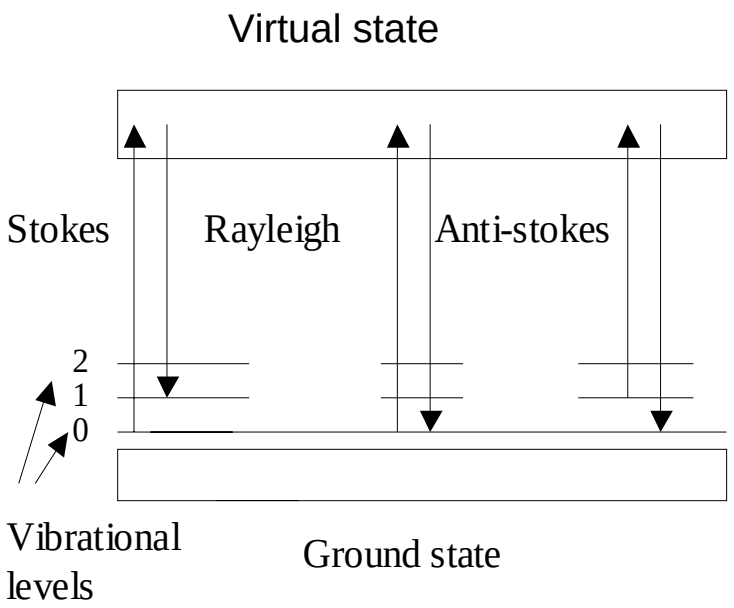
Scattered radiation, resulting from incident laser light of frequency $\mathbf{v_o}$, is of two types:

Rayleigh (NO frequency change, strong)

Raman (Frequency change, weak)

Stokes ($\mathbf{v_o}$-$\mathbf{v_m}$)

Anti-stokes($\mathbf{v_o}$+$\mathbf{v_m}$)



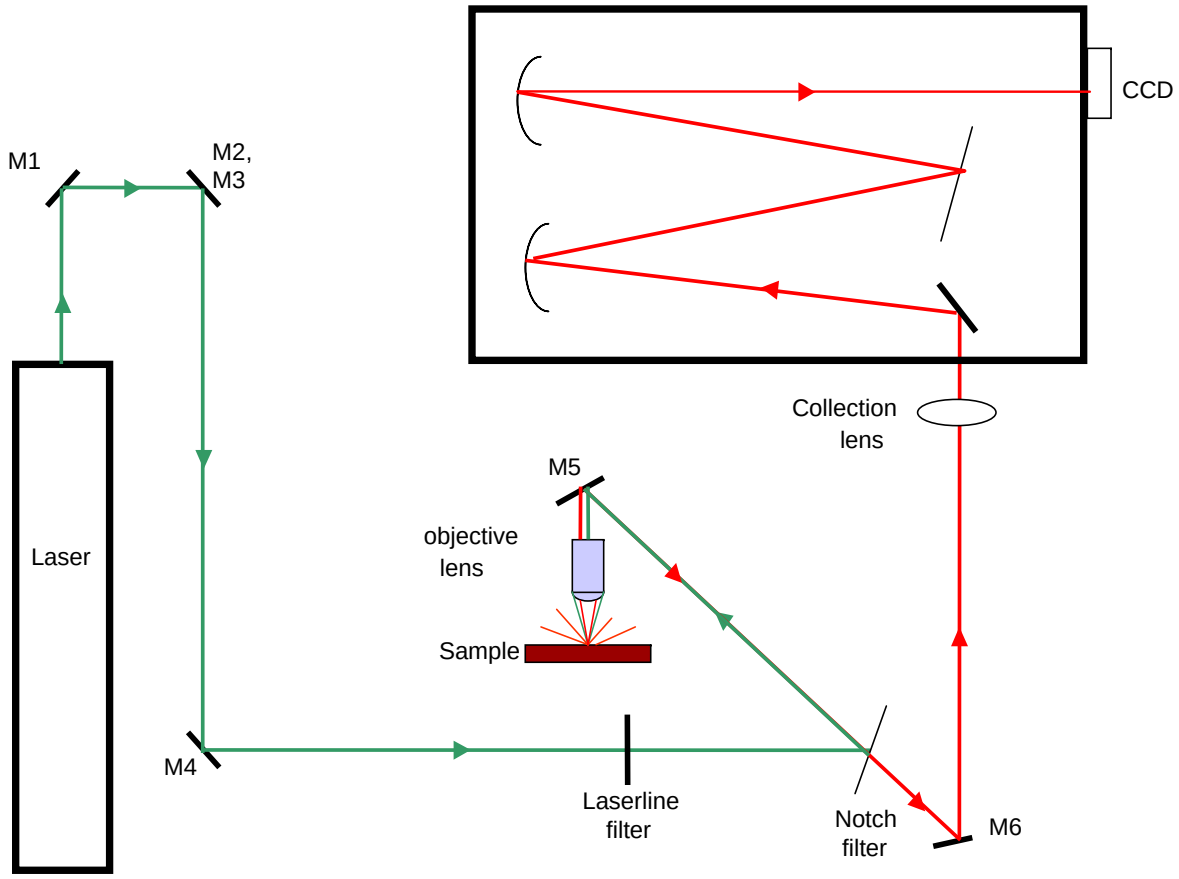
Schematic of Raman scattering

Raman vs IR spectroscopy

- Since water is a weak Raman scatterer, Raman spectra of sample in aqueous solution can be obtained without major interference from water vibrations. In contrast IR spectroscopy suffers from strong absorption of water.
  - . Raman spectroscopy depends on polarizability
  - . IR spectroscopy depends on dipole moment
- A small sample size is adequate to obtain Raman spectra. This is a great advantage over conventional IR when only a small quantity of sample is available.

J.R.Ferraro, K. Nakamoto, and C.W.Brown, *Introductory Raman Spectroscopy*, second Ed, Academic press, 2003.

Static Raman Setup



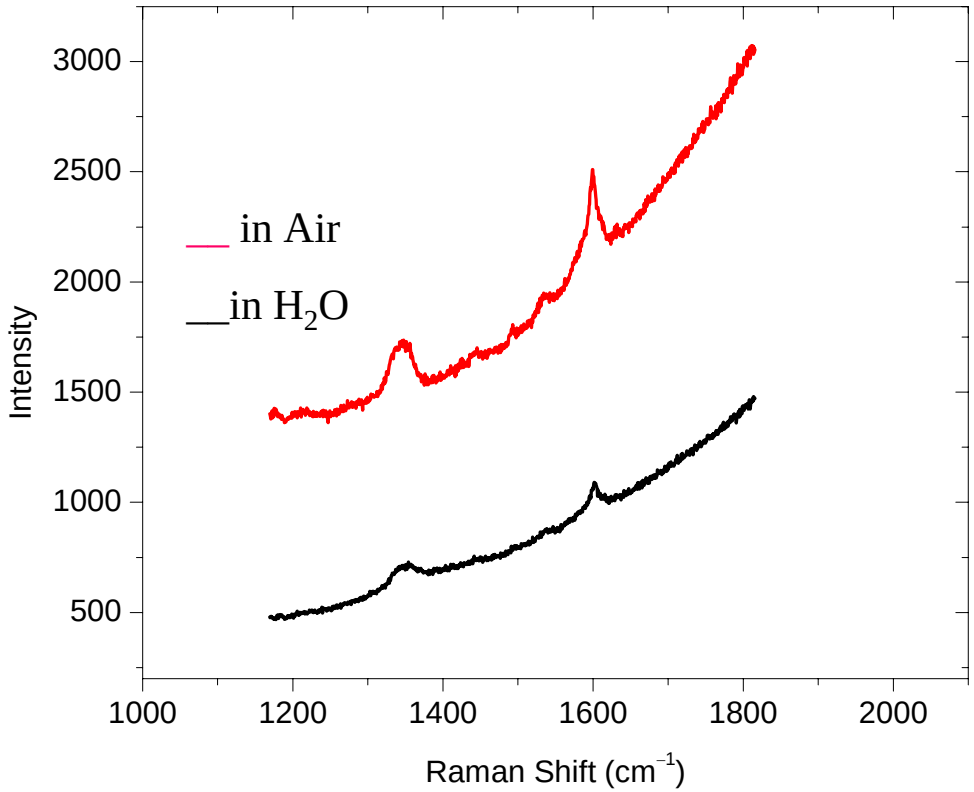
Raman spectrometer

Jobin Yvon HR 640, equipped with liquid N_2 cooled CCD.

Ar laser at 514.5 nm.

Diode laser at 784.85 nm

SiLK spectra in Air and Water



- Source:Diode Laser at 784.85nm
- Power: ~290 mW
- Confocal Hole = 300 µm
- Spectrometer Slit = 100 µm
- Collection Time: ~15 s
- Equipment : LabRam

Thickness of water layer: ~2mm

•Peaks due to the aromatic vibrations in SiLK appeared even in water medium, but less intense than those obtained in air.

•Peak intensity would be higher during CMP as the slurry thickness is much lower (~20 microns)

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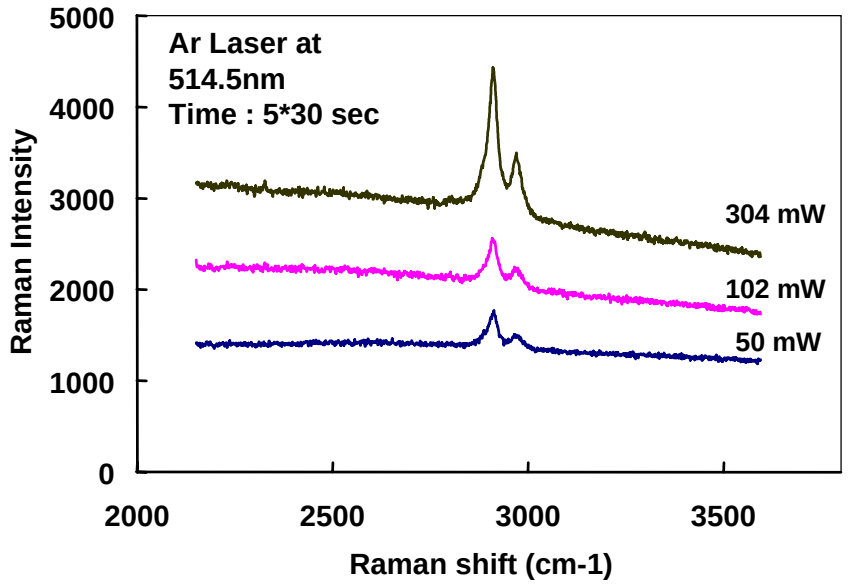
Raman spectra of CDO-I

- Strong peak at 2911 cm^{-1} and a shoulder peak at 2972 cm^{-1} are due the symmetric vibrations of C-H bond in CH_3 and CH_2 groups respectively.
- Same peaks observed in CDO-II.
- Increase in peak intensity with increase in laser power.
- Fluorescence was observed in CDO-I samples.



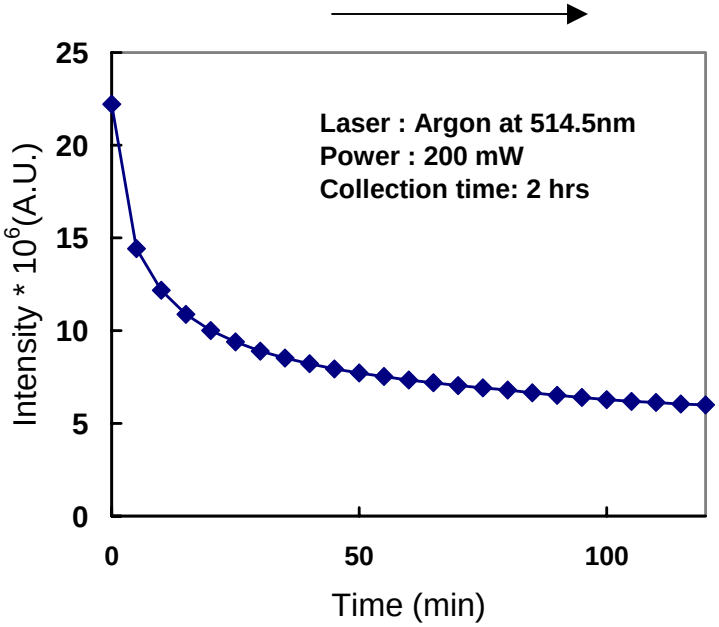
Raman spectra of CDO material at different laser powers.

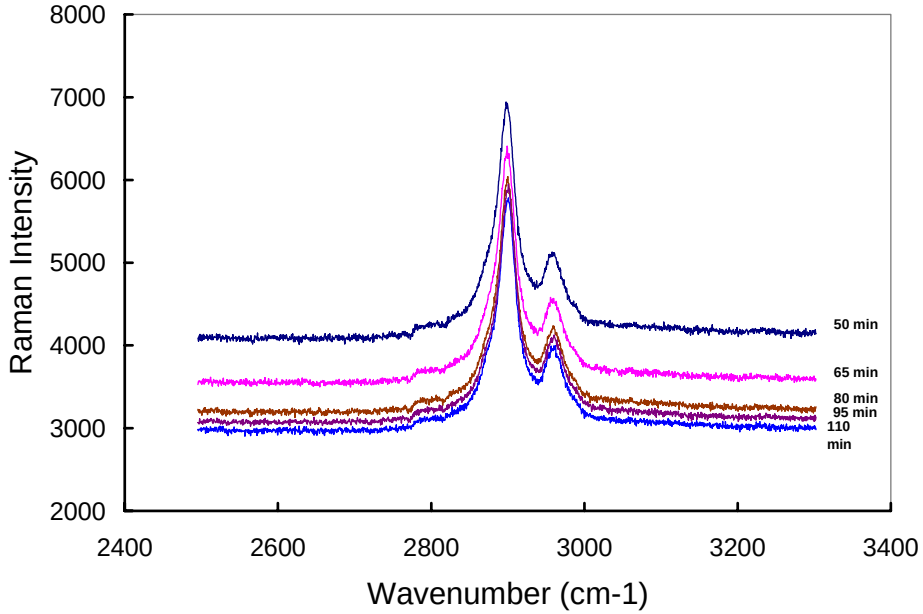
Additional Characterization of CDO Films

- Fluorescence
- Presence of liquid media
- Thickness of CDO layer

Fluorescence

- Fluorescence was observed when one type of CDO sample was exposed to the laser, and it eventually decreased with time.



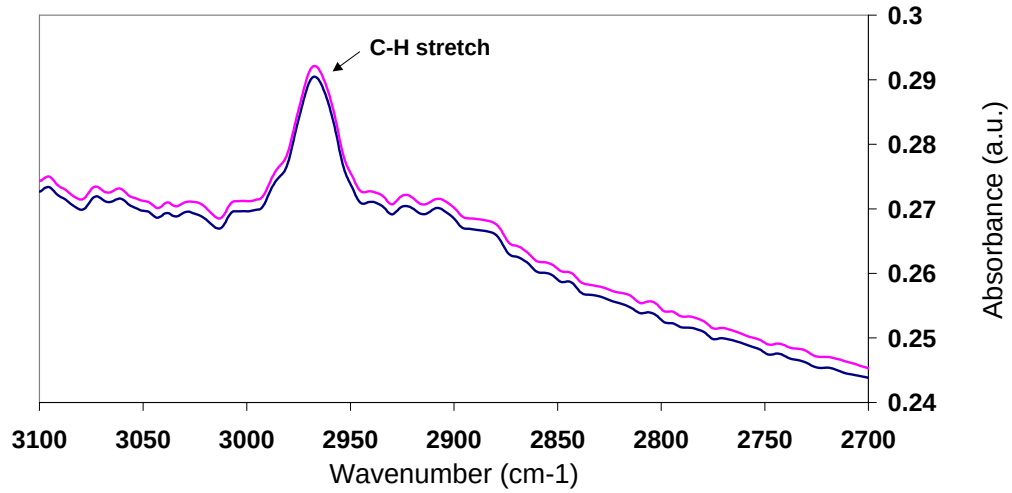


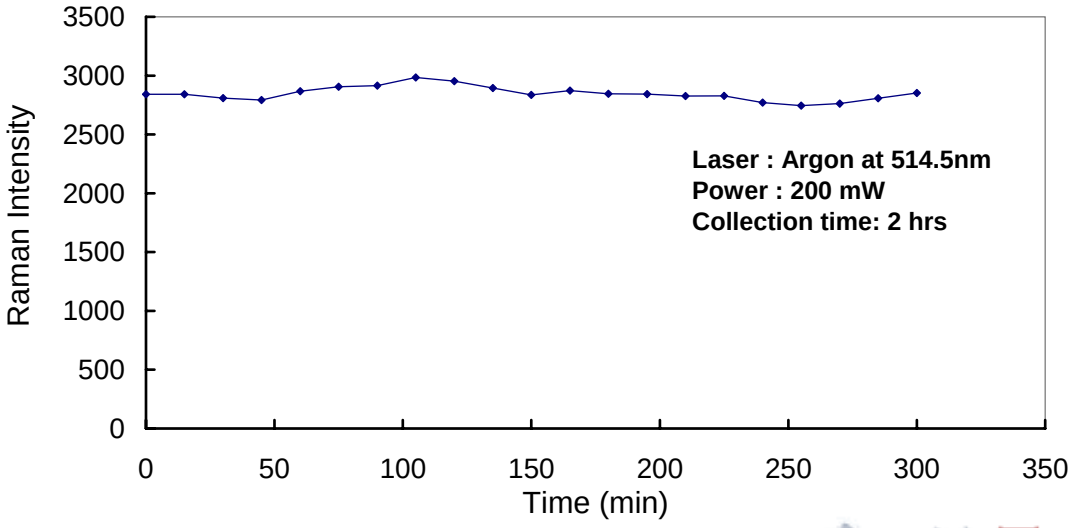
Fluorescence vs Time.

(Data points are the highest peak points in every spectrum taken at equal intervals of time).

Study on Fluorescence

- FTIR spectra, before and after, were checked to make sure there is no chemical change in the sample due to the quenching of fluorescence.





• No marked change in the peak height was observed as the fluorescence decreased with the time.

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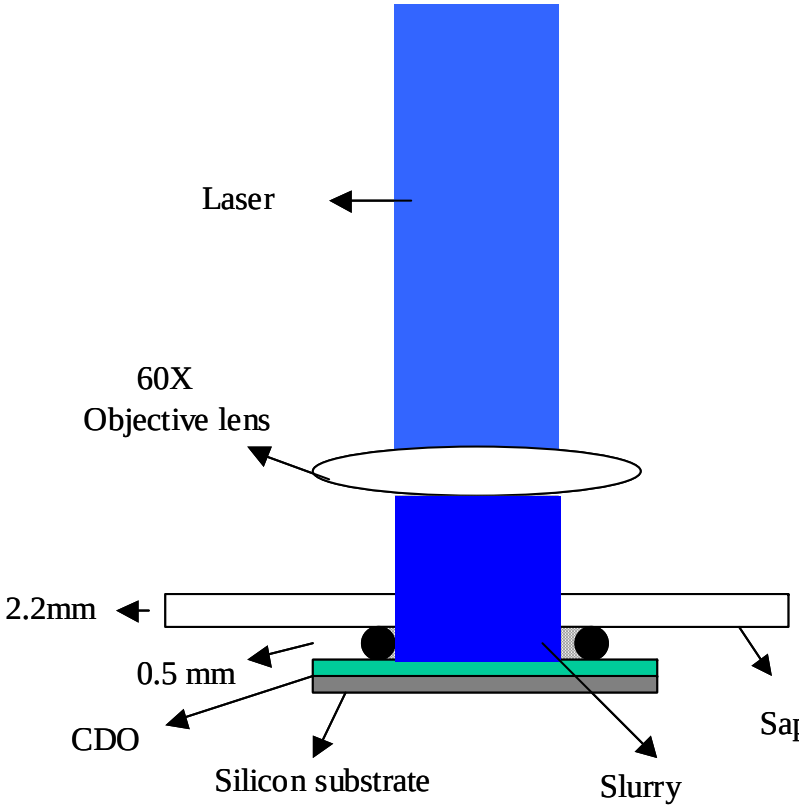
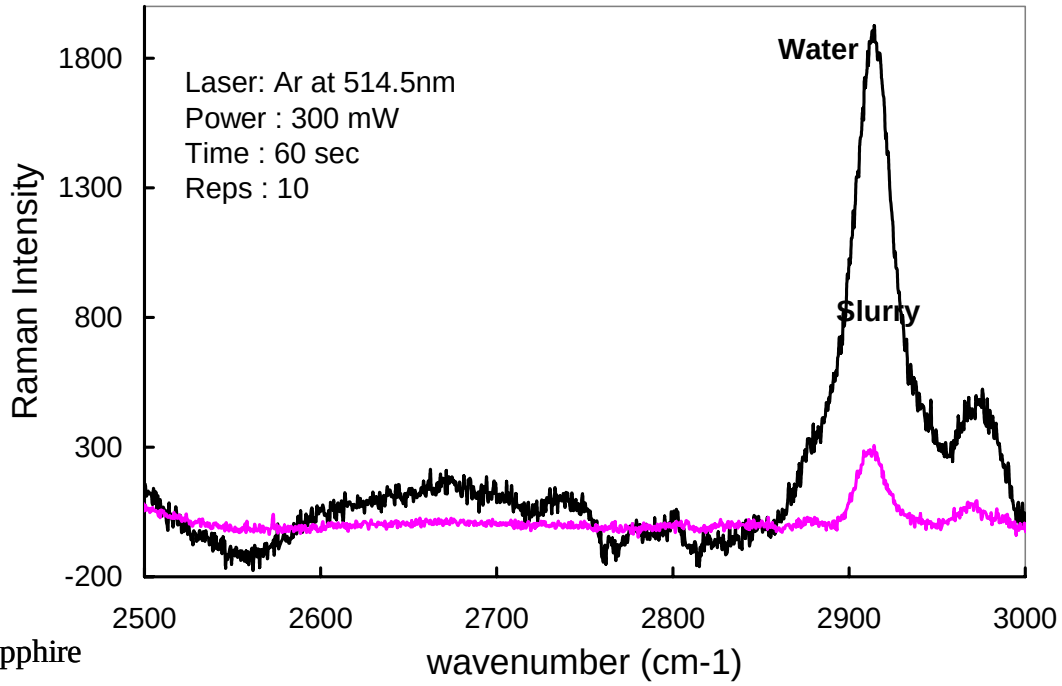
Effect of liquid layer (slurry)



(3 % H2O2 3 % SiO2 particles)



Raman setup to collect spectrum of CDO sample through slurry/water and sapphire.

Raman spectrum of CDO sample, after subtracting the baseline (water peak)

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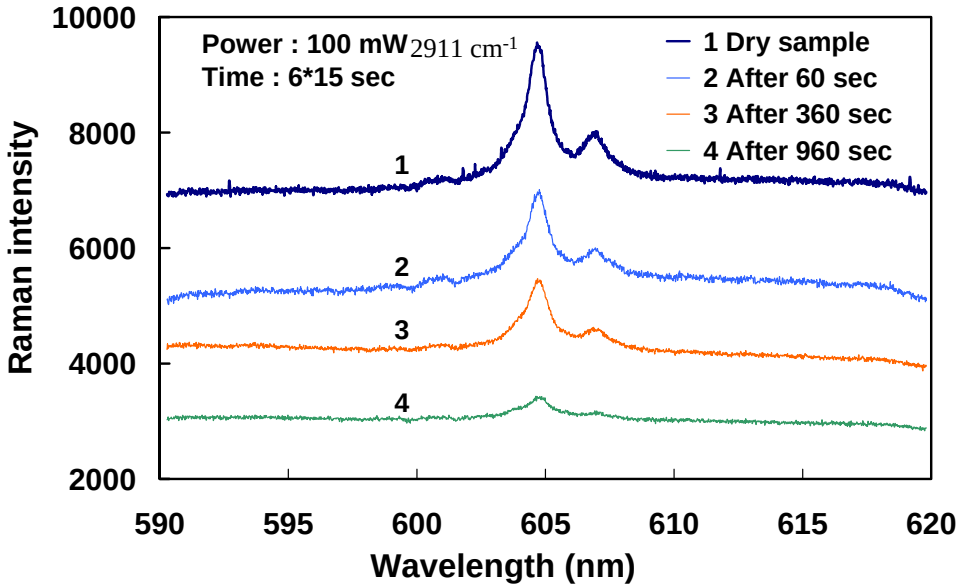
Effect of thickness on Raman intensity

- CDO thickness was decreased by etching the samples in 9.8%HF.
- Thickness measurements were performed using ellipsometer.
- Correlation between CDO peak intensity and thickness.
- This was also confirmed by performing CMP on CDO-I samples.

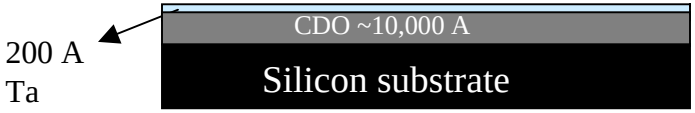


Decrease in CDO-I peak intensity with etching time

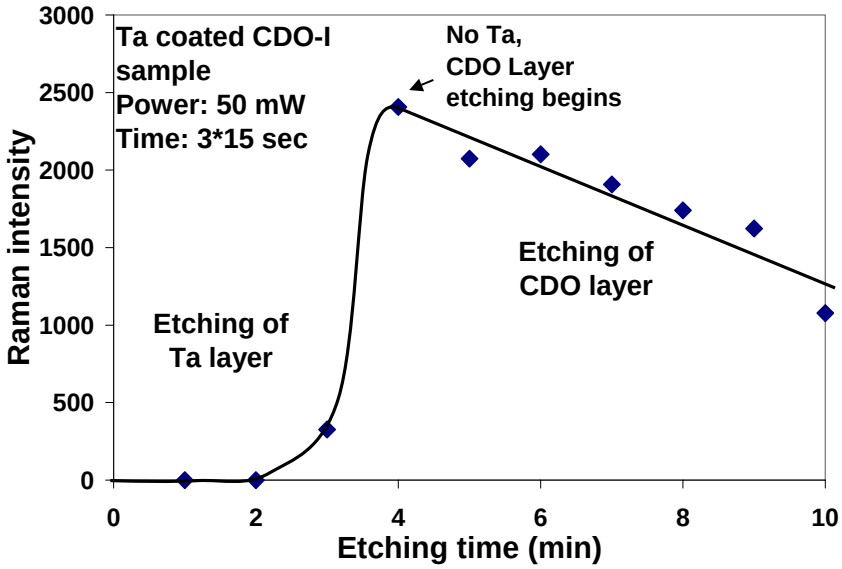
End Point Detection

Raman monitoring of barrier layer breakthrough (using CDO peak)

- Samples: 20 nm Ta coated on CDO-I



- Ta layer thinned by etching in KOH
- Evolution of CDO peak as Ta overlayer is thinned
- Over etching (after Ta overlayer removal) resulted in decrease in CDO peak intensity



Evolution of CDO peak (2911 cm^{-1}) during etching of Ta overlayer.

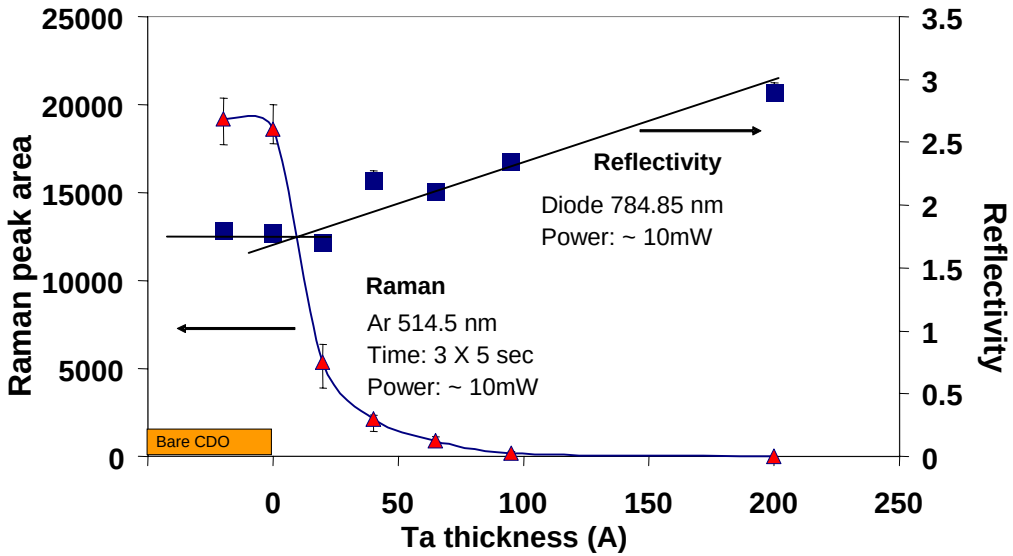
Raman vs. Reflectivity measurement
(using Si peak)

- Samples: 20 nm Ta coated on CDO-I.

- Raman Technique:

  Evolution of Si peak (bottom) as Ta overlayer is etched away.

  Exponential increase in Si peak intensity ; VERY SENSITIVE
- Monotonic linear decrease of signal in reflectance technique.



Comparison of Ta to CDO transition using reflection and Raman (Si peak at 520 cm^{-1}) techniques.

Measurements Under Abrasion

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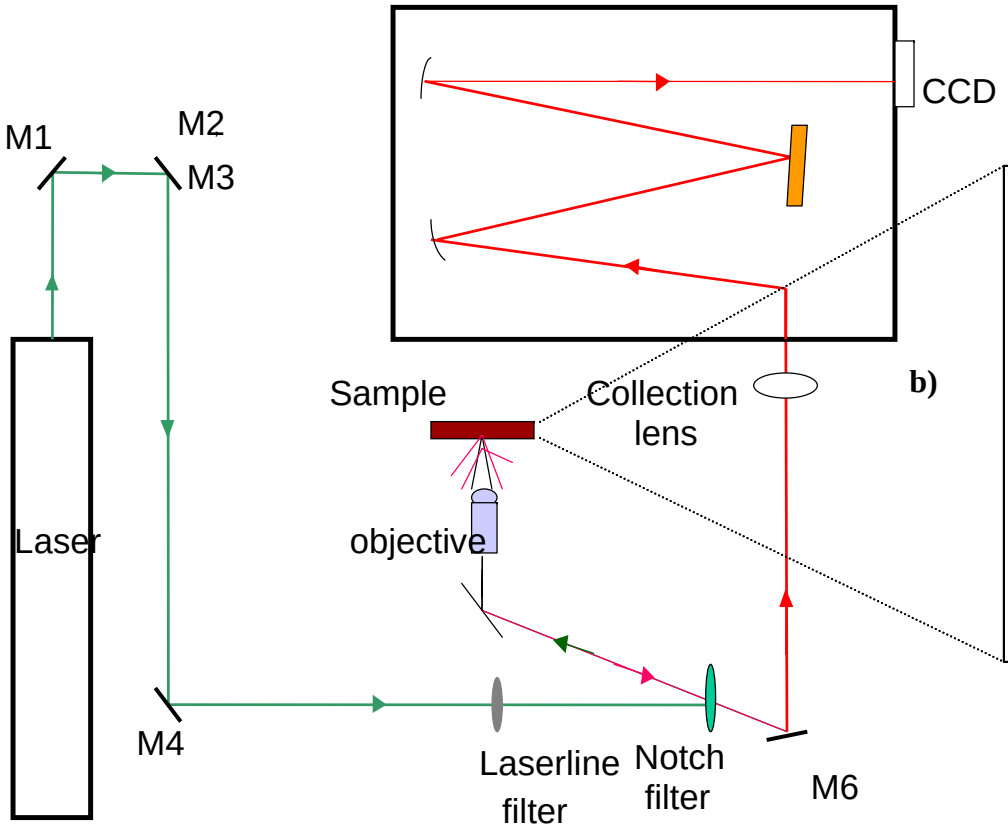
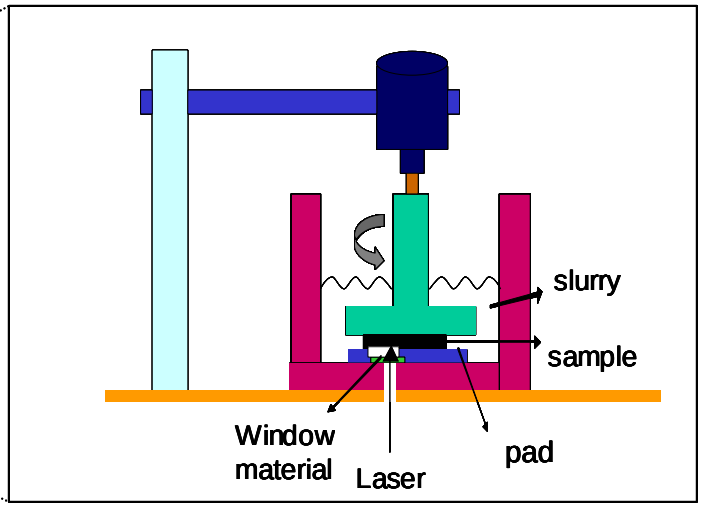
New Raman setup integrated with an abrasion cell



b)

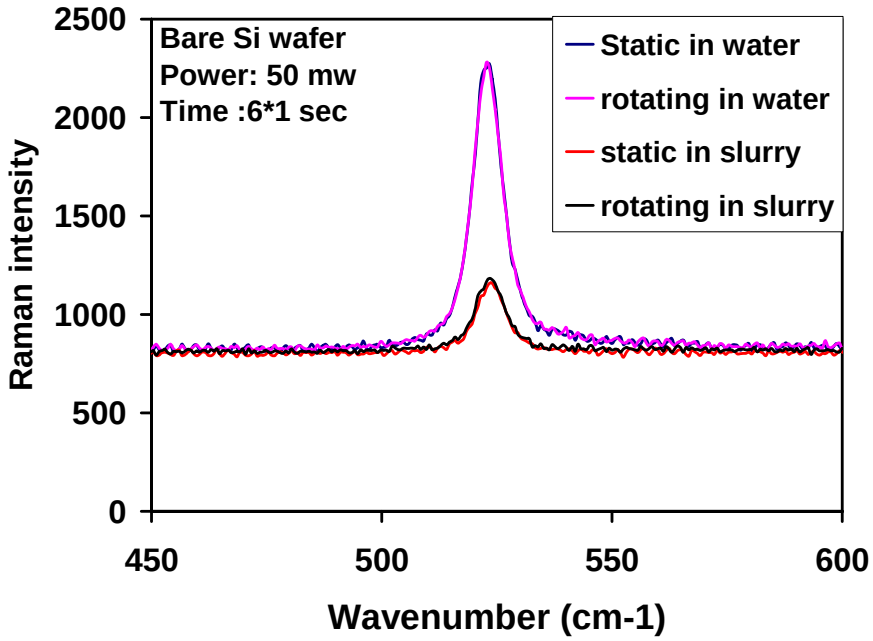


Abrasion cell with polyurethane pad and sapphire window

Raman spectrometer Jobin Yvon HR 640, equipped with liquid N_2 cooled CCD.

In-situ measurements

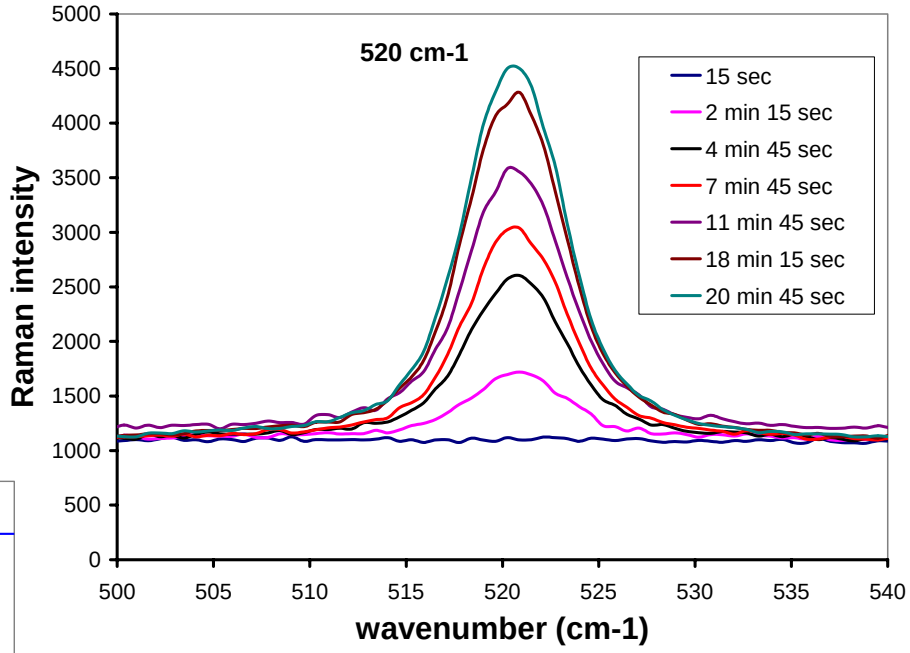
- Three inch silicon wafer was rotated and pressed against a polyurethane pad .
- Slurry composition: 3% silica particles (90 nm) in 3% H_2O_2, pH 10.
- Thickness of the slurry layer : (between the window and wafer) ~ 1 mm
- Raman spectra collected through a sapphire window
- No significant effect on Raman signal by abrasion.

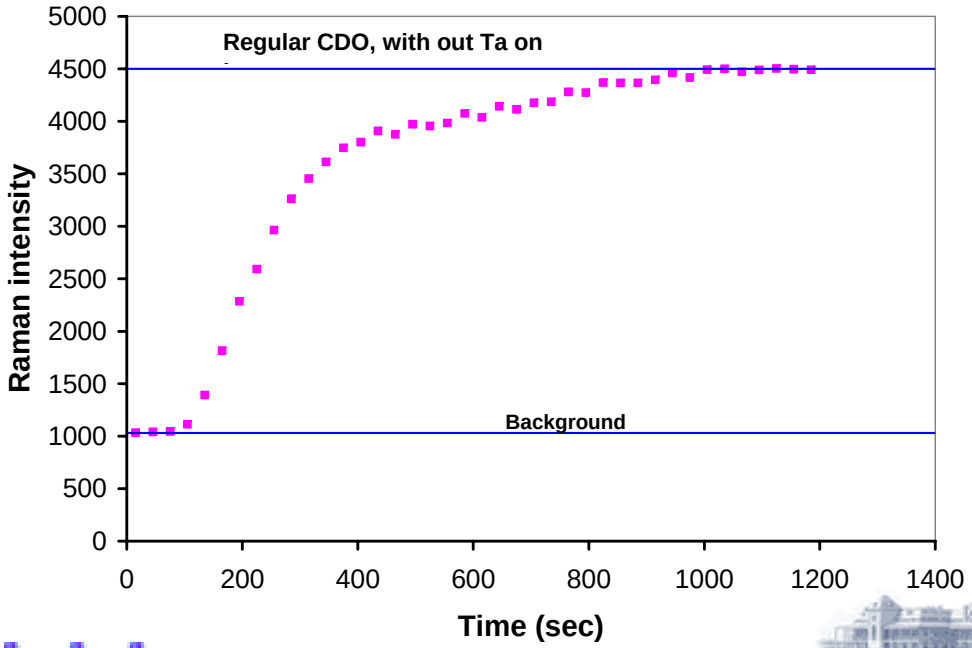


Si-Si Raman peak collected in abrasion cell in static and rotating modes.

In-situ monitoring of Si peak

- In-situ monitoring of barrier layer to CDO transition using Si peak at 520 cm-1.
- Si peak at 520 cm-1 is from the substrate underneath the CDO film.





Experimental conditions

Slurry: 3% SiO_2 particles, 3% H_2O_2, pH 10.

Laser power: 50 mW

Time: 3 X 5 sec

Load : ~0.5 psi at 124 RPM

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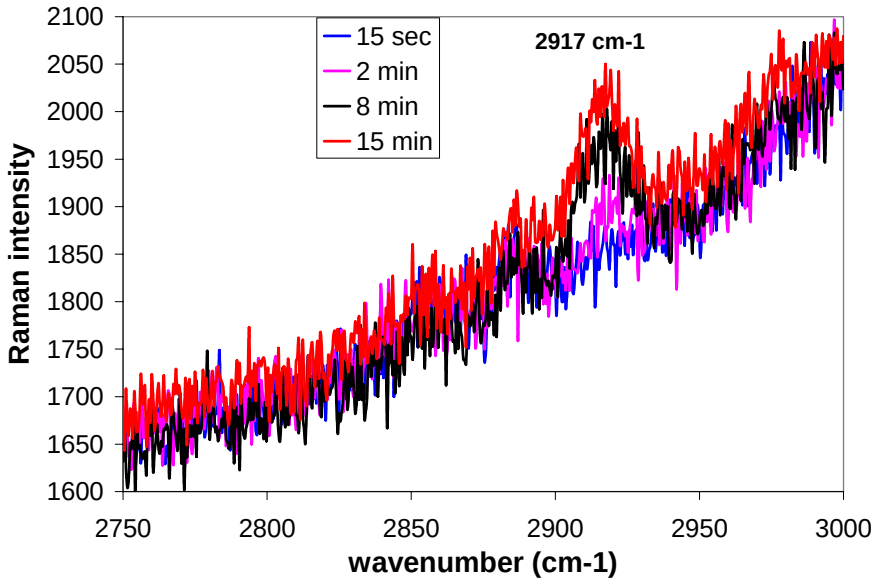
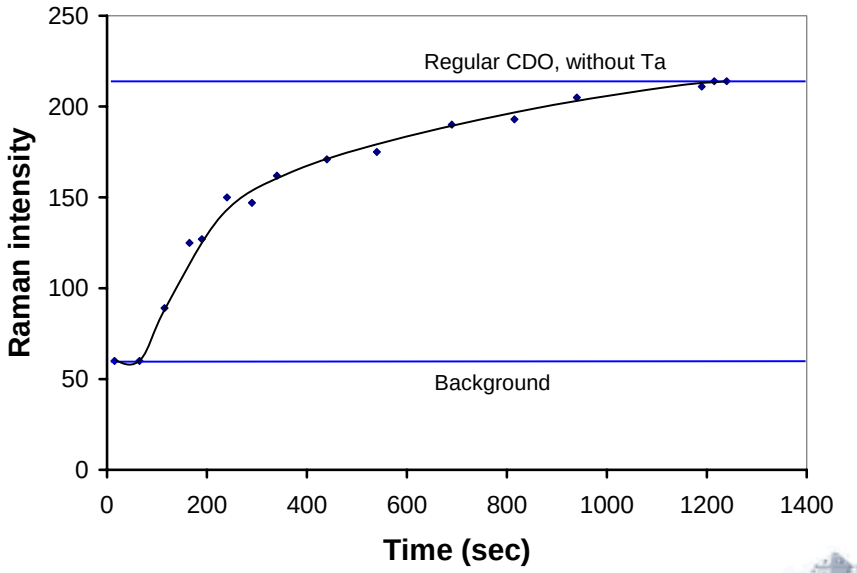
In-situ monitoring of CDO peak

- In-situ monitoring of barrier layer to CDO transition using CDO peak at 2917 cm-1.
- Increase in the CDO peak intensity as the Ta layer is removed





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Load : ~0.5 psi at 124 RPM

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Chemical Analysis

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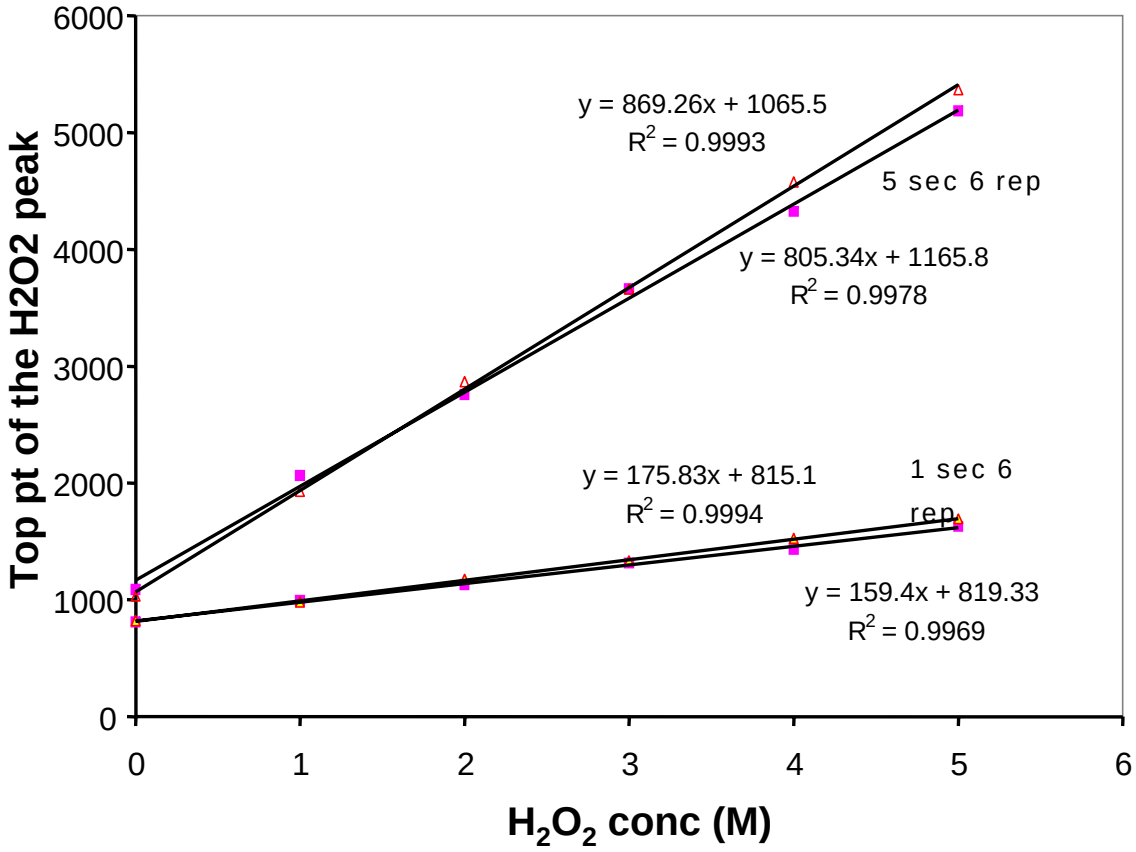
H_2O_2 Concentration vs Raman Intensity

. Ar laser (50mW)

. Peak at 877 cm^{-1}.

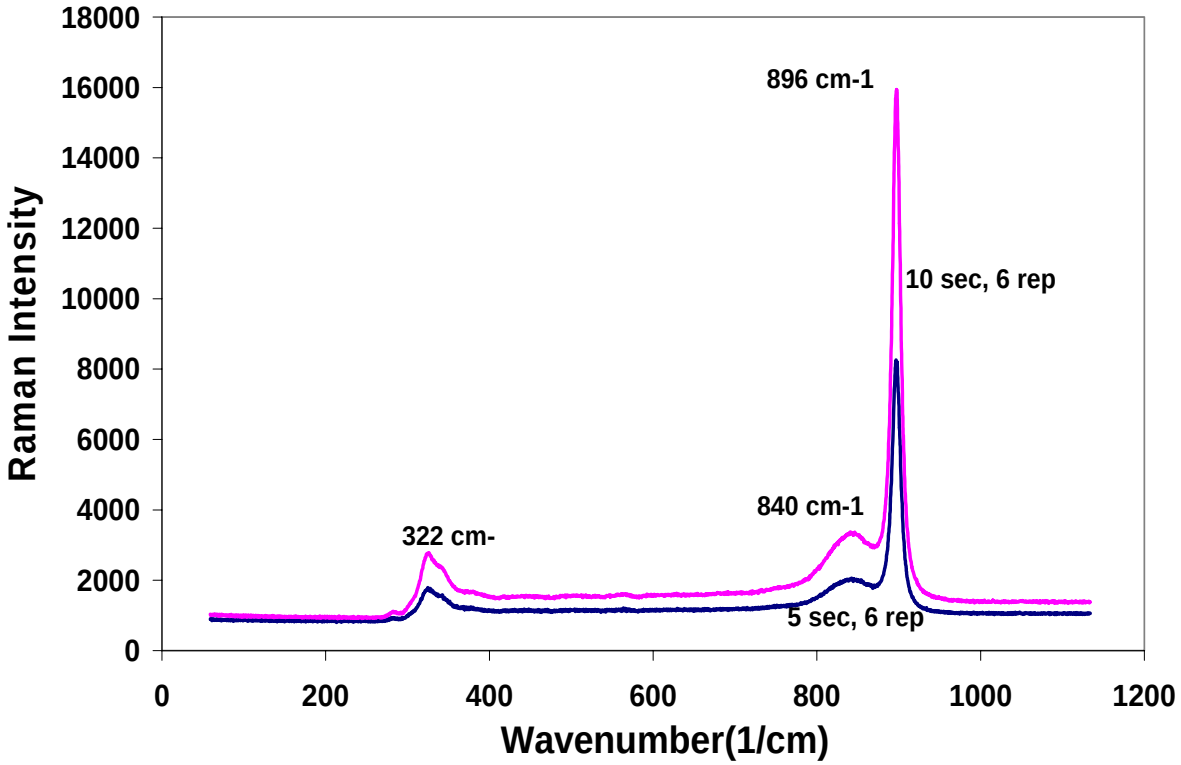
. Clear correlation between Raman intensity and the concentration.



Detection of Molybdate Species

- Novel oxidants/slurries based on Mo have been patented

  (Climax Engineered Materials, Sahuarita, AZ)
- 1M sodium molybdate hydrate at 9.56 pH.
- Ar laser at 50 mW.
- Peaks are in agreement with literature values*.



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1) * M. Arab, D. Bougeard, J. M. Aubry, J. Marko, J. F. Paul and E. Payen, *J. Raman spectrosc*, **33**, 390 (2002).

N. Weinstock, H. Schulze, and A. Muller, *J. Chem. Phys.*, **59**, 5063 (1973)

Conclusions

- Raman signal from CDO materials shows promise in detecting Ta to CDO transition.
- Raman technique is more sensitive than the currently popular reflectance technique.
- Raman signal (of Si and CDO) can be collected in the presence of a slurry and during abrasion.
- Raman spectroscopy has potential to identify and perhaps quantitative chemical species present in the region close to wafer.

Acknowledgements

- Thanks to Intel Corporation for Financial Support.
- Mentorship of Paul Fischer, Andrea Oehler and Mansour Moinpour is highly appreciated.

Questions