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Aging of self-assembled monolayers for anti-stiction coatings studied by near edge x-ray absorption fine structure

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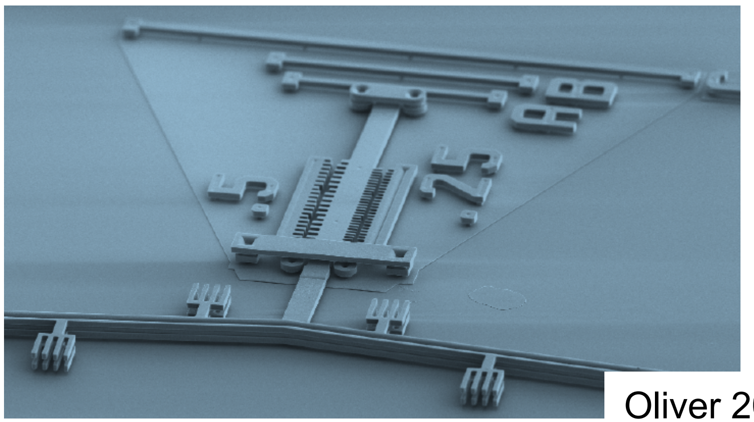
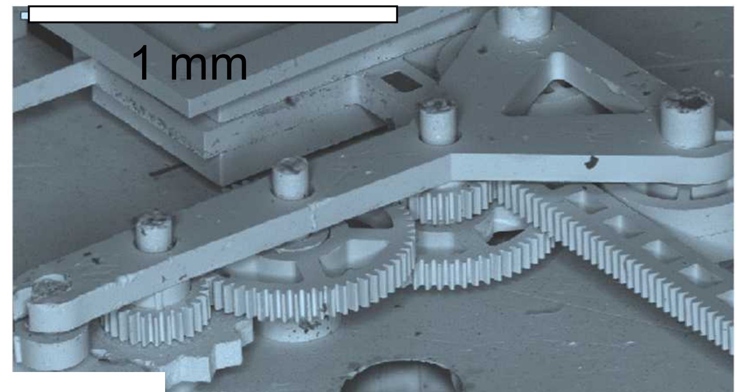
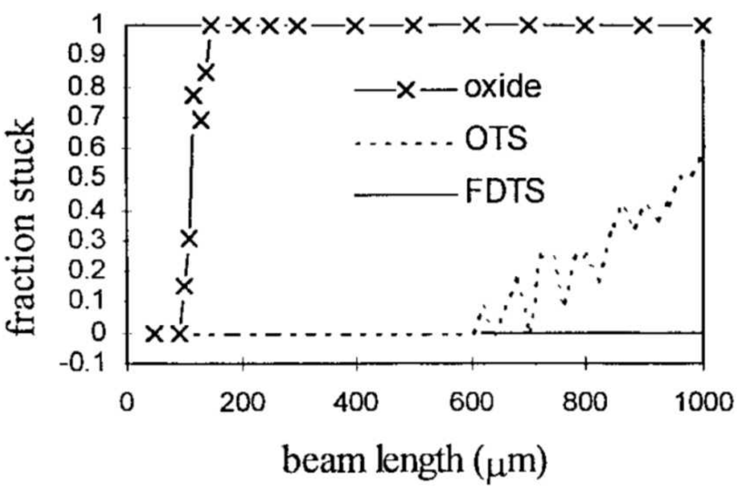
SAMs for anti-stiction of MEMS

- Motivation: Class III and IV MEMS devices (impacting/rubbing surfaces)
  - Untreated MEMS last for 10^2 to 10^3 cycles
  - MEMS with single-layer SAMs last for 10^4 to 10^5 cycles
  - Reliable devices require 10^6 to 10^8 cycles

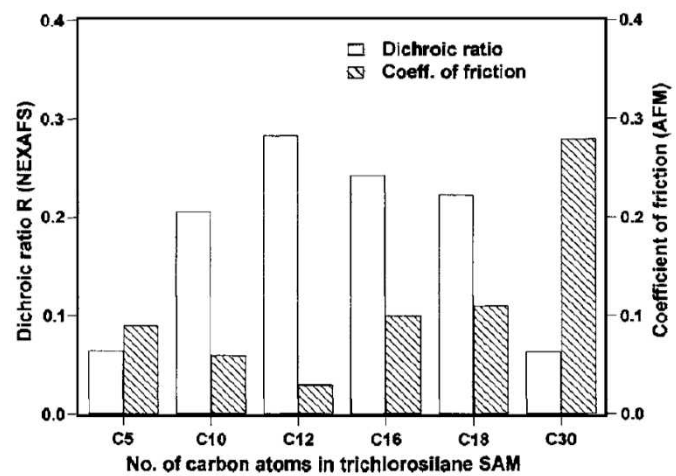




Oliver 2002 *Sand Report*

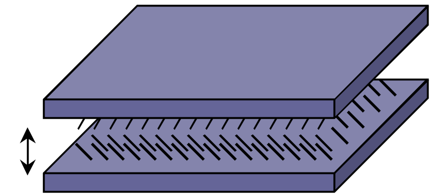


Srinivasan 1998 *J MEMS*



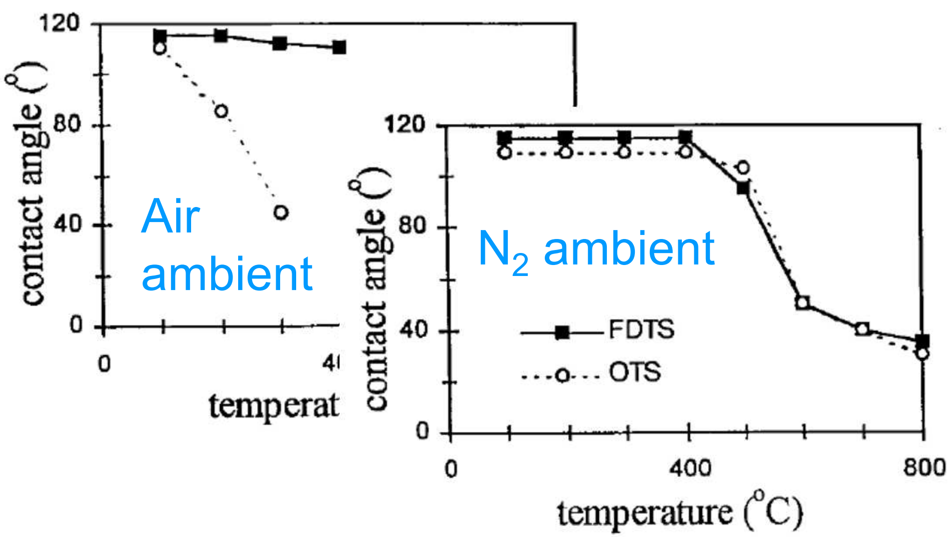
Sambasivan 2006 J Vac Sci Tech A

SAM wear leads to device failure



~2 nm separation between surfaces

- 3 routes envisioned to SAM failure
  - Wear leads to local heating, cleaving C-C bonds
  - Wear scratches silicon surface and ‘uproots’ SAMs
  - Mechanical heating and humidity hydrolyzes Si-O-Si bonds
- Investigate surfaces before and after: (1) dry heating, (2) mechanical wear, and (3) humid heating
  - NEXAFS gives local orientation, types of bonds, and bond composition
  - Other techniques: contact angle, grazing incidence FT-IR, and ultimately cycling of MEMS



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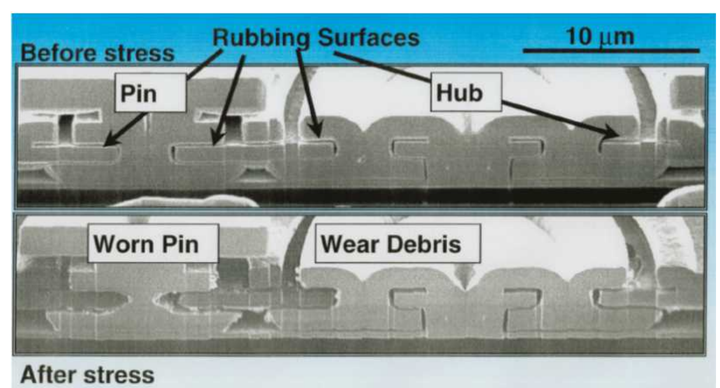
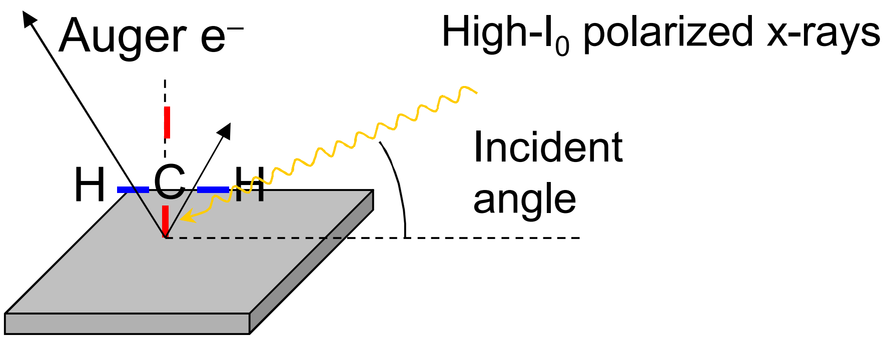


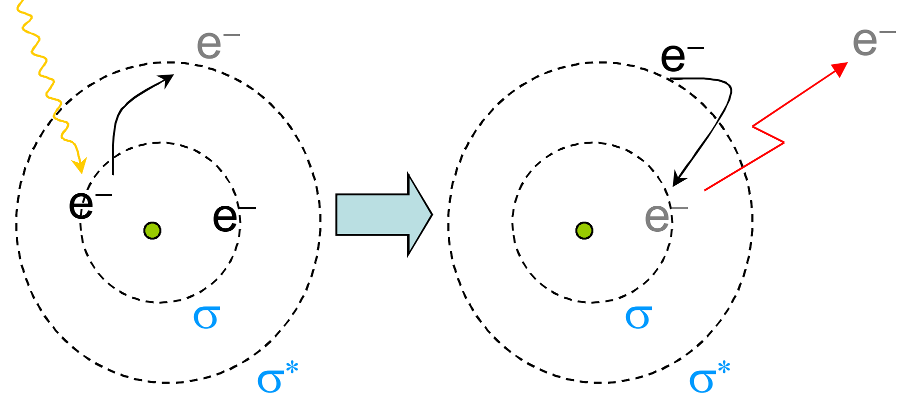
Jenkins 2004 *Sand Report*

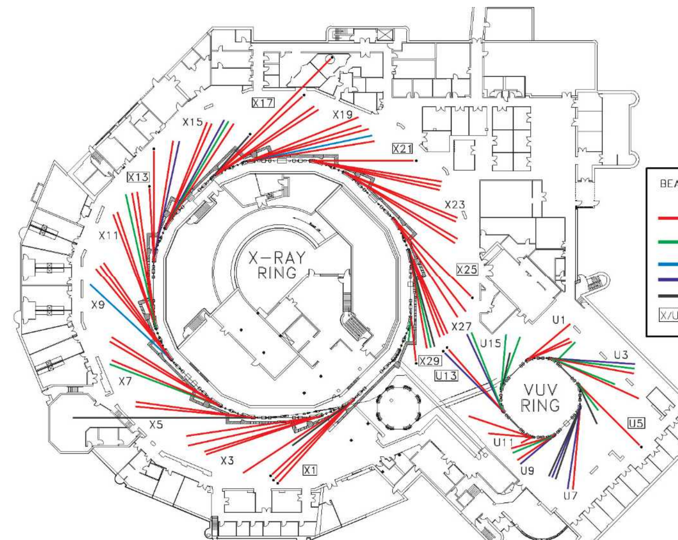
Near edge x-ray absorption fine structure

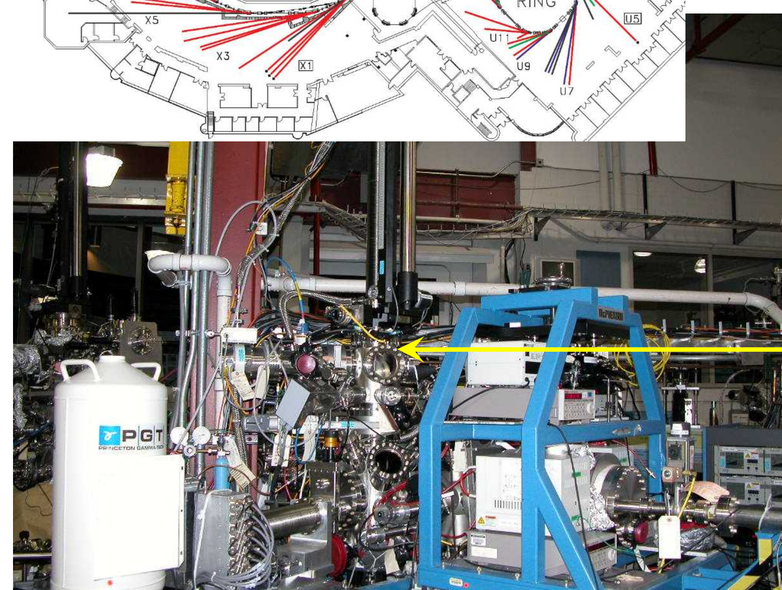
- High intensity, polarized x-rays lead to the ejection of core-shell electrons at energies separating the bonding and anti-bonding orbitals



excitation $h\nu = E(\sigma^*) - E(\sigma)$

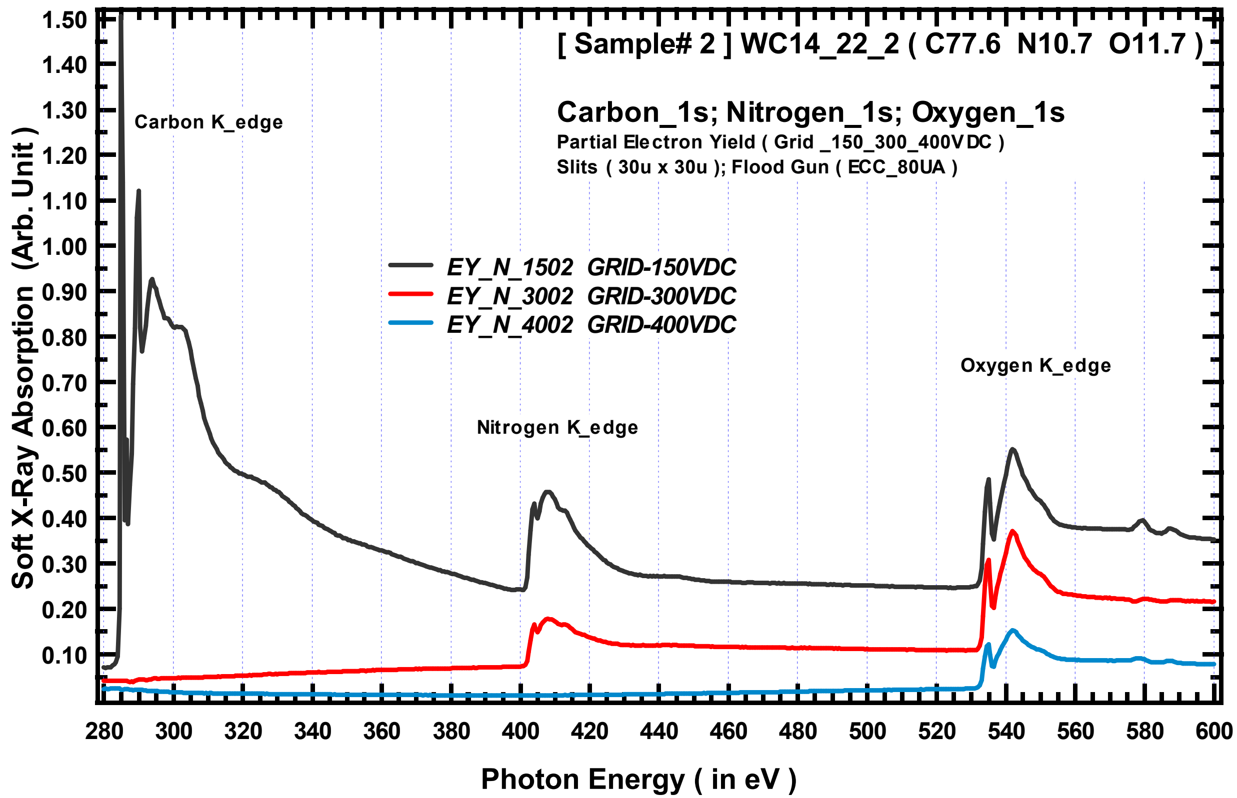






Typical NEXAFS spectra

- Scanning the incident x-ray energy (x-axis) gives elemental edges in the partial electron yield (y-axis)
  - Peak energies sensitive to local bonding characteristics
  - Intensity dependent on bond orientation

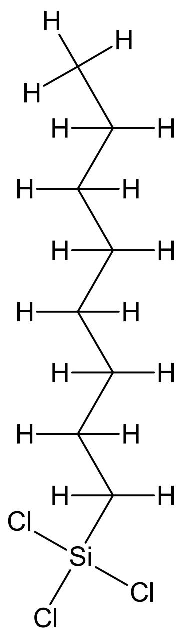


Courtesy of Zugen Fu (Brookhaven/NIST)

Silane surface treatment

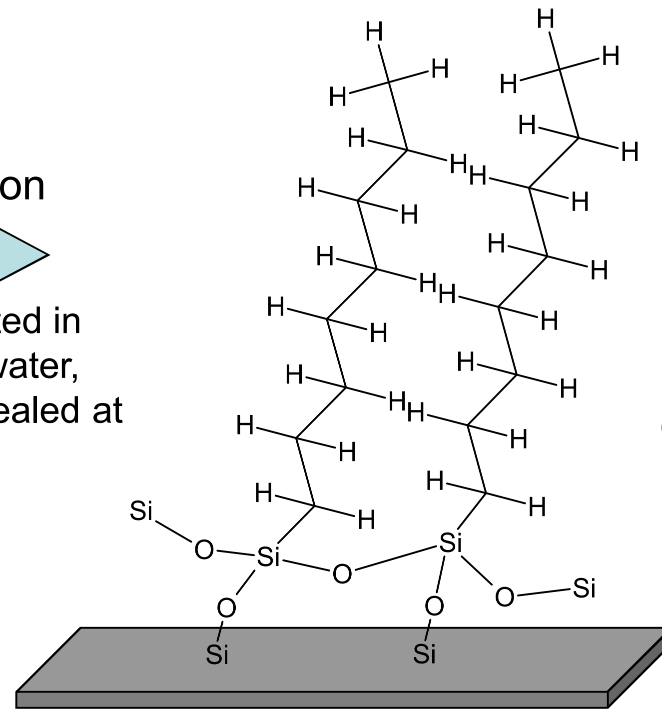
- Octyltrichlorosilane (OTS): simple hydrocarbon silane
  - Second and third siloxyls can bond to other molecules or the surface
  - Order depends on length of hydrocarbon chain: < C_5 and > C_{25} near random*
  - Monolayers typically oriented slightly off normal

Si wafer



Condensation

Vapor deposited in presence of water, rinsed, and annealed at 120 ^oC

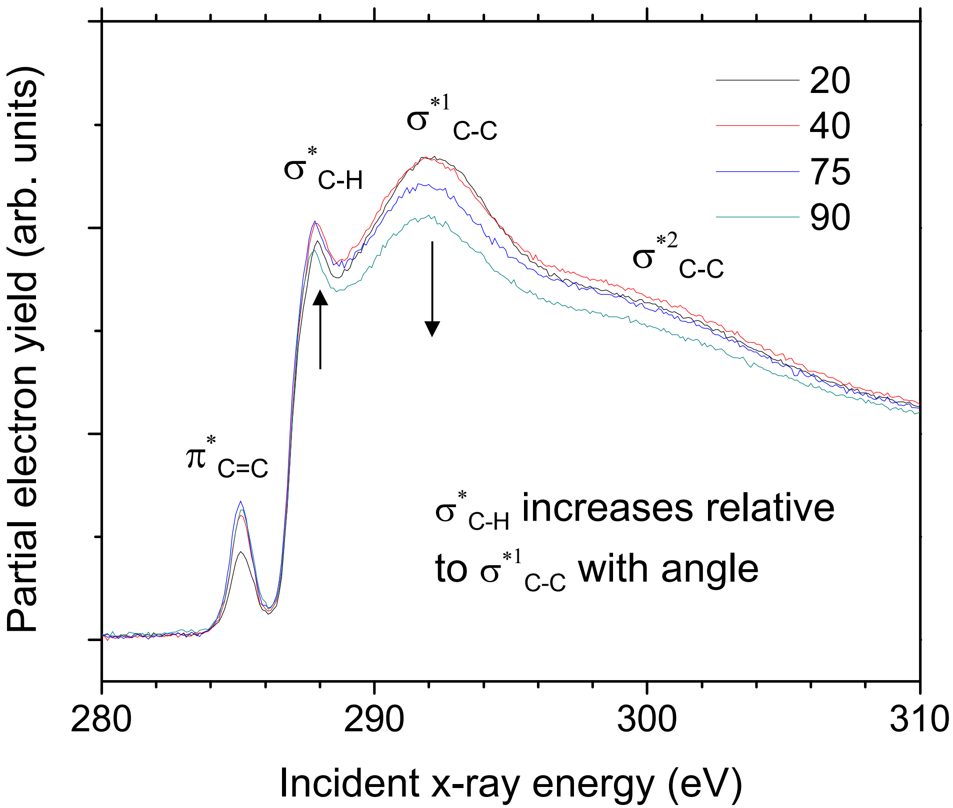


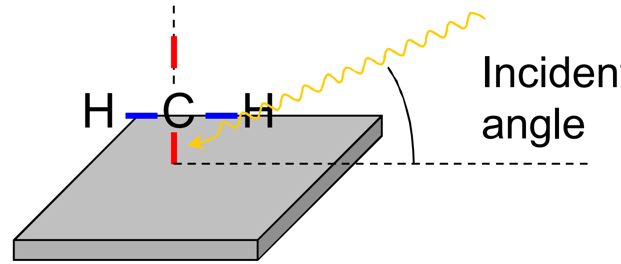
OTS on Si

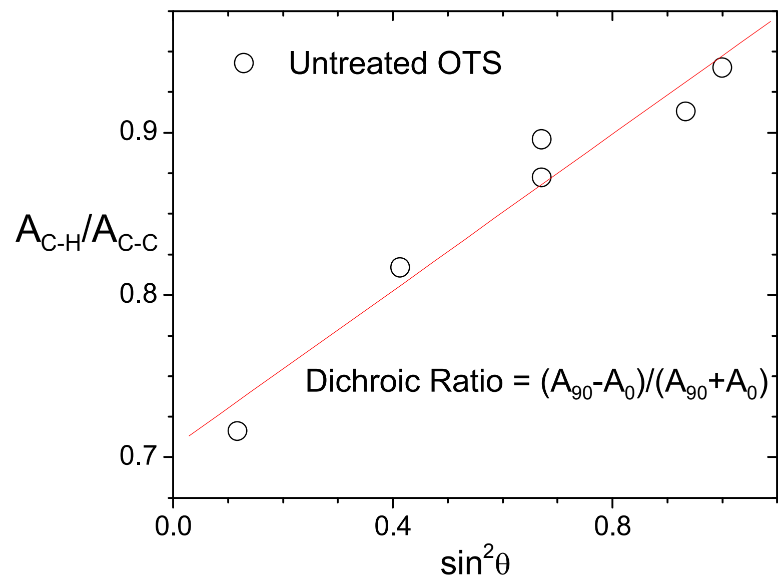
* Sambasivan 2006 J Vac Sci Tech A

Measuring orientation

- OTS orientation: normalized PEY of untreated OTS
- Dichroic ratio ≈ 0.14, somewhat oriented (-1 < DR < 0.75)



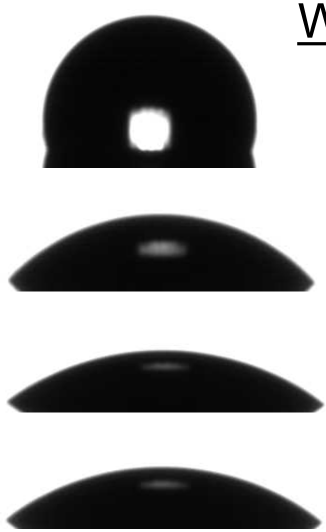


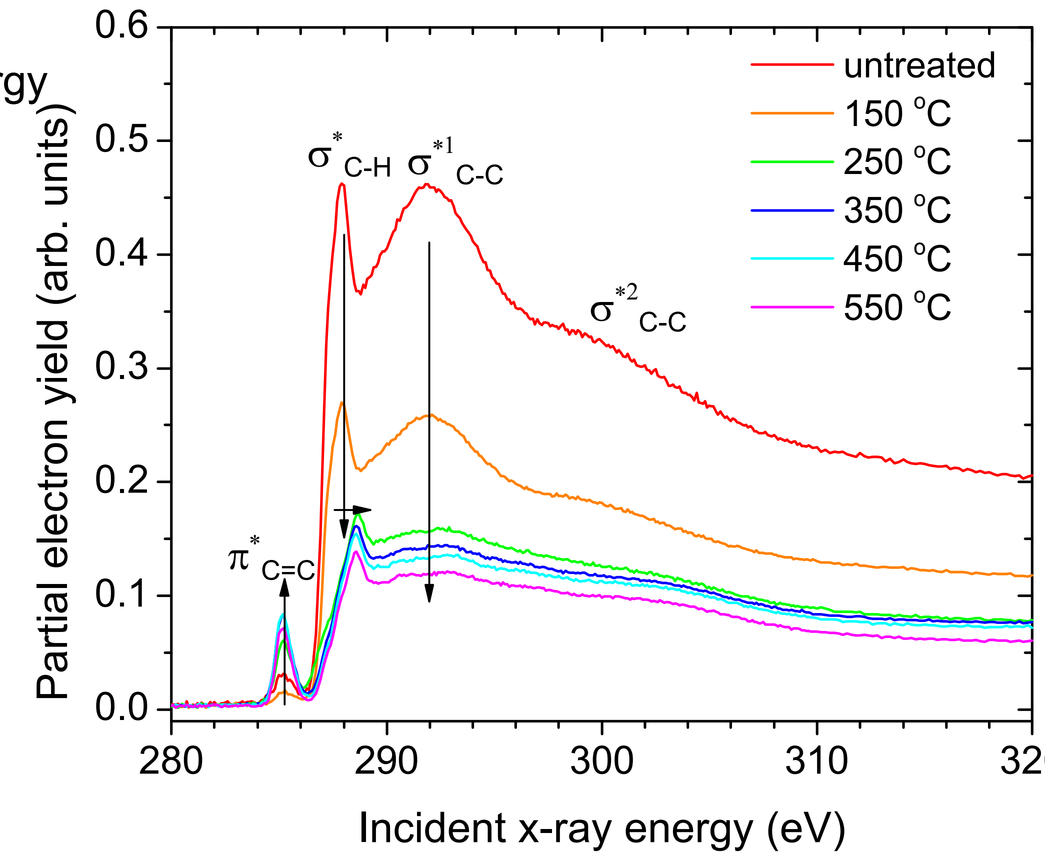


Heat treatment of OTS

- 1 h at 150-550 °C under air
- Carbon edge jump intensity decreases dramatically, but bond types are not dramatically affected
  - Significant C=C (and C=O?) formation
  - C-C peaks broaden
  - C-H peak shifts to higher energy (likely from proximity to C=C)
- Suggests cleaving of C-C bonds with incr. T

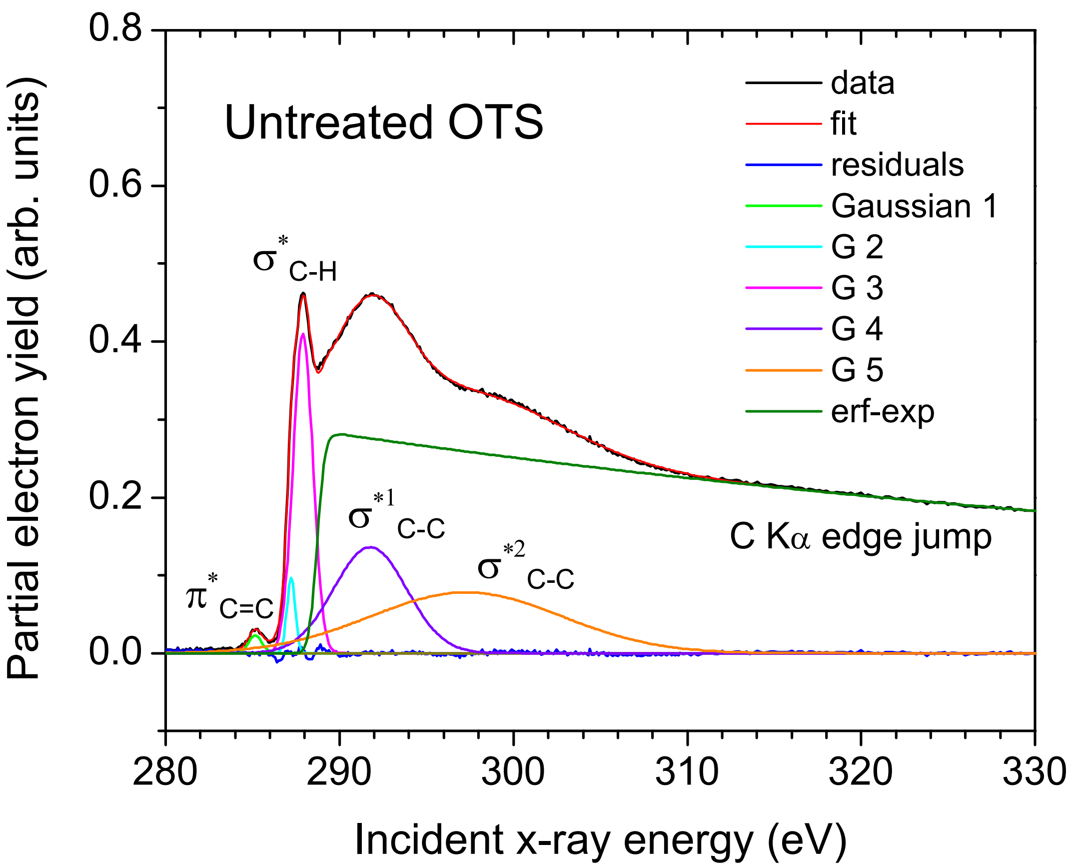
T (°C)	Water CA (°)
150	105
250	46
350	36
450	40



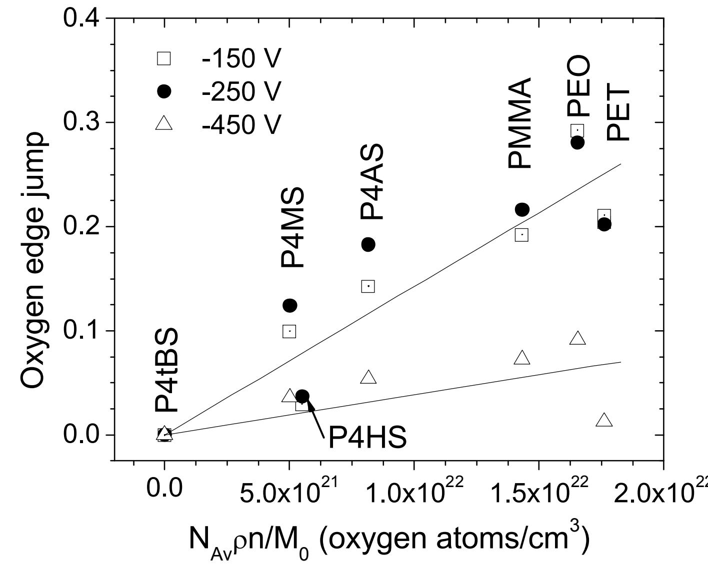


NEXAFS peak fitting

- Peak fitting* quantifies the fraction of specific bond types
- With standards, can obtain atomic concentrations



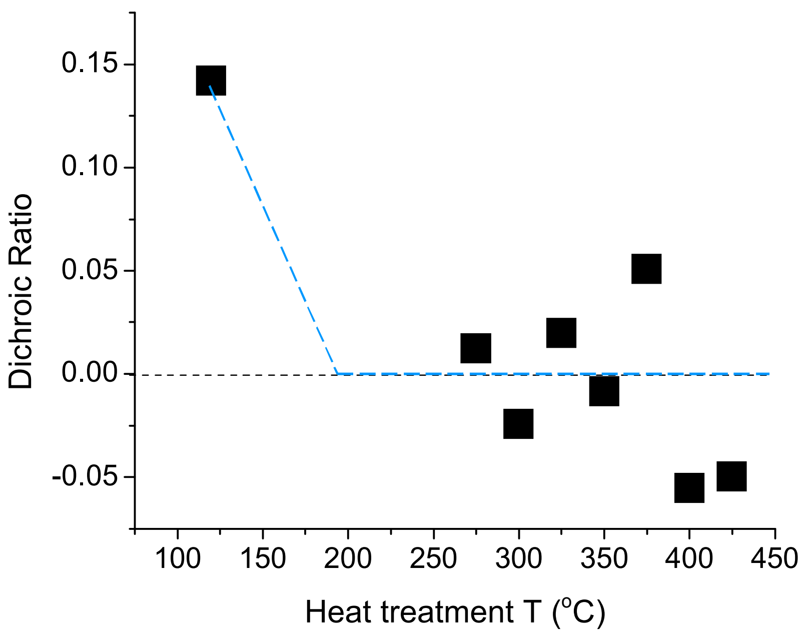
E.g., using reference polymers to obtain oxygen calibration curve

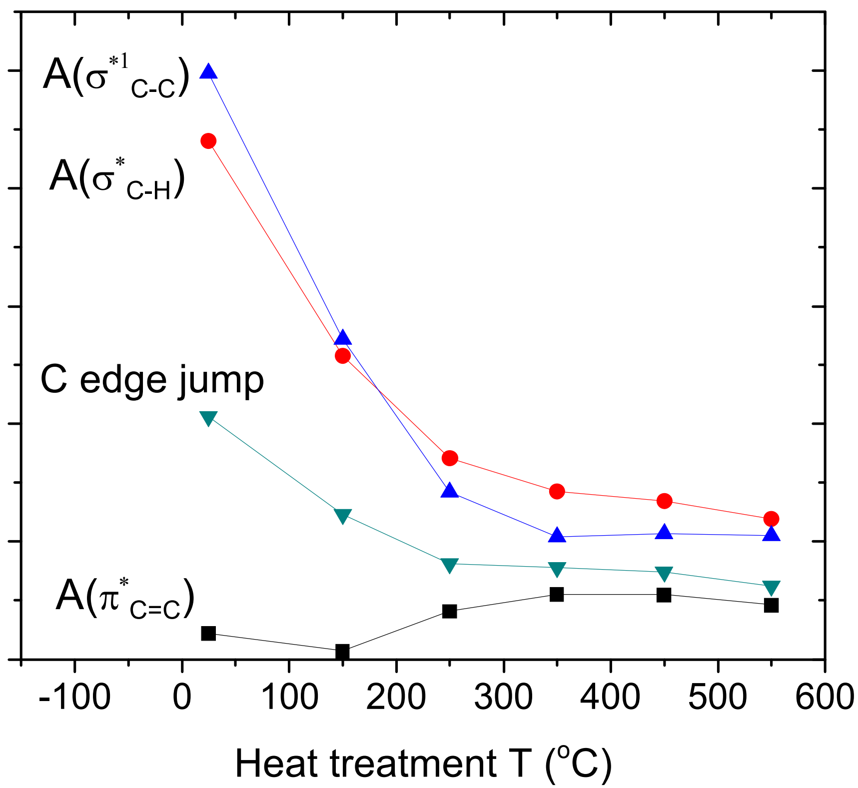


*Stohr, NEXAFS Spectroscopy 1992
Outka, Stohr JCP 1988

OTS after heat treatment

- Orientation removed by 275 °C
- OTS decomposes by breaking C-C bonds
  - Oxygen assisted reactions likely occur at the CH_3 end group*
- Some double bond formation occurs, by removal of H or addition of O



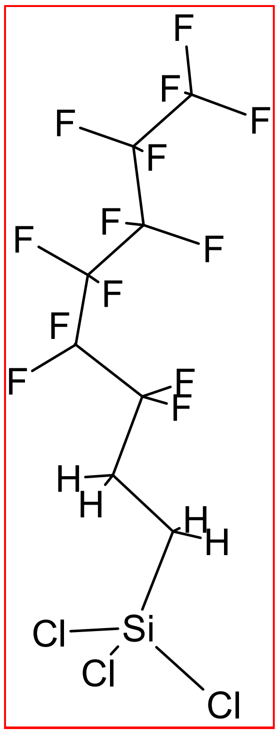


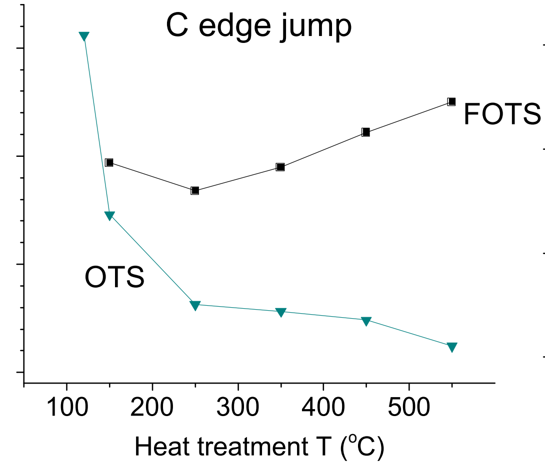
*Mowery et al *Macromolecules* 2005

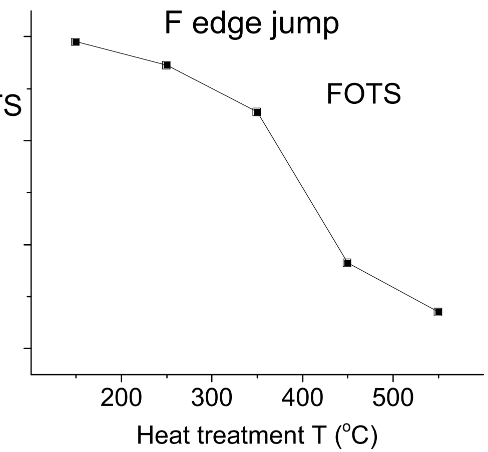
FOTS, FODS, and FOMS

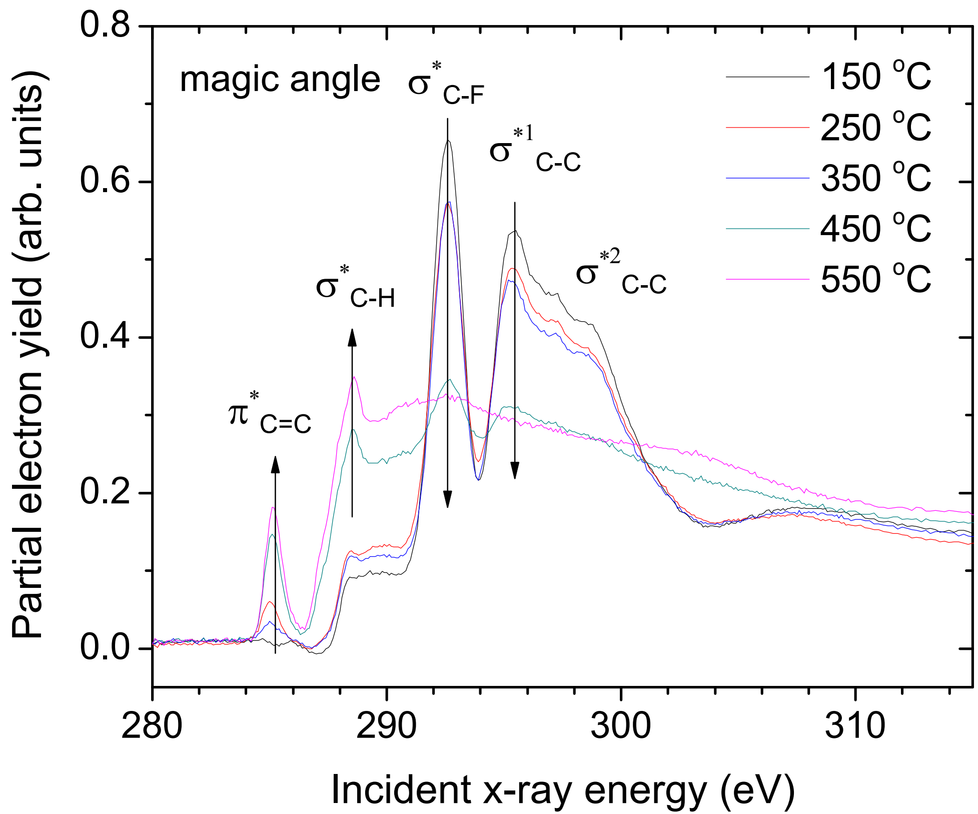
Fluorinated octyl trichlorosilane

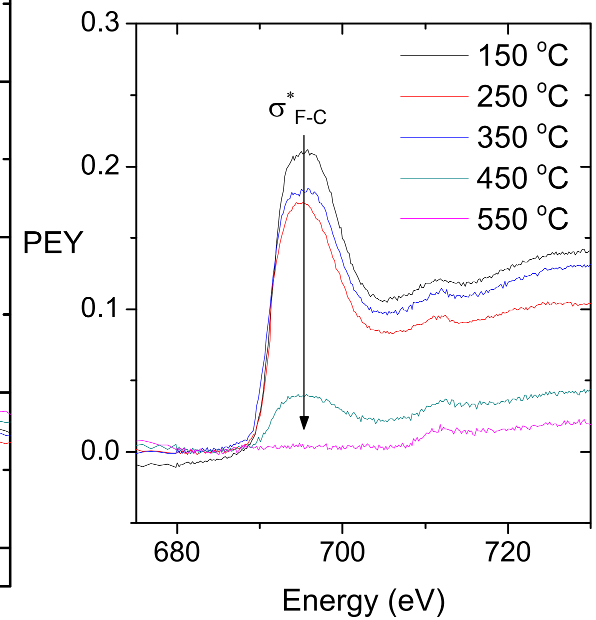
FOTS





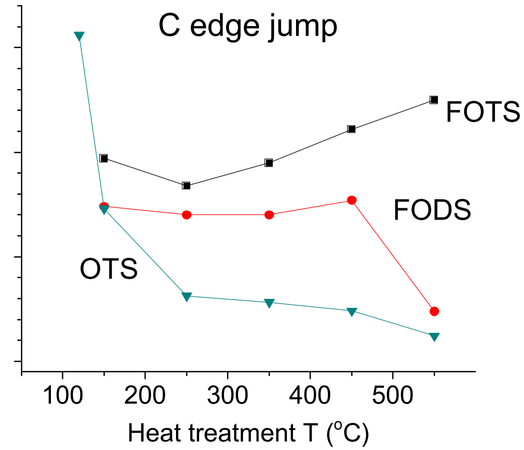


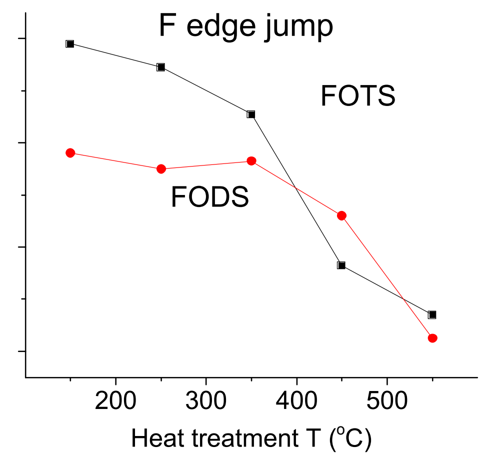




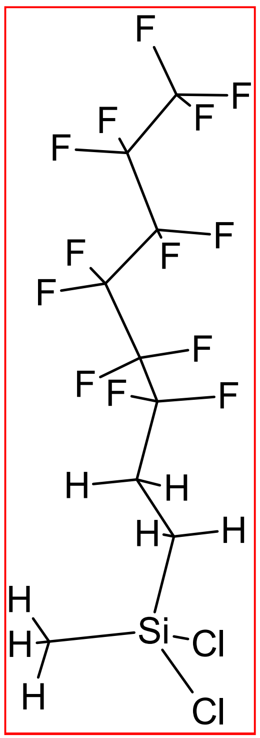
FOTS, FODS, and FOMS

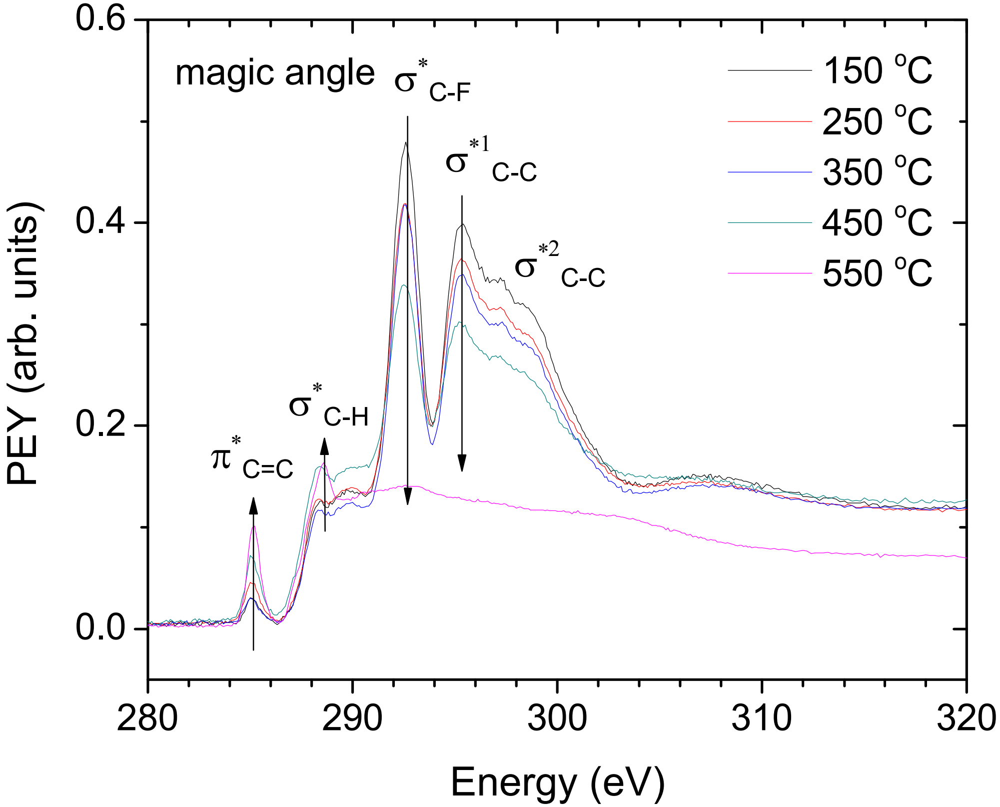
Fluorinated octyl methyl<u>di</u>chlorosilane

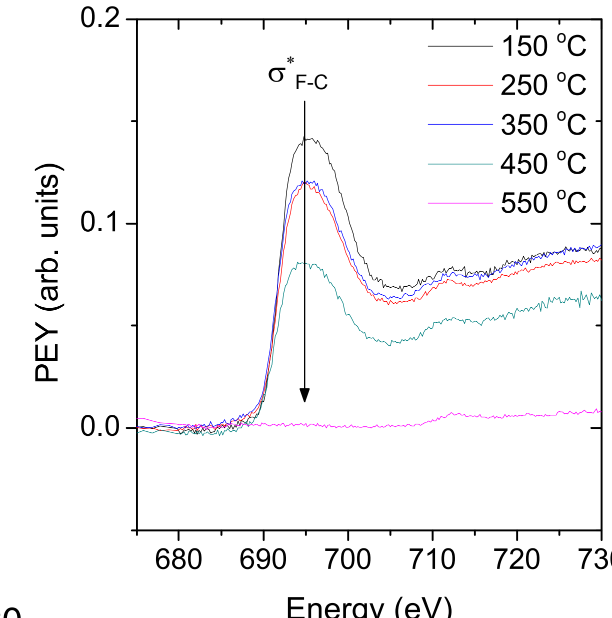




FODS



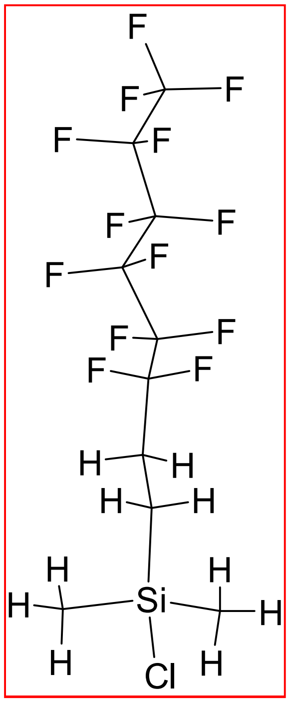


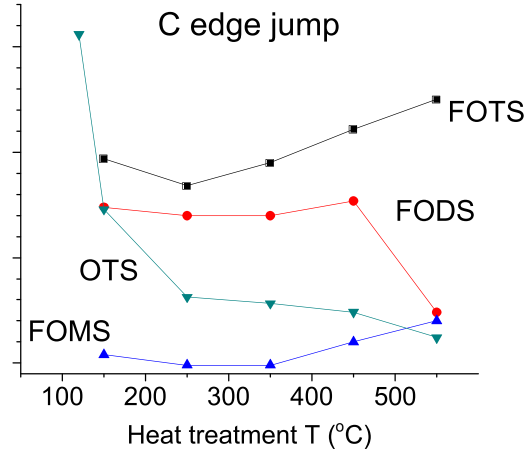


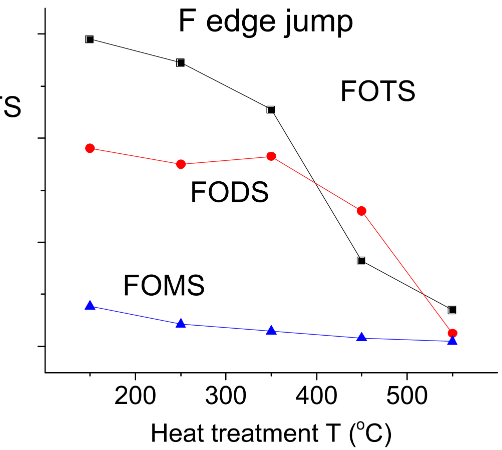
FOTS, FODS, and FOMS

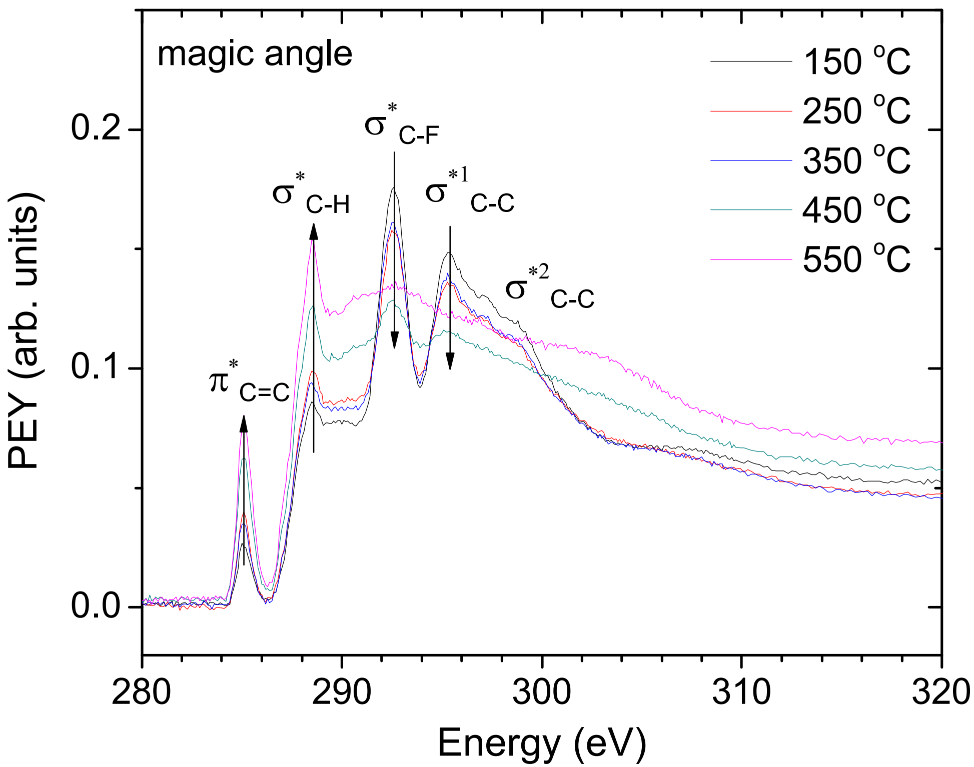
Fluorinated octyl dimethyl<u>mono</u>chlorosilane

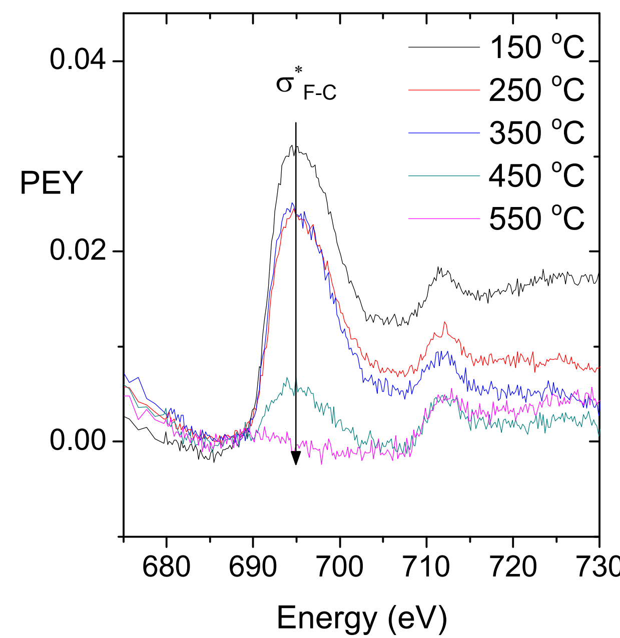
FOMS





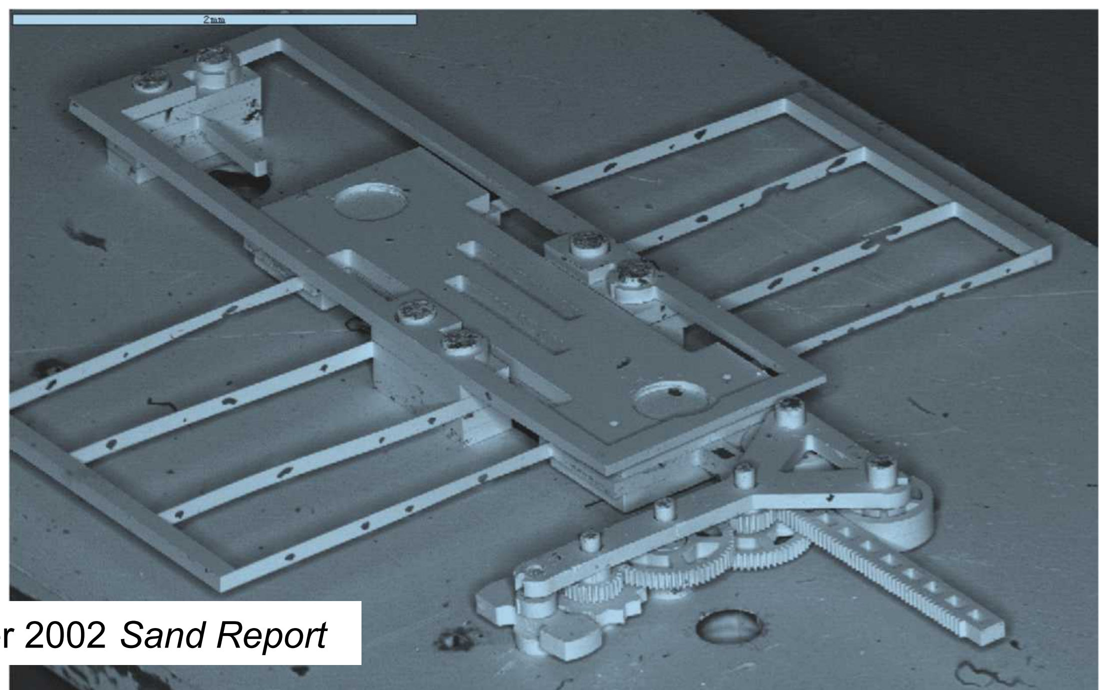






Future work

- Wear vs temperature: mechanisms and products of degradation
- Effect of water?
- SAMs designed for wear reduction
  - Multilayers



Oliver 2002 *Sand Report*

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