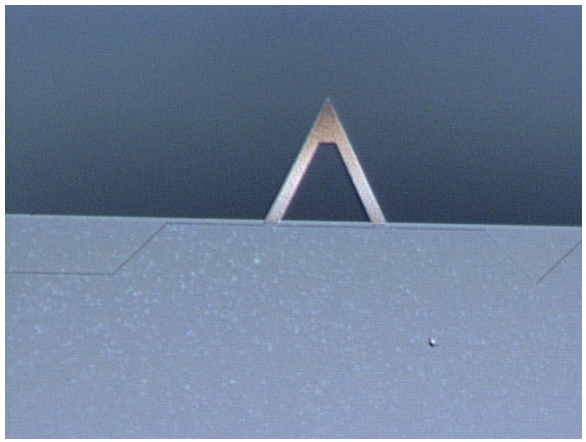
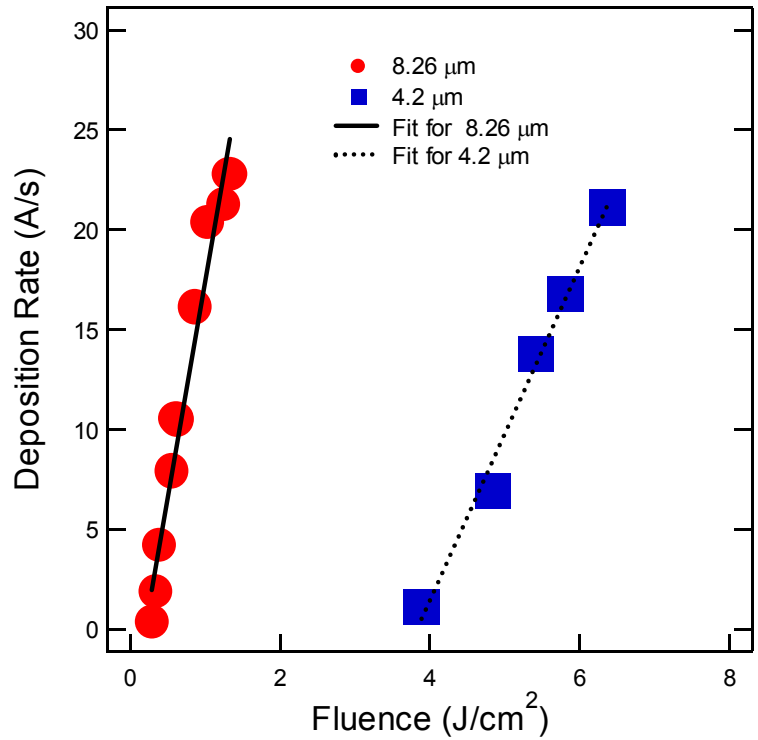
IR pulsed laser deposition: electronics, biotechnology, sensors, opto-electronics





A prescient comment …

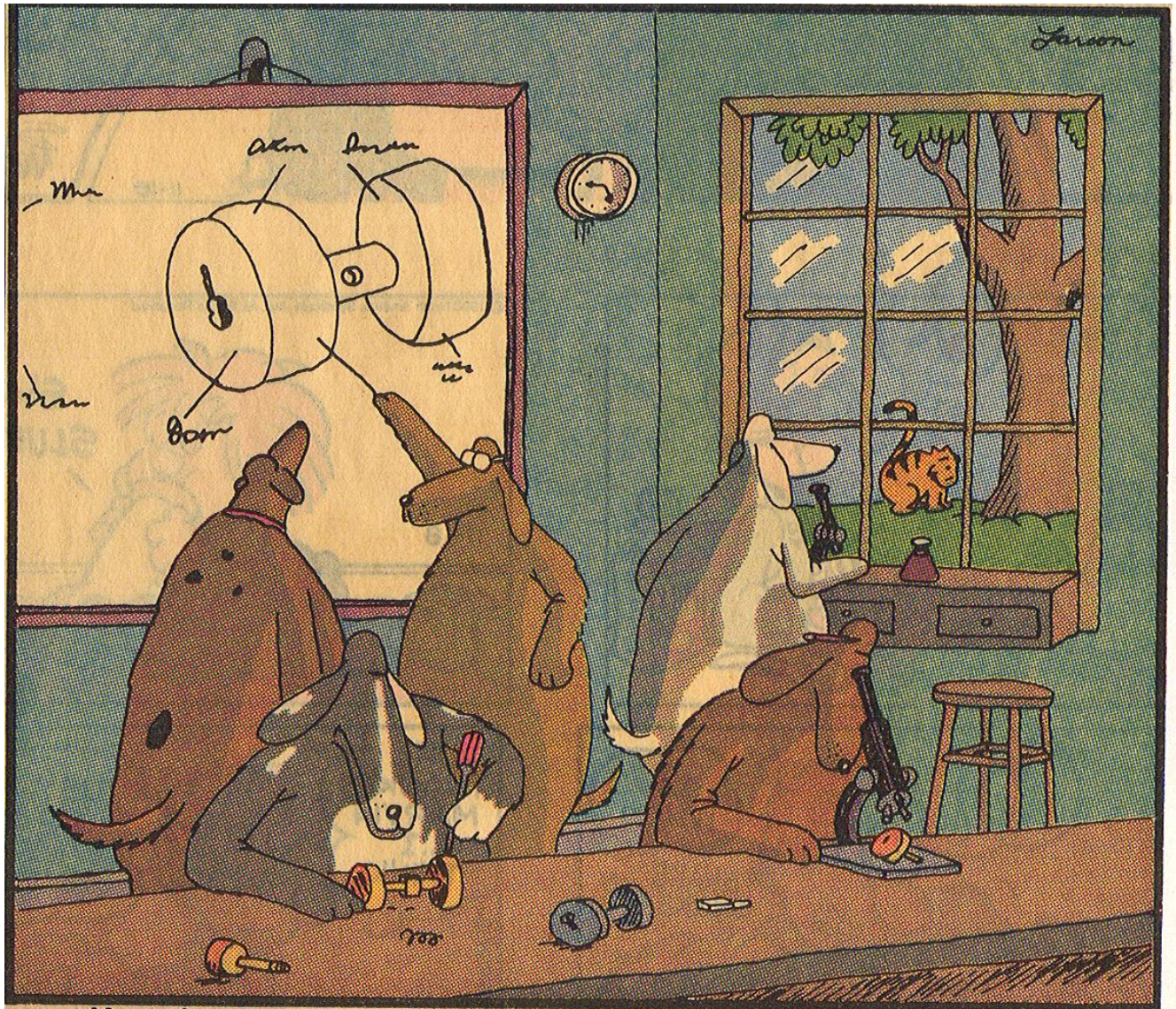
"Construction of an oscillator for any given radiation frequency will greatly extend the region of application of lasers. It is clear that if we make a laser with a sweep frequency, we apparently shall be able to influence a molecule in such a say that definite bonds will be excited and, thus, **chemical reactions will take place** in certain directions.

"However, this problem will not be simple even after design of the appropriate lasers. But one thing is clear: the problem is extremely interesting and perhaps its solution will be able to make a revolution in a series of branches of chemical industry."

A. M. Prokhorov, Nobel Lecture, December 11, 1964

What if the effect of exciting specific bonds is not chemical?

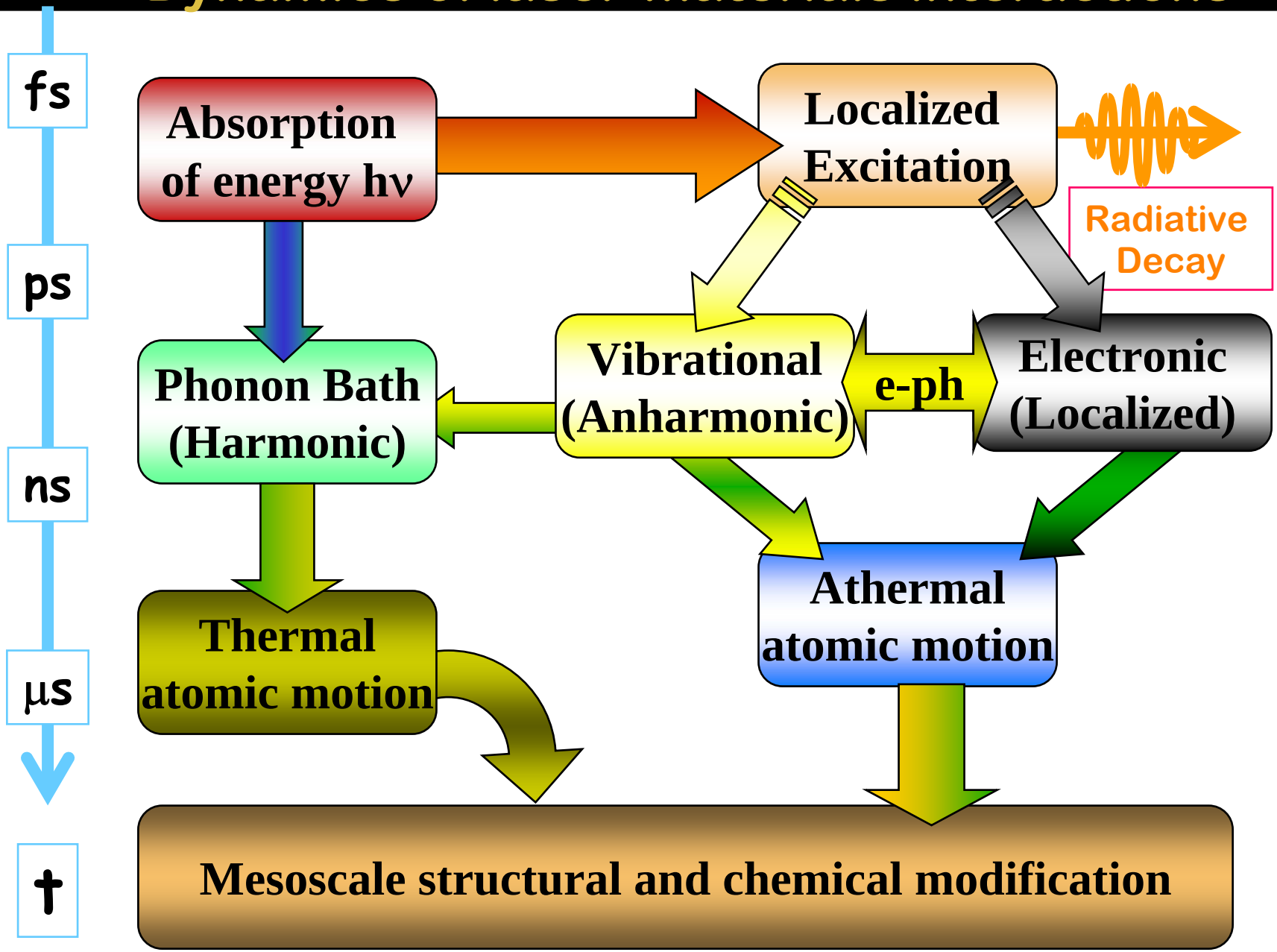
Is ps IR laser ablation a thermal process?



What you are about to hear …

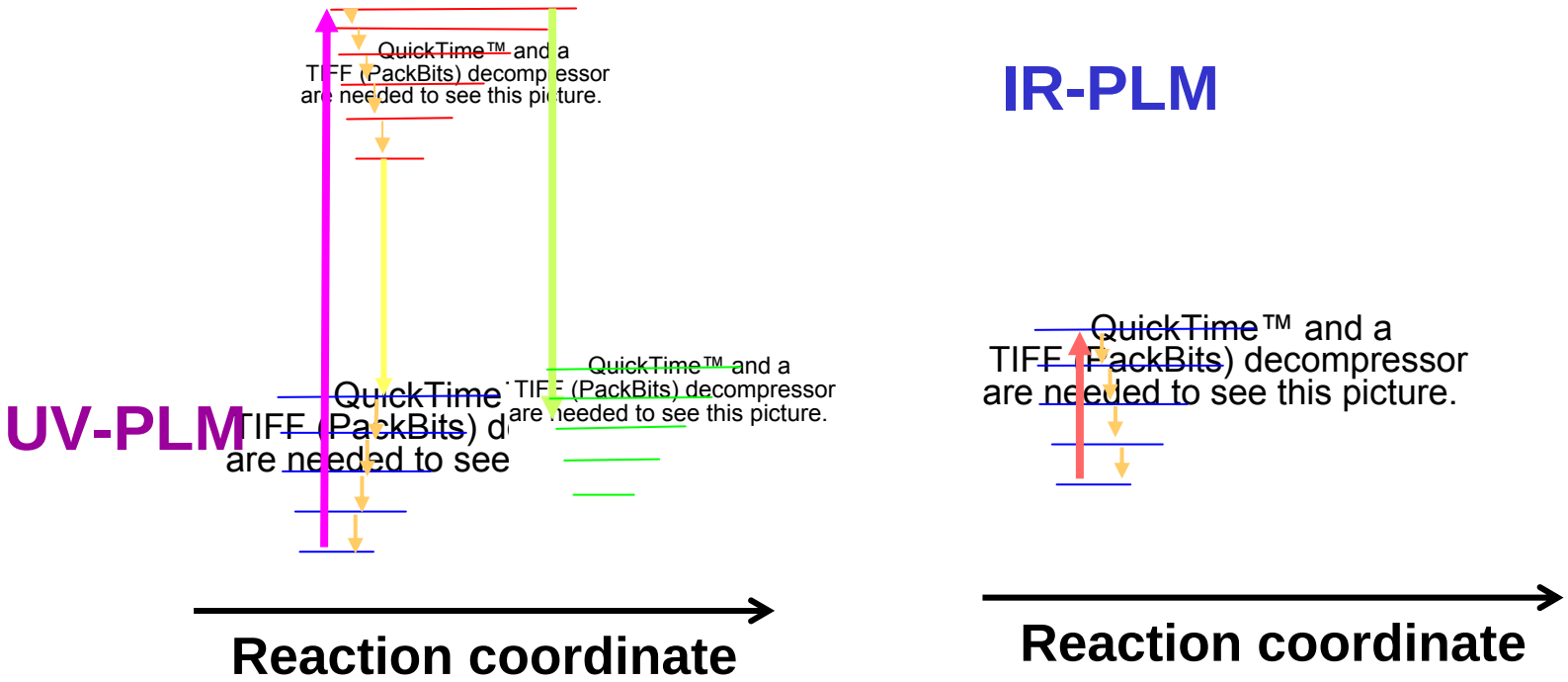
- A new paradigm: resonant infrared pulsed laser deposition (RIR-PLD) of polymers
- Some case studies …
  - Biomedical applications: PEG, PLGA, Teflon
  - Sensors: fluoropolyol, SXFA
  - Electronic applications: Polyimide
  - Opto-electronic applications: MEH-PPV
- Evidence for low-temperature, non-thermal character of RIR-PLD … and some thoughts about a substitute for the FEL

Dynamics of laser-materials interactions



A novel paradigm for materials modification

- UV-visible-NIR processing begins with *electronic* excitation — but many materials modifications require *vibrational* energy.
- Relaxation of UV-visible-NIR energy often leads to undesirable, photolytic or photochemical products.



Efficient laser deposition

- Requires an ablation process which
  - Produces vapor, rather than particulates or clusters
  - Localizes vibrational energy long enough to break bonds
  - Converts photon energy into desired material modification
- Efficiency requires spatio-temporal energy localization:
  - Thermal confinement $\tau_L < L_{opt}^2 / D_T$ and/or
  - Mechanical or stress confinement $\tau_L \leq L_{opt} / C_s$
  - Minimal "leakage" of energy into heat (phonons), defect formation
- The processing rate and total yield are

$$\frac{dn_{\text{proc}}}{dt} = \eta n_{\text{target}} \sigma_{(k)} I^k \Rightarrow n_{\text{proc}} \propto \frac{E_{\text{abs}}}{V} \propto F_{\text{abs}} \alpha(\omega, I)$$

- In the IR, the process yield is frequency and intensity-dependent!

Why ultrashort, high repetition rate pulses?

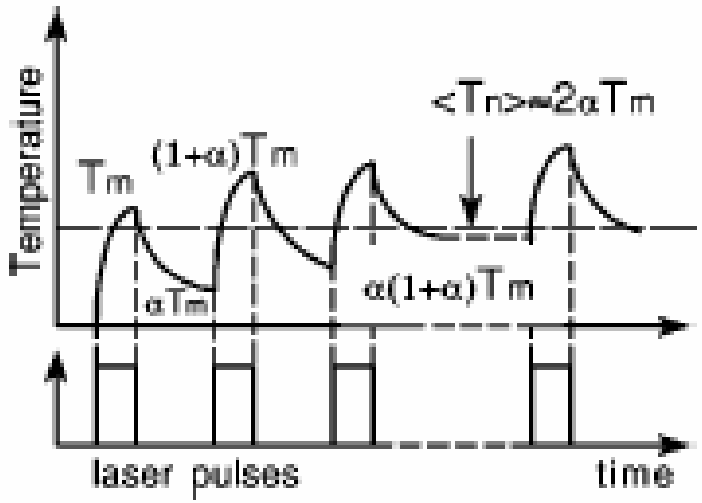
- Need to deliver laser energy before thermal confinement breaks down and heat diffuses - so …
- Use ultrashort, low energy pulses (≤1-5 ps, 3-15 μJ) to generate a high density of vibrationally excited states, and
- Run at high pulse-repetition frequencies for efficient processing (high through-put) of material.

$$T_{\max} = \sqrt{\frac{2}{\pi}} \frac{I_{\text{abs}} \left(D_{\text{therm}} \tau_{\text{L}}\right)^{1/2}}{\kappa}$$

After n pulses, *T is*

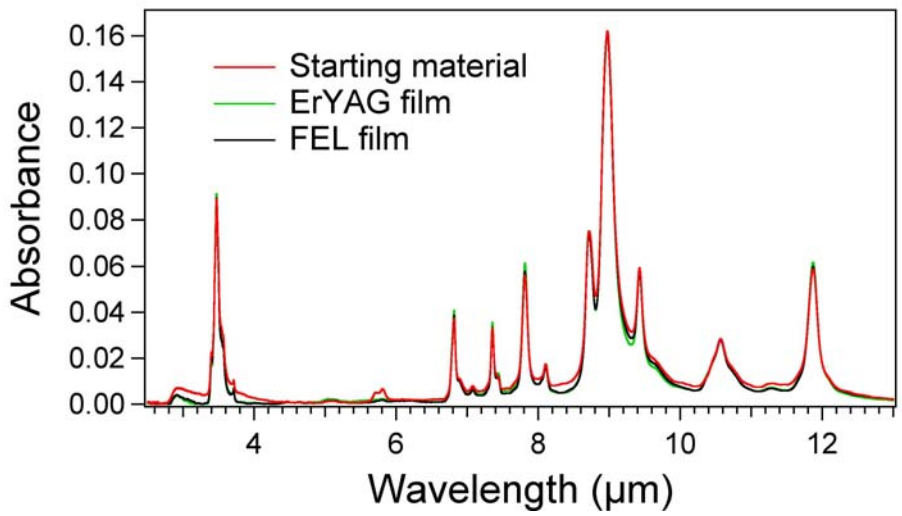
$$T_{\text{n}} = 2T_{\max} \sqrt{\tau_{\text{L}} \cdot \nu_{\text{PRF}}}$$

Ergo, low temperature, high yield!



Gamaly, Rode, Luther-Davies, J. Appl. Phys. **85**, 4213 (1999)

Why a tunable, mid-IR laser?



Er:YSGG
2.79 μm

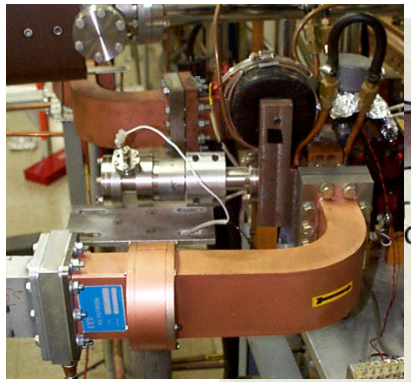
Er:YAG
2.94 μm

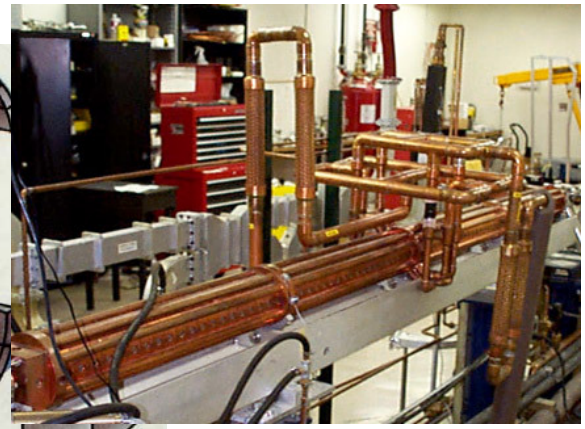
CO_2
9.4-10.6 μm

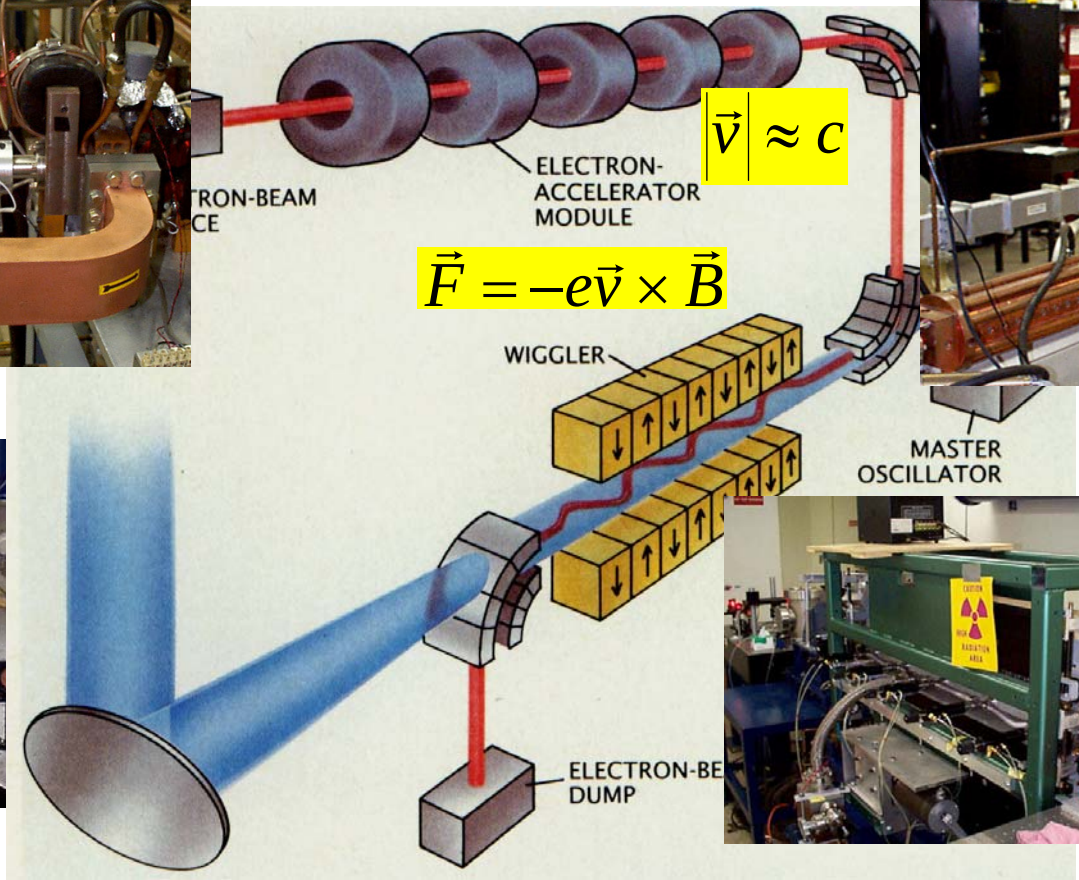
OPO
(1.5-4.0 μm)

Vanderbilt rf-linac FEL
1.8-10.2 μm

- Many organic and inorganic materials have rich vibrational spectra in the 1-10 μm region
- Tuning wavelength means controlling *density of vibrational excitation* in the absorption zone
- Tuning *may* limit **selective pathways** for laser energy
- BUT fixed frequency IR lasers do not cover many vibrational bands of interest, and
- Solid-state laser devices (*e.g.*, OPOs, OPAs) still have limited tuning range, fluence, intensity

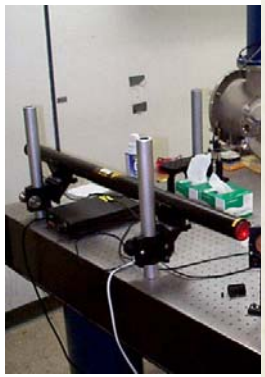






$$\left|\vec{v}\right| \approx c$$

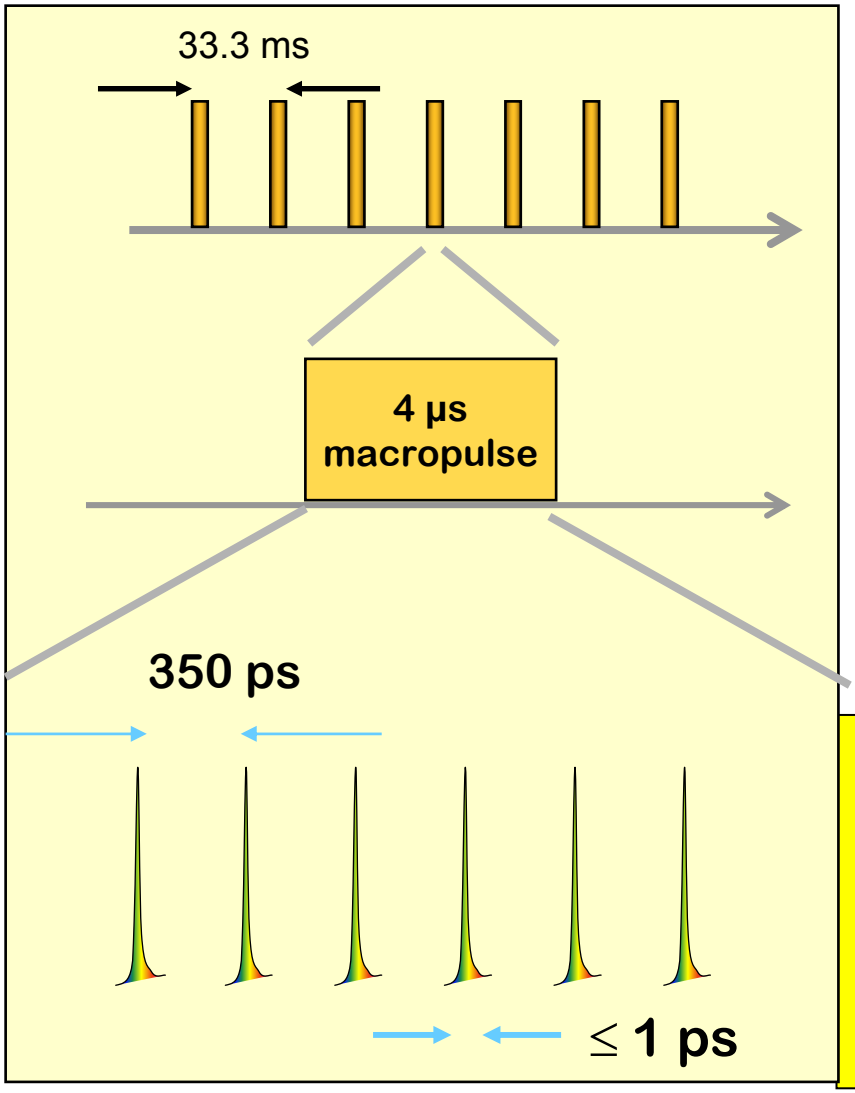
$$\vec{F} = -e\vec{v} \times \vec{B}$$

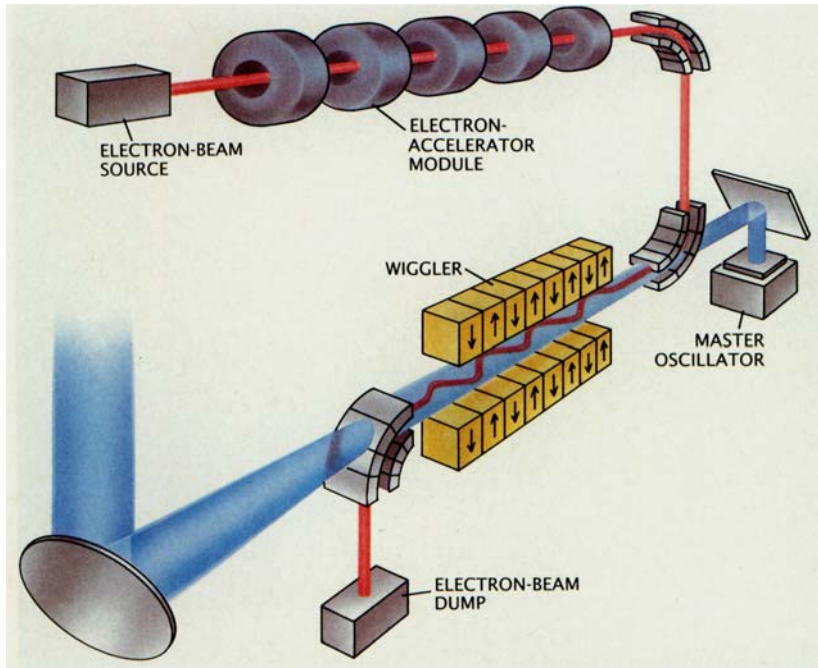


$$\lambda_{FEL} = \frac{\lambda_{Wiggler}}{2\gamma^2}\left[1+\kappa^2(B)\right] \quad \gamma = \frac{E_{beam}}{m_0 c^2} \approx 80$$

$$\Rightarrow \quad 2 \ \mu\text{m} \le \lambda_{FEL} \le 10 \ \mu\text{m}$$

"To him who has a hammer, …"





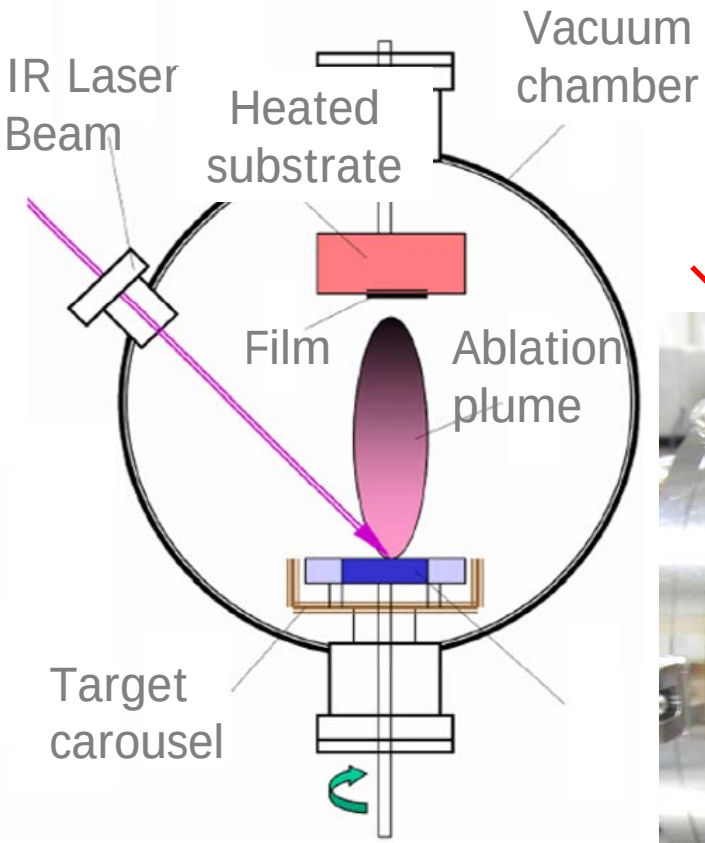
Tuning range 2-10 μm
Macropulse energy 30-150 mJ
Micropulse energy 3-15 μJ
Spot size ~ 10^{-2}-10^{-4} cm^2
Switched macropulse 50-4000 ns

FEL irradiation parameters

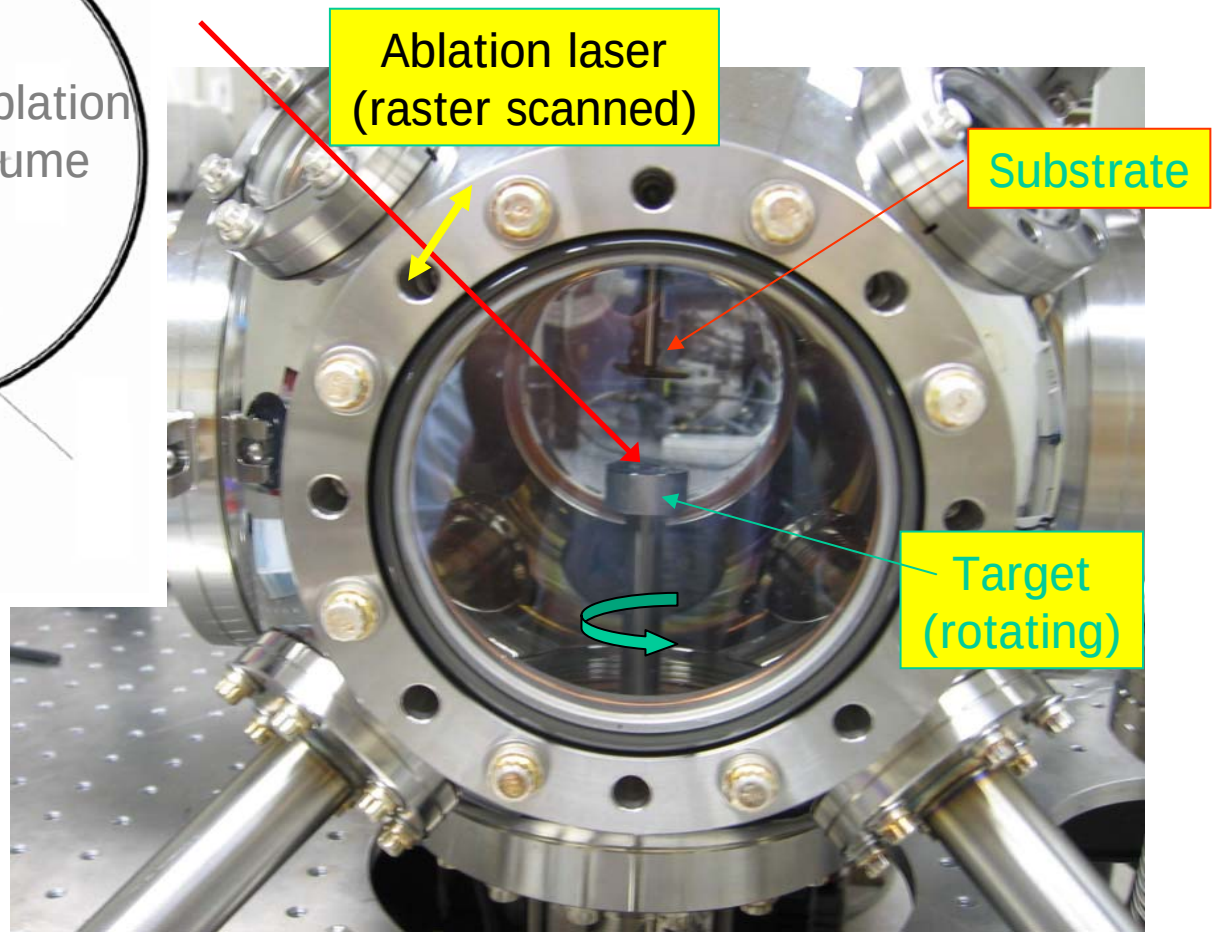
	Micropulse	Macropulse
Pulse duration	1 ps	4 μs
Pulse energy	1-30 μJ	10-300 mJ
Fluence	$\leq 5 \times 10^{-3}$ J·cm^{-2}	—
Intensity	$1\text{-}10 \times 10^{9}$ W·cm^{-2}	—
Photon flux	$\leq 5 \times 10^{29}$ cm^{-2}s^{-1}	
Photon density*	$\leq 5 \times 10^{22}$ cm^{-3}	
Dose		1-100 J/cm^2

* Scales with absorption (penetration depth)!

Experimental geometry



Thin-film deposition
by pulsed laser evaporation.



A sampling of case studies …

- A new paradigm: resonant infrared pulsed laser deposition (RIR-PLD) of polymers
- Some case studies …
  - Biomedical applications: PEG, PLGA, Teflon
  - Sensors: fluoropolyol, SXFA
  - Electronic applications: Polyimide
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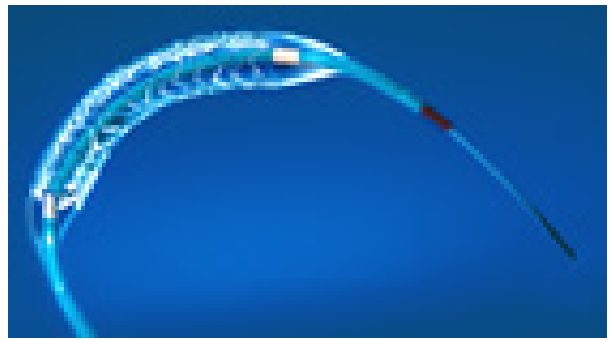
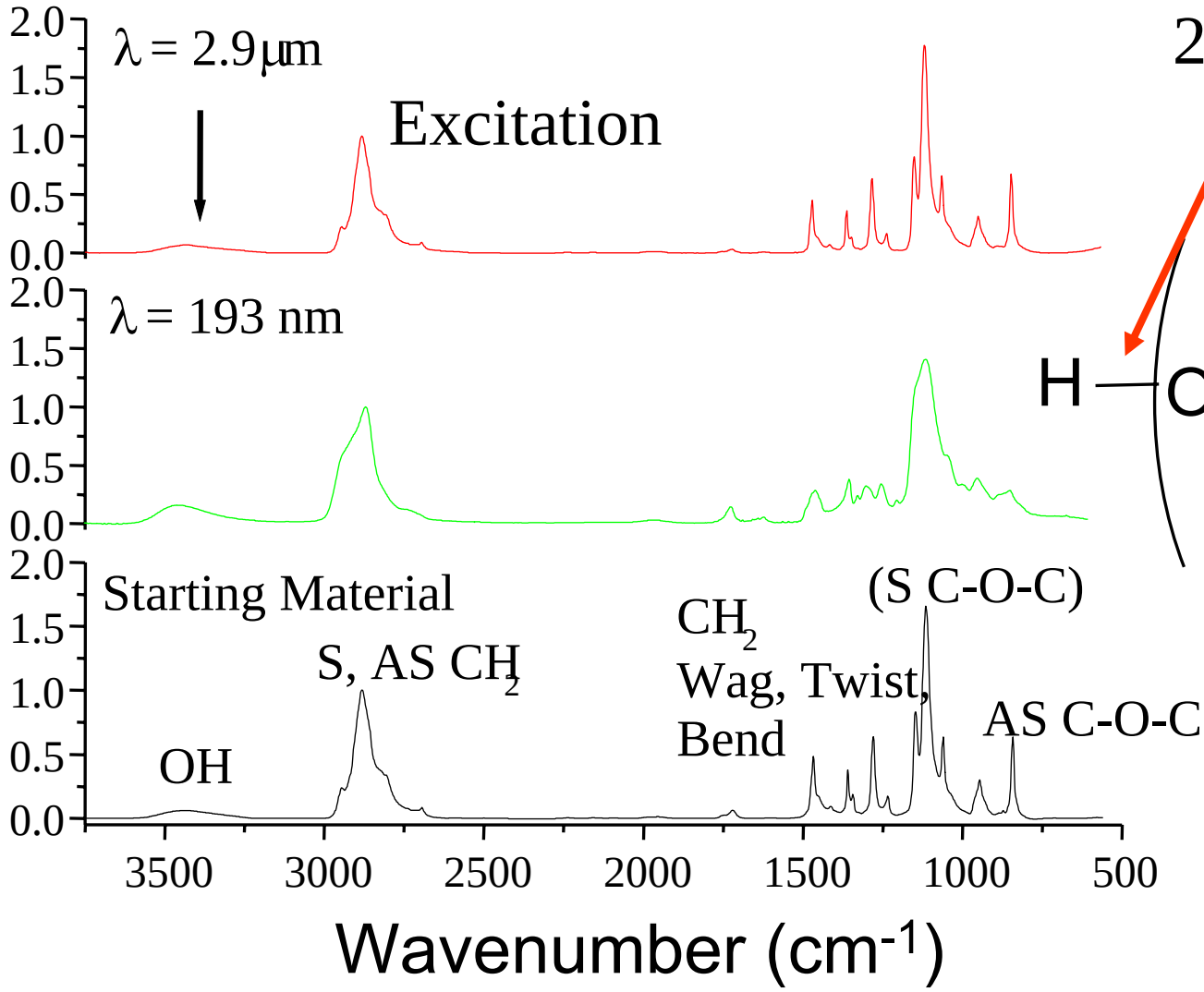
- Evidence for low-temperature, non-thermal character of RIR-PLD … and some thoughts about a substitute for the FEL

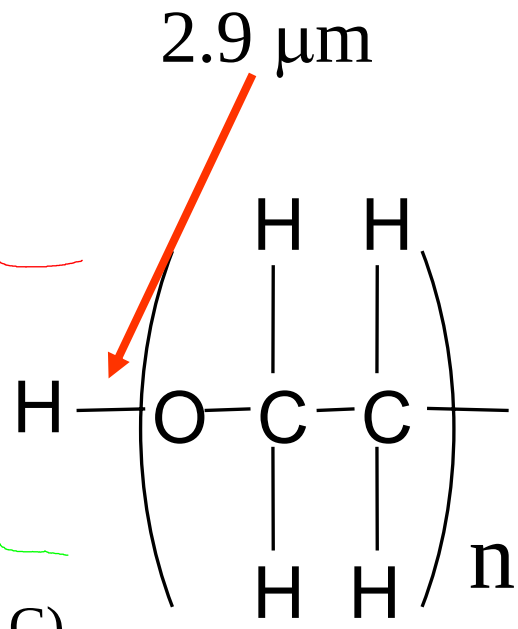
Thin films for biomedical technology

- Applications: drug delivery, medical device packaging, biodegradable coatings, temporary use objects, … and micro-electro-mechanical systems (MEMS)
- Requirements: precise thickness control to manage release time, coat irregular shapes (conformal coating), deliver functionalized moeties
- RIR-PLD shown to work on several interesting systems: PEG, PLGA, Teflon®, …



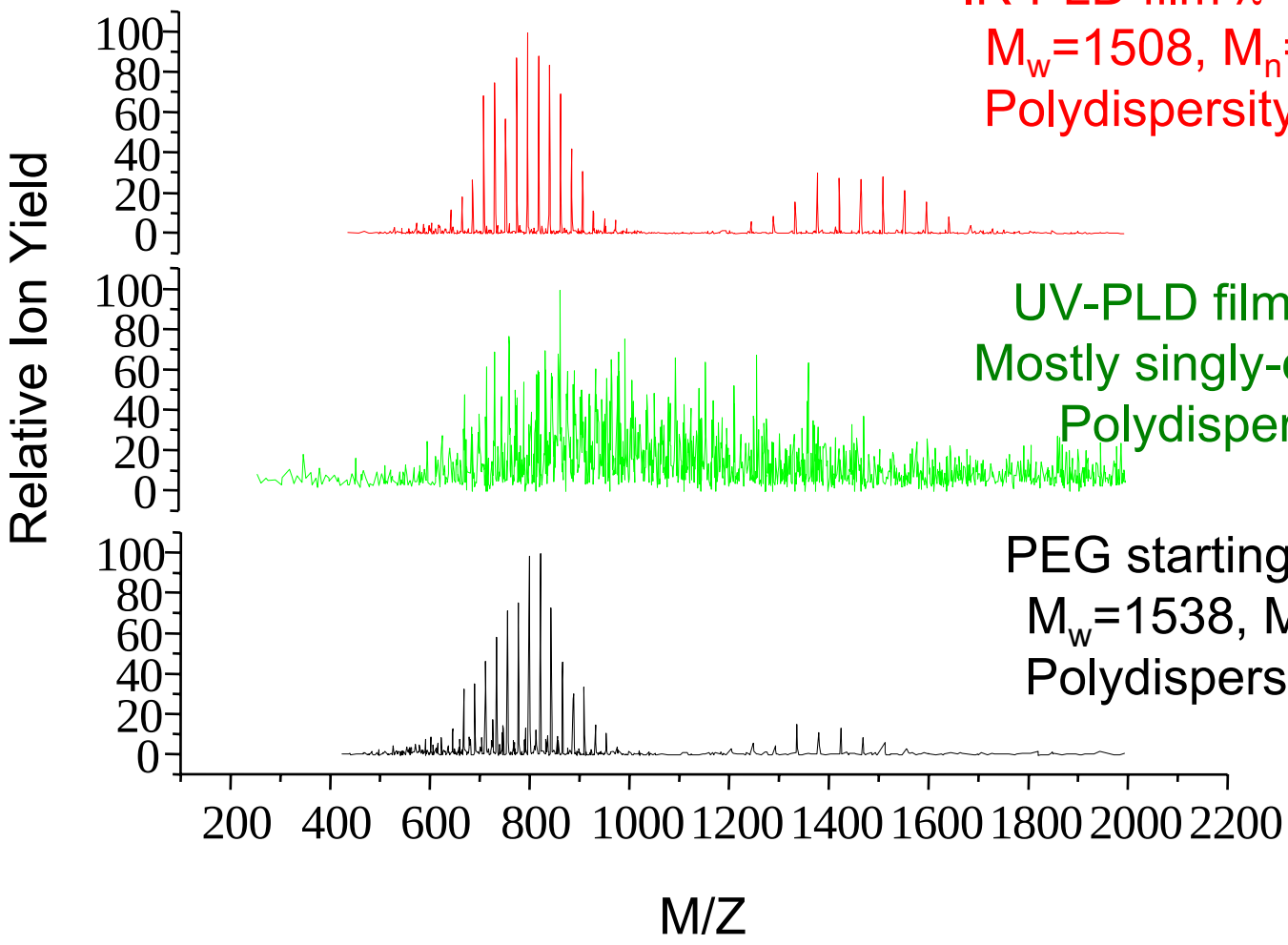
First try: PEG (1500 MW)





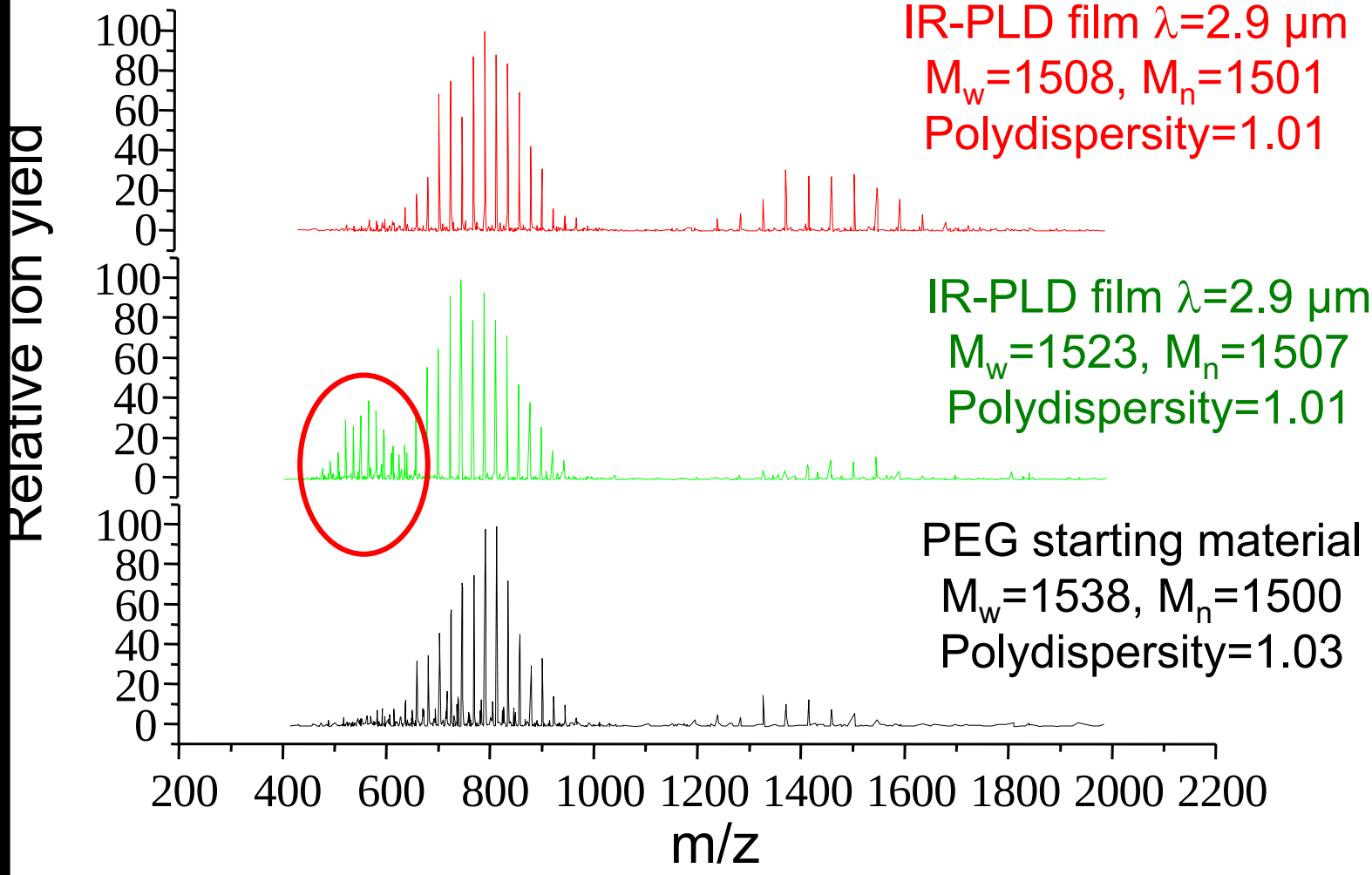
UV PLD is tough on polymers

Electrospray ionization mass spectra of PEG (1450) films



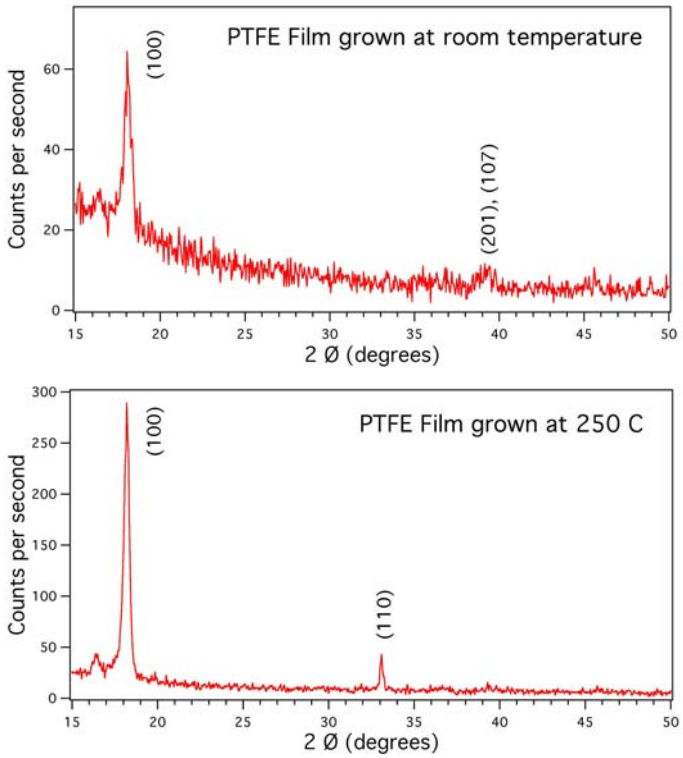
Off-resonance IR is also bad

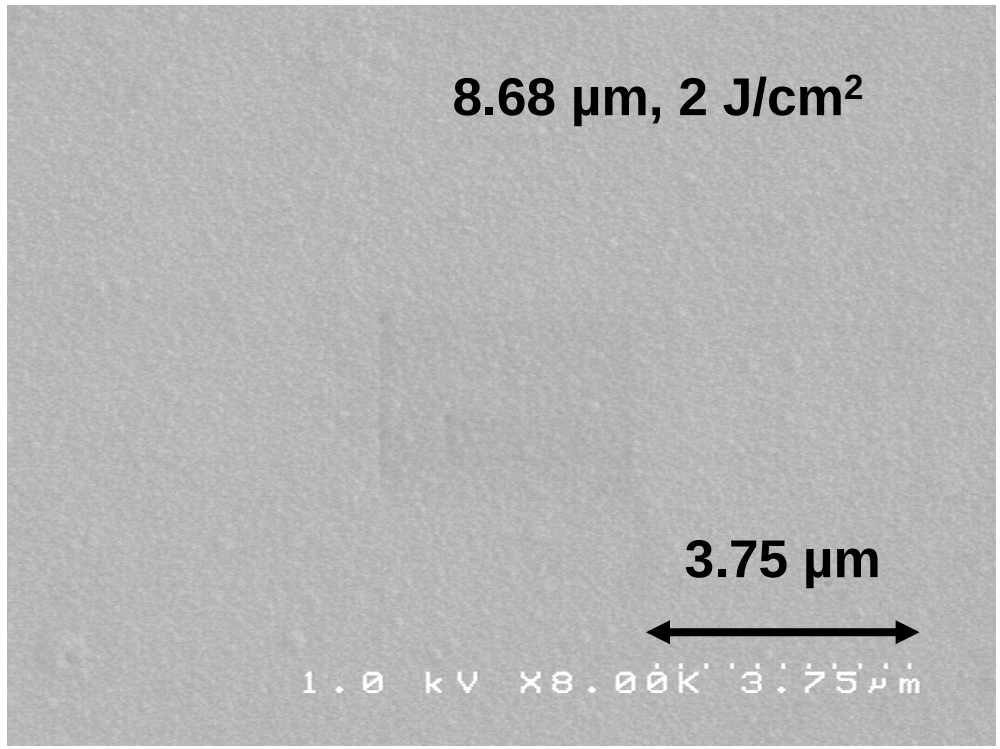
Electrospray ionization mass spectra of PEG (1450) films



RIR-PLD PTFE Films on Si Substrates

Why PTFE films? Dielectric properties, low friction coefficient, chemical inertness, biocompatibility, …

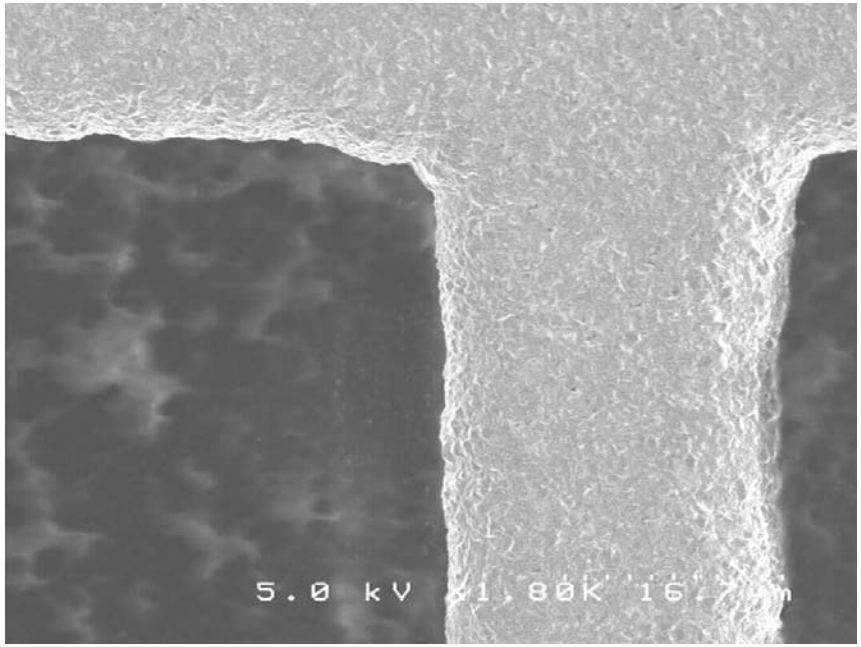




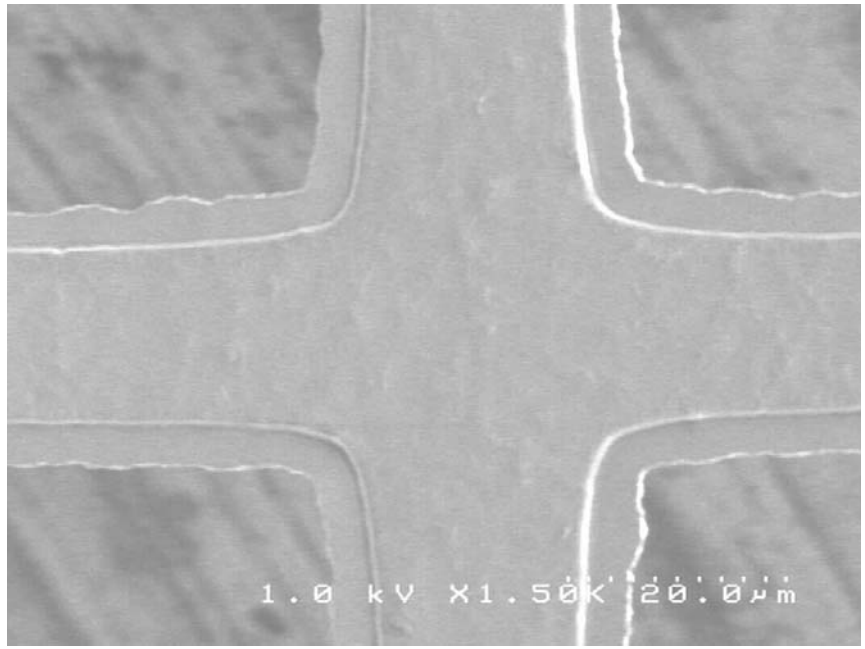
Films have no large scale particulates, RMS roughness = 12 nm. XRD shows increased crystallinity, smoothness with moderate heating

PTFE coated microstructures

Uncoated Ni wire mesh

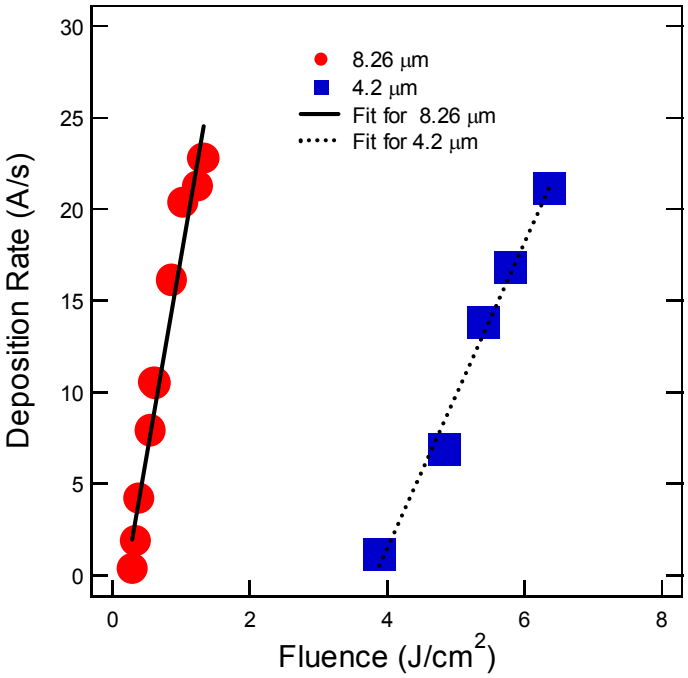


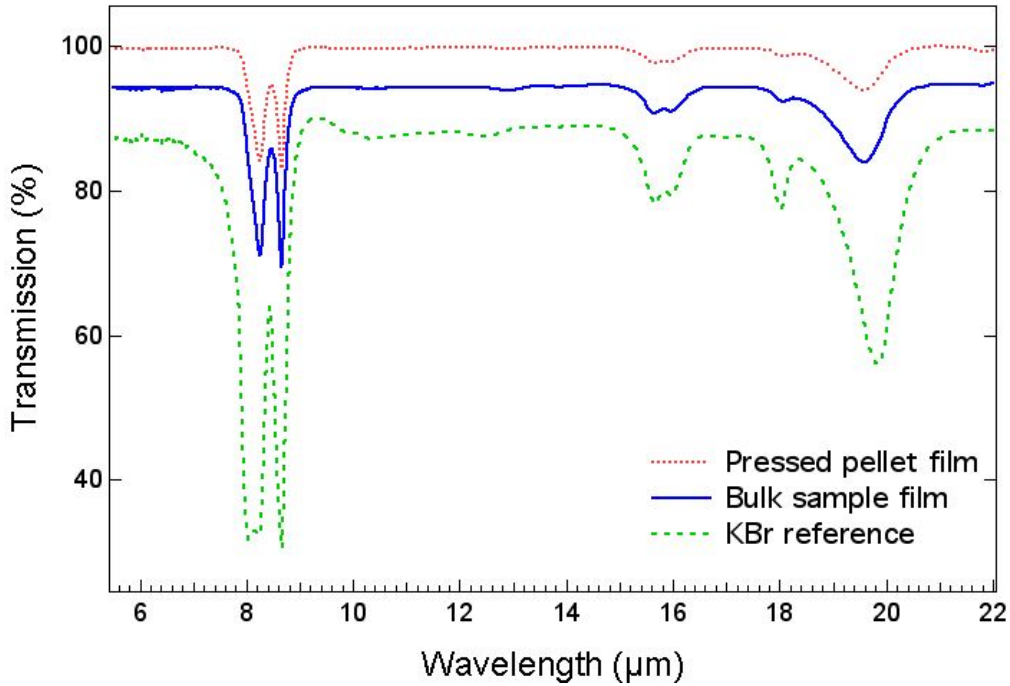
Coated with 200 nm PTFE



- Deposited 135-nm thick coating in 5 min at F=0.5 J/cm^2, λ=8.26 µm. No significant particulate formation.
- Note sharp edge of PTFE film on Ni mesh structure.

RIR-PLD of poly(tetrafluoroethylene)





- Penetration depth is 1.5 μm at 8.26 μm, 30 μm at 4.2 μm, suggesting strong *vs* weaker local excitation, respectively.
- One-dimensional heat-flow calculations show that T_{melt} is not reached, but final target temperature higher at 4.2 μm.
- Low threshold at 8.26 μm corresponds to smoothest films; at 4.2 μm, ablation may be dominated by droplet formation.

A schematic sensor device

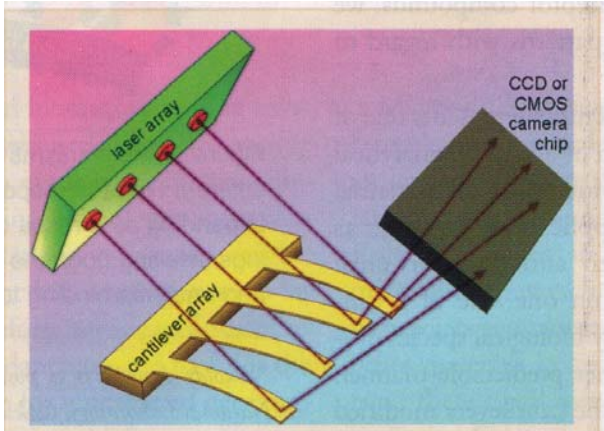


Figure 1 Multi-cantilever sensor with an advanced version of the optical lever read-out uses an array of VCSELs for the source and a CCD or CMOS camera as a read detector sensor.

- Cantilever sensor
- Optical detection
- Mechanical or chemical response, depending on mechanism

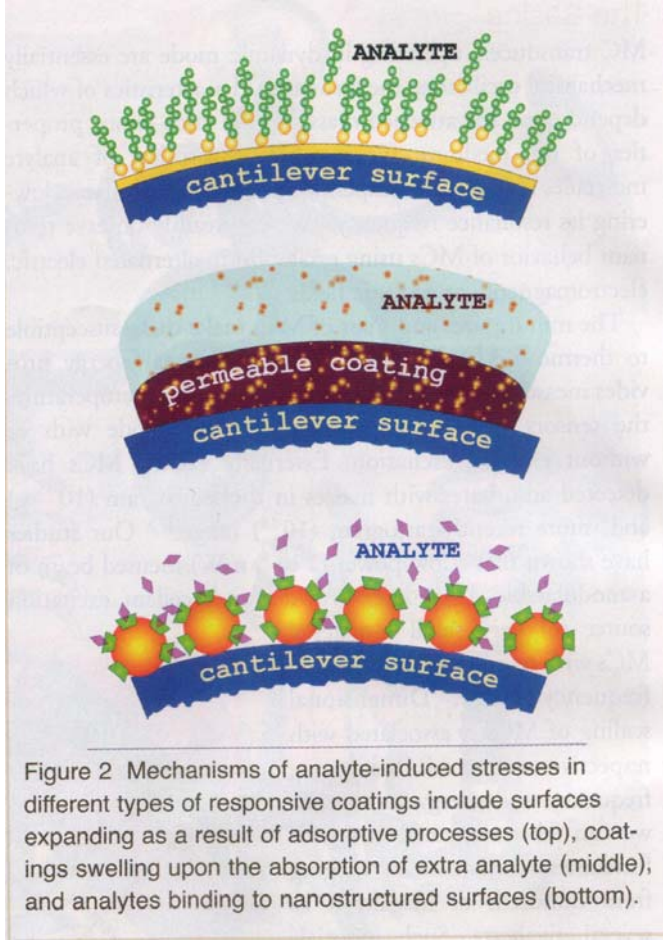
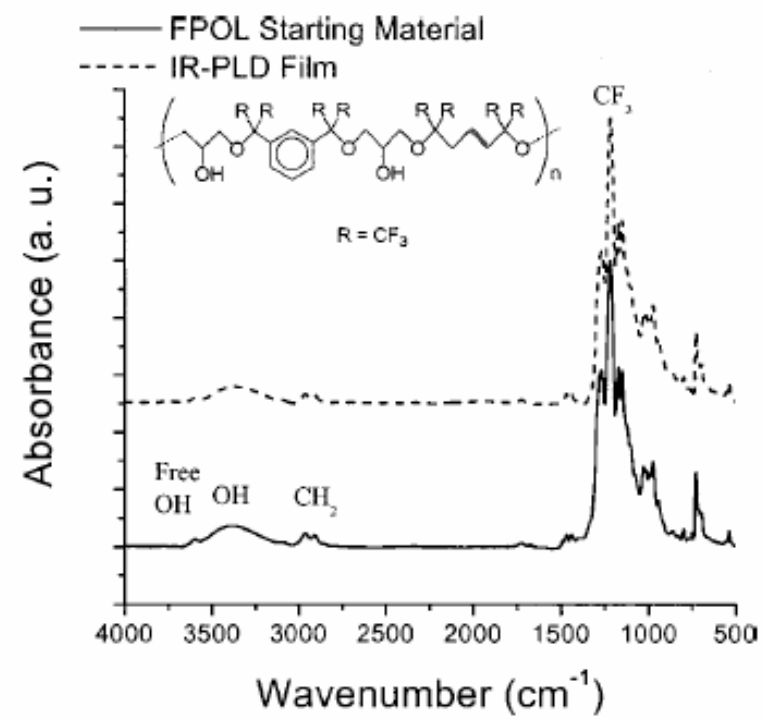


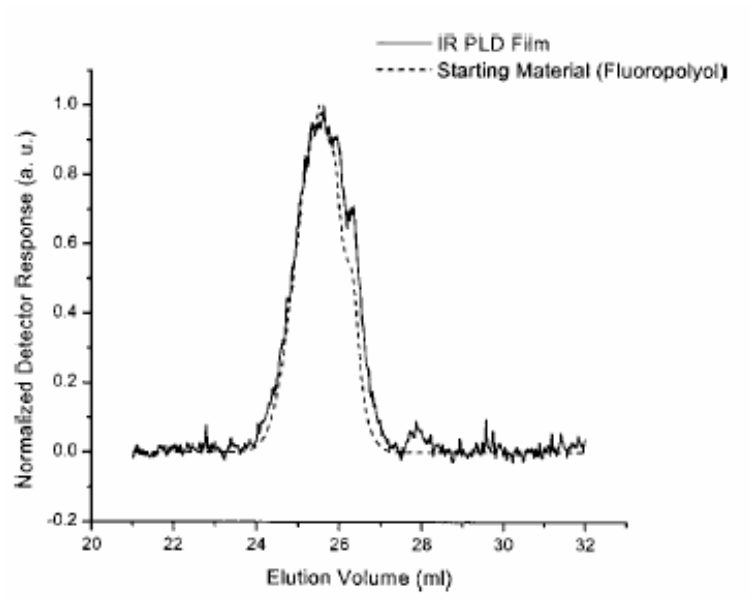
Figure 2 Mechanisms of analyte-induced stresses in different types of responsive coatings include surfaces expanding as a result of adsorptive processes (top), coatings swelling upon the absorption of extra analyte (middle), and analytes binding to nanostructured surfaces (bottom).

Functionalized polymer deposition

Appl Phys Lett **79**, 2847 (2001)

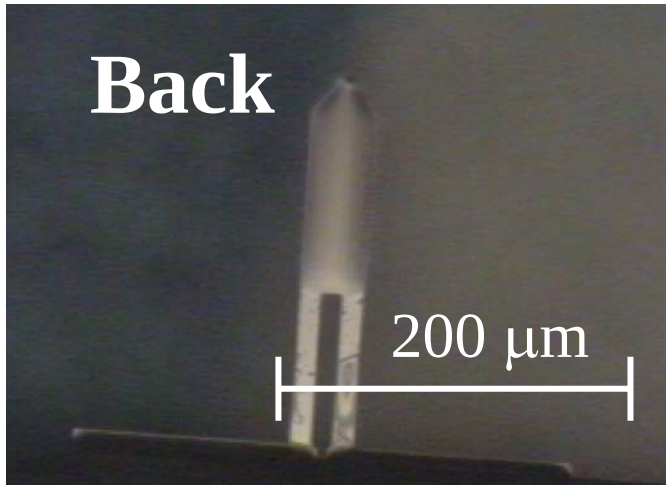
- SAW or cantiliver sensors require coatings of precise thicknesses
- Solubility and selectivity controlled by pendant groups attached to backbone

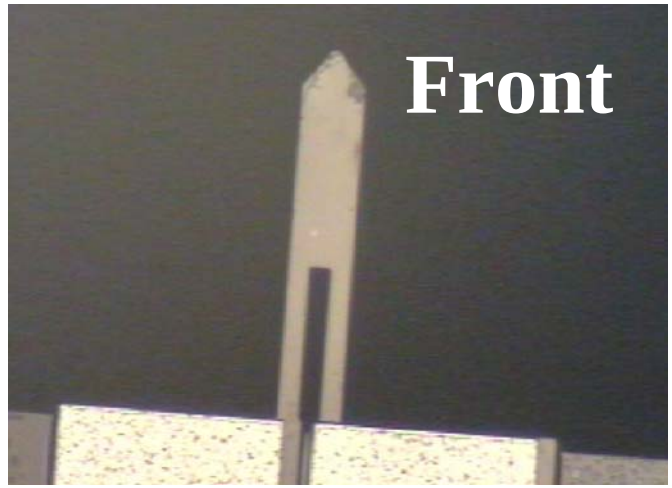




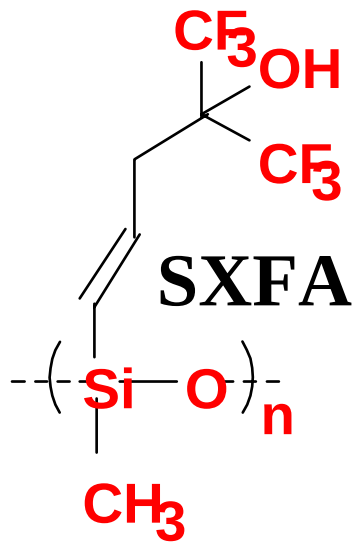
- Nearly identical FTIR spectra of target and film at 2.90 μm (O-H stretch)
- GPC gives polydispersity M_w/M_n is 1.24 for native material, 1.21 for the PLD film.
- Deposition rate is 0.3 nm/macropulse - or 30x that of UV-MAPLE.

Microcantilevers for sensors

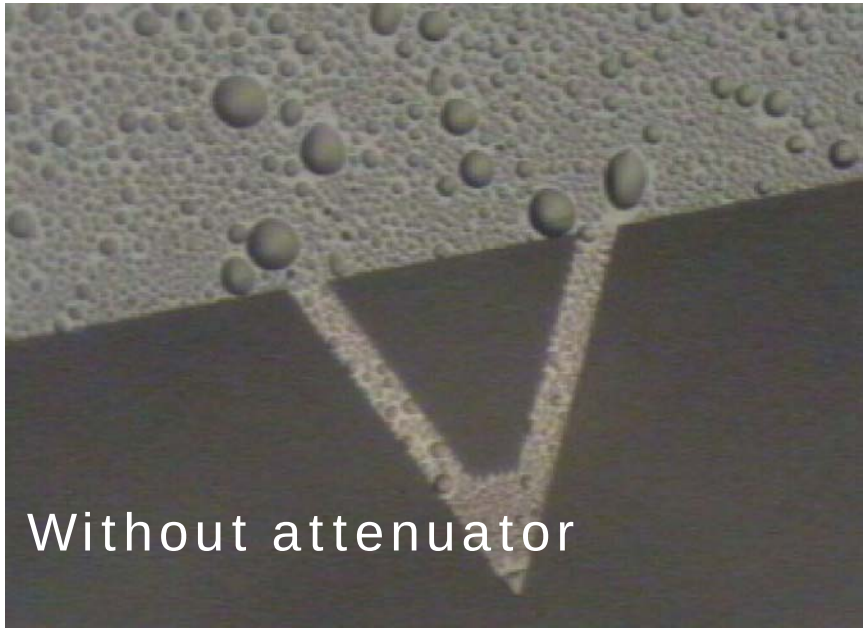


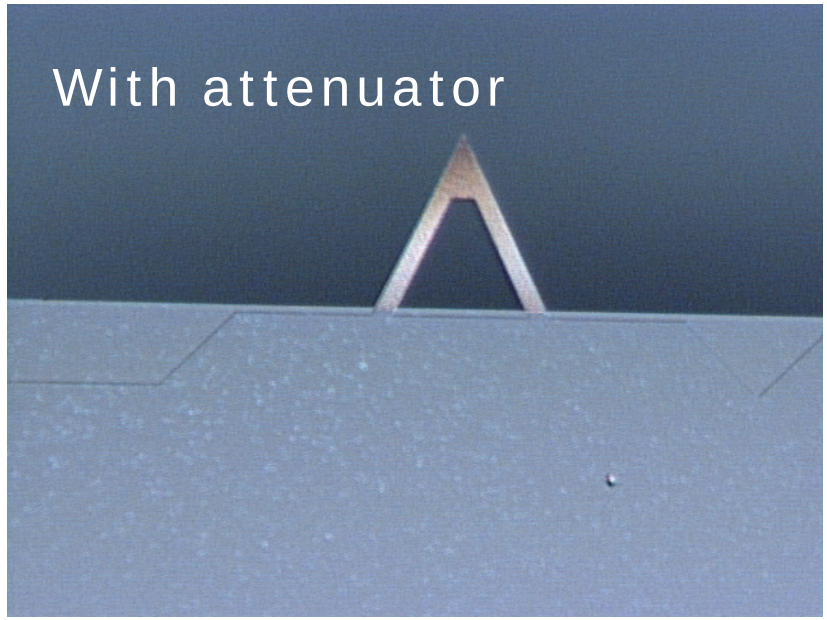


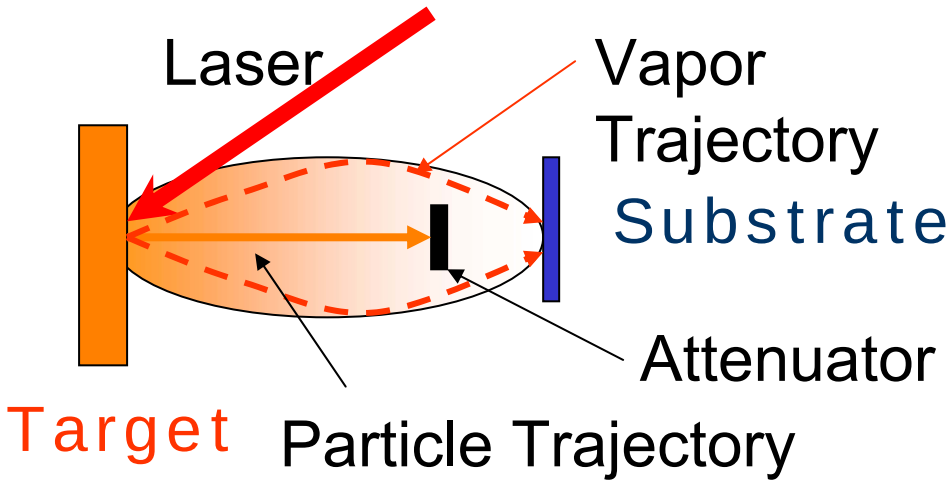
- Strain based sensor REQUIRES coating only one side
- RIR-PLD used to deposit 500 nm of SXFA
- Successful challenge with DMMP simulant vapor
- Device requirements **can not** be met by any other organic film technology (solvents, thickness control)



Improved carbosilane morphology





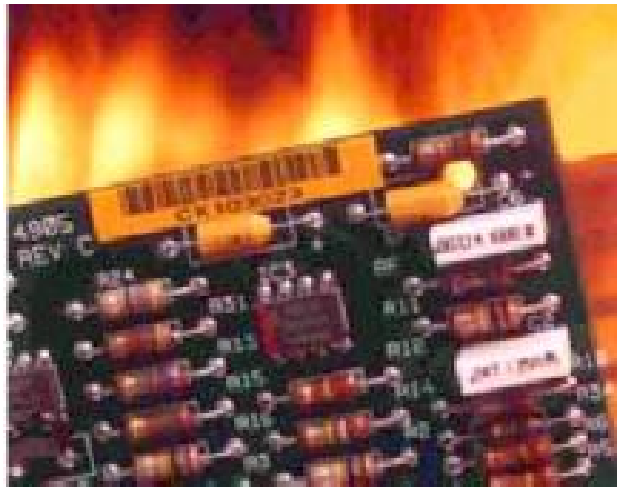


Pulsed laser passive filter deposition system
US Patent 5,458,686
Pique et al., NRL, 1995

Polyimide - a thermoset polymer

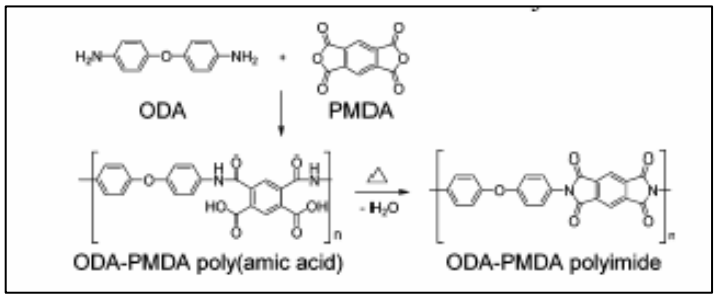
DUPONT

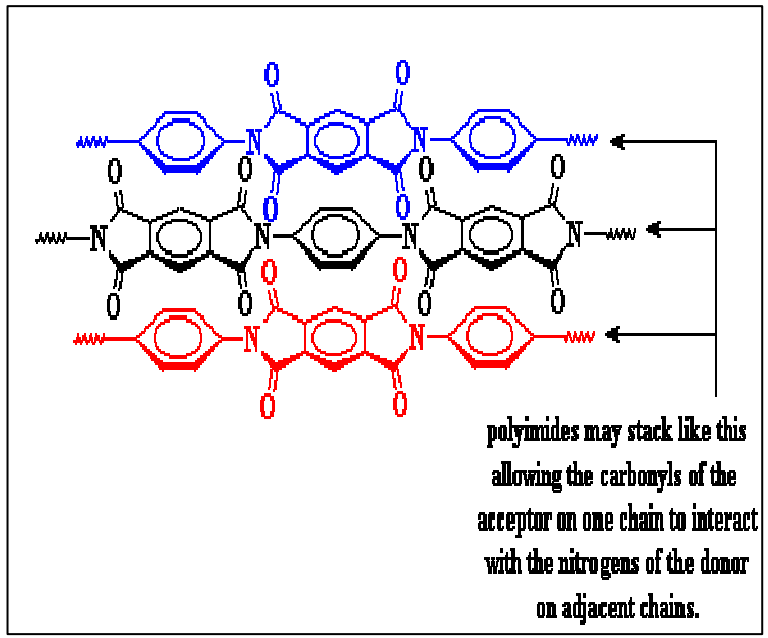
Kapton®
polyimide film



- Withstands huge extremes of temperatures
- Can be fabricated in many different forms
- Excellent insulating properties
- Chemically inert, mechanically hard
- Widely used in electronics industry

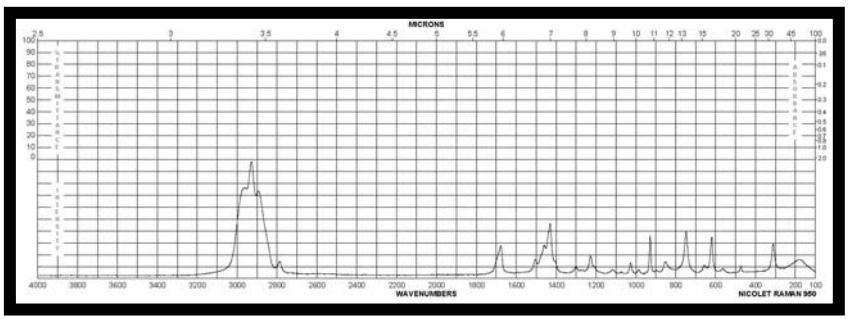
Synthesis and IR-PLD of PAA



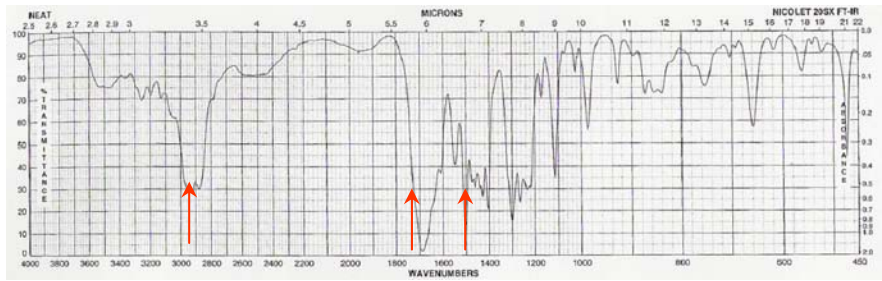


- Normal synthesis requires heating to make “thermoset”
- RIR-PLD with FEL attempted at 3.45, 5.95 and 6.67 μm (see arrows)

n-methyl pyrrolilidone (NMP)



FTIR spectrum of PAA in MNP



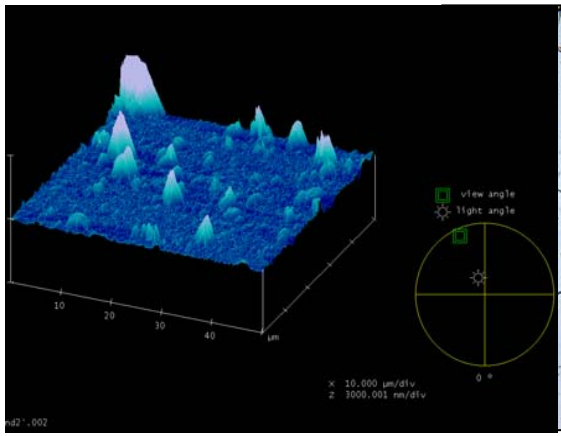
Plume photography of MNP and PAA-MNP

Ablation plume evolution, FEL wavelength 3.45 µm fluence ~3J/cm^2: Top NMP; bottom, PAA solution

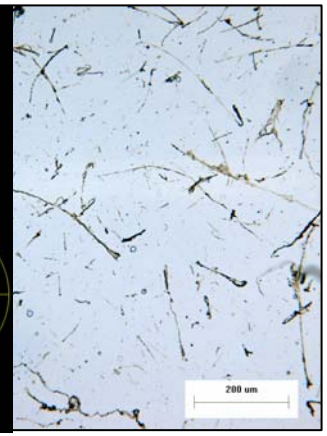
- Clear difference between the NMP matrix solution, and the more viscous NMP-PAA solution.
- Ablation phenomenology strongly resembles the behavior of liquids (*á la* Vogel, Jansen, Venugopalan)
- Suggests an important role for viscosity in the non-destructive ablation of polymers …

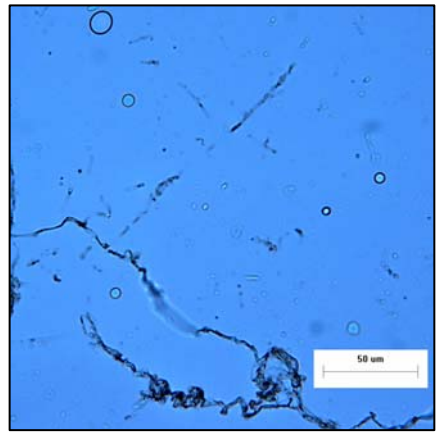
Results of RIR-PLD of PAA in NMP

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.



Thick RIR-PLD film

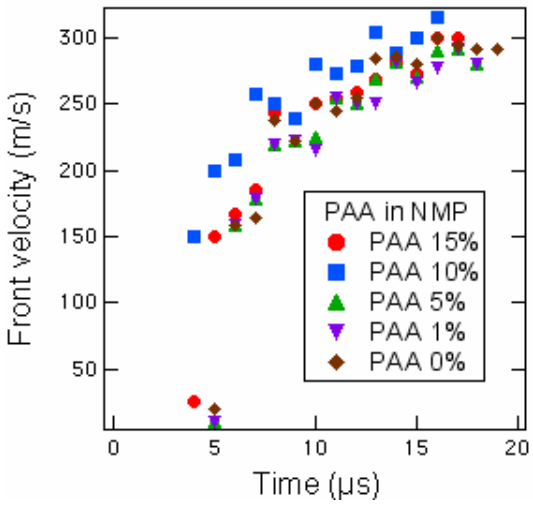


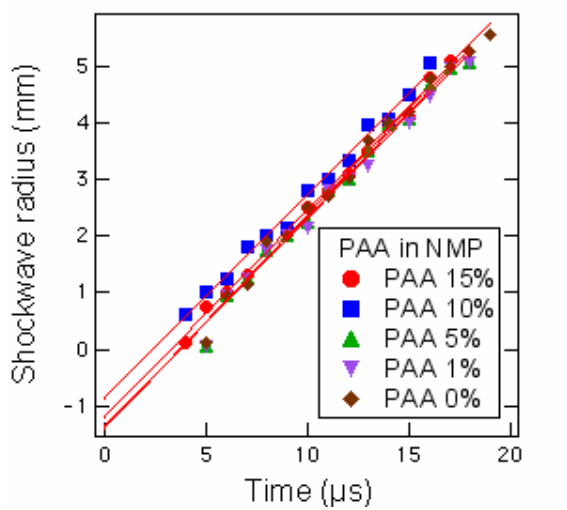


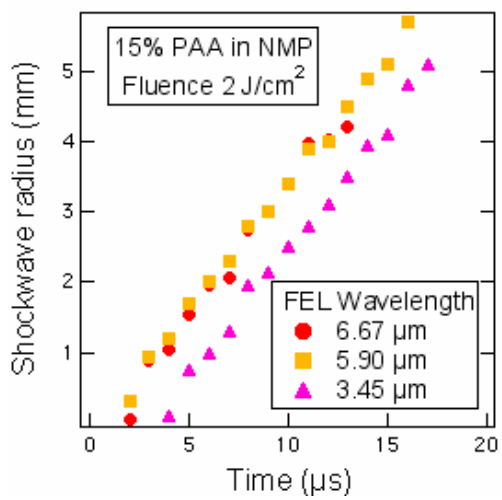
RIR-PLD in vacuum

- Threshold for deposition is ~0.5 J/cm^2 in vacuum and in air. (Scale bar above, right is 200 µm.)
- Photomicrographs show string (only in vacuum) and droplet (in air and vacuum) morphologies for low fluence.
- At higher fluence, films become thicker, but are still uncured until heating.
- Post-deposition methanol wash removed PAA-NMP.
- Curing of the PAA only occurred following heating!

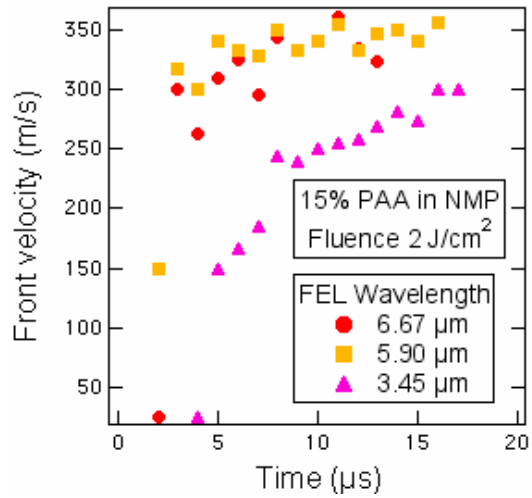
Shock-wave data at 2 J·cm^2







- Data from shadowgraph experiments carried out in air as function of delay time
- Shadowgraph apparatus calibrated by machinist's ruler
- At any given wavelength, shockwave velocity is relatively independent of PAA concentration
- Clear dependence of velocity on wavelength; note that 3.45 μm ablation produces slower shock wave.



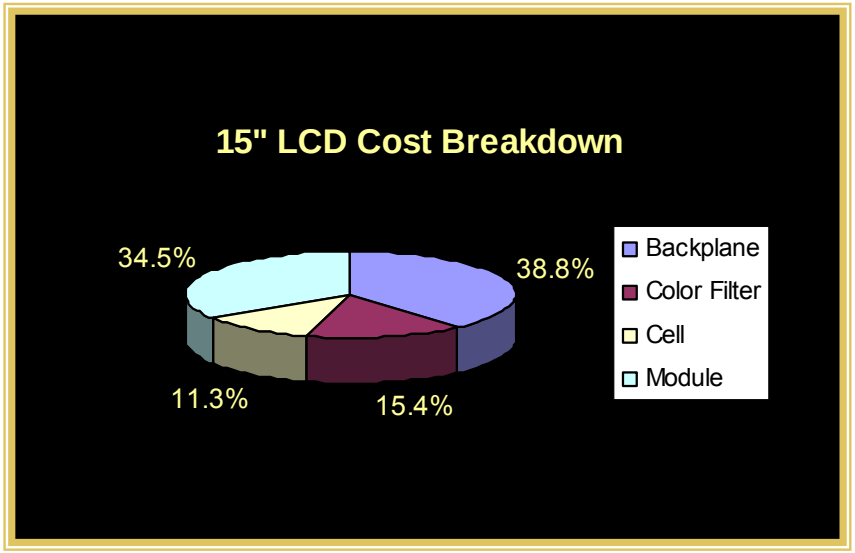
OLED Manufacturing

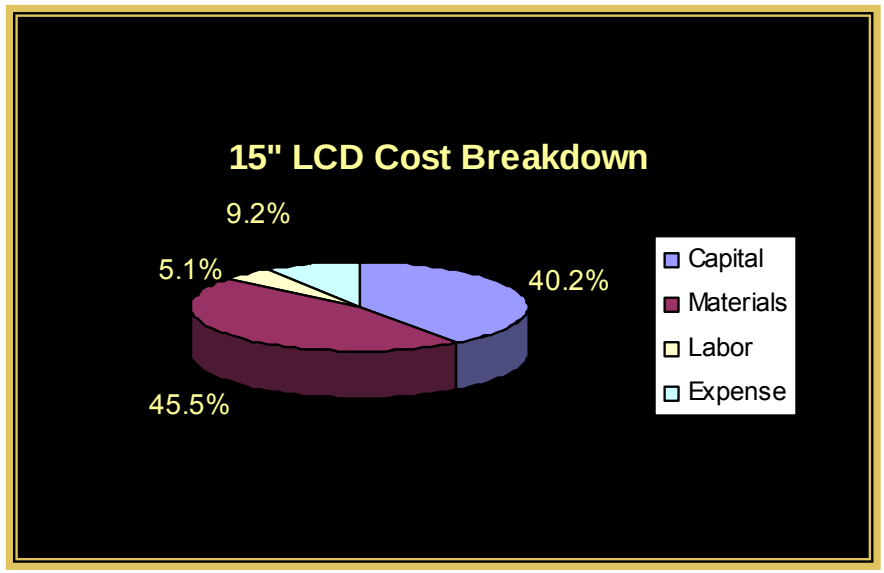
- Cost Driver

Year	2004	2007	2010
Fab cost ($/sq in)	5.00	1.00	0.50

  - Source: U.S. Display Consortium Roadmap

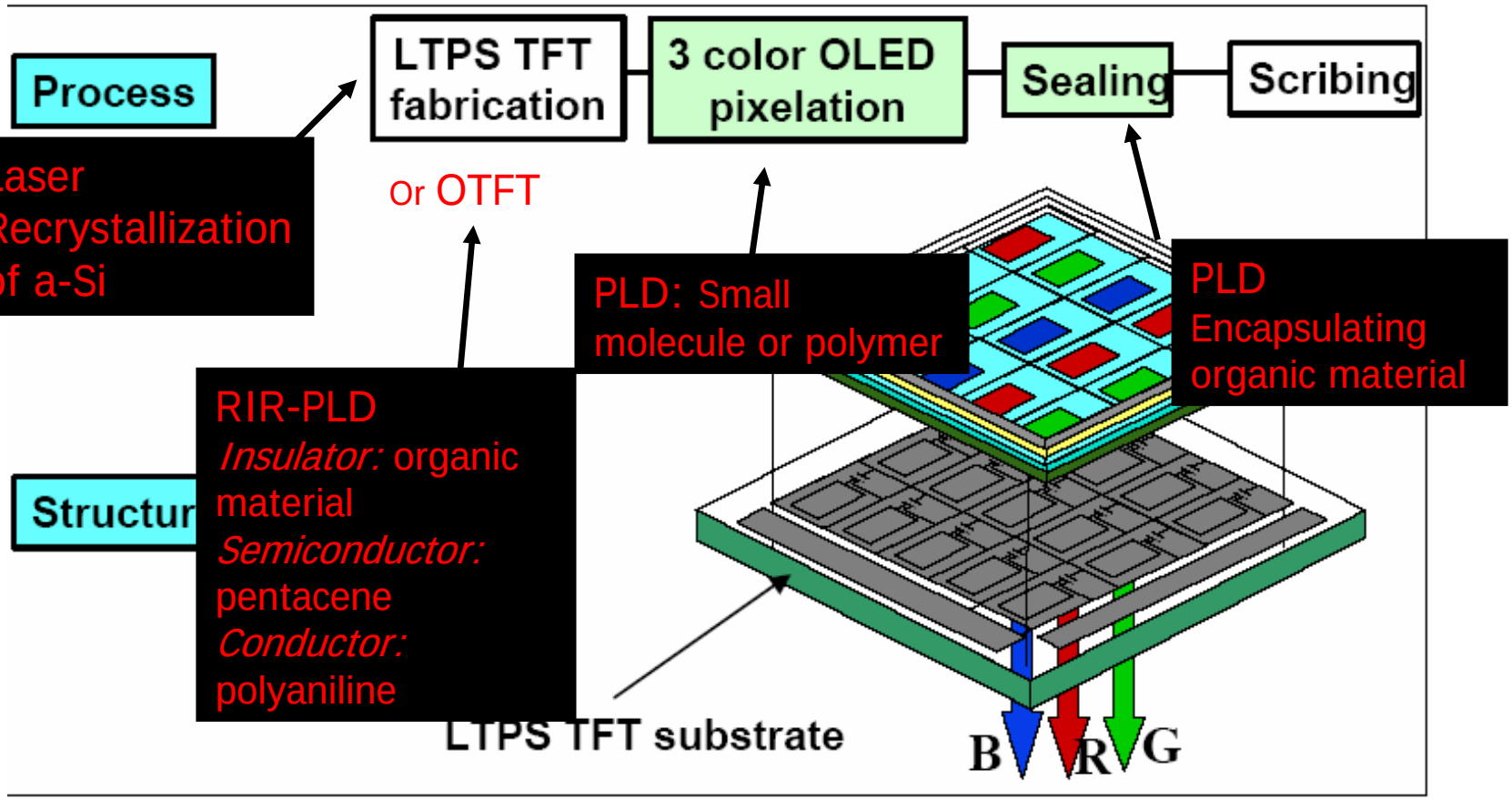
- Cost Breakdown



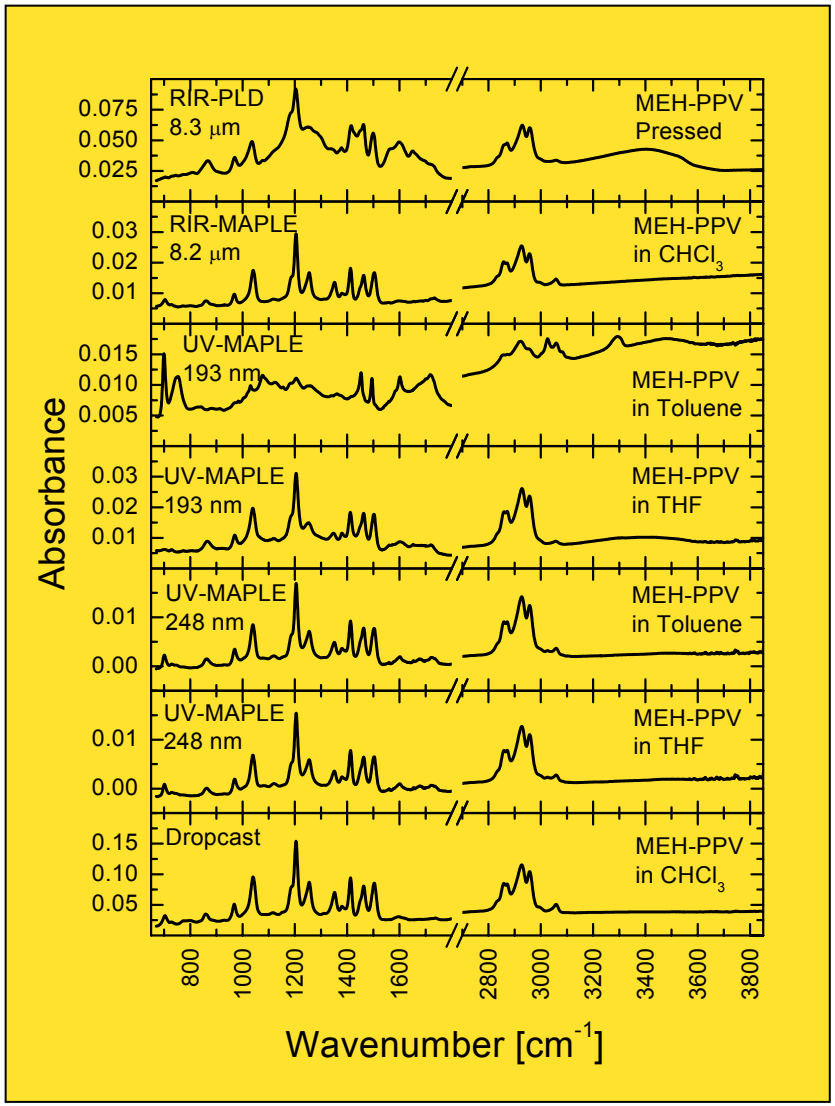


- Conclusion: Improvements that focus on (1) simpler fabrication process and (2) reduced material consumption will very likely be of interest to industry.

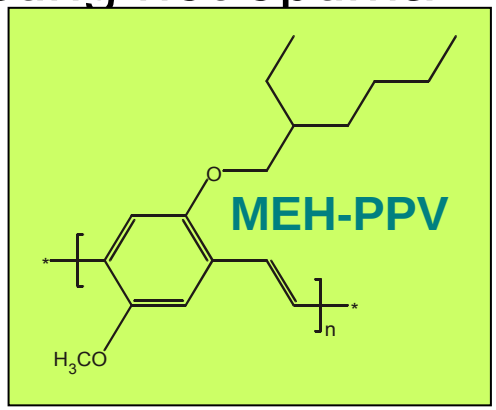
RIR-PLD for OLED processing …



RIR-PLD of MEH-PPV



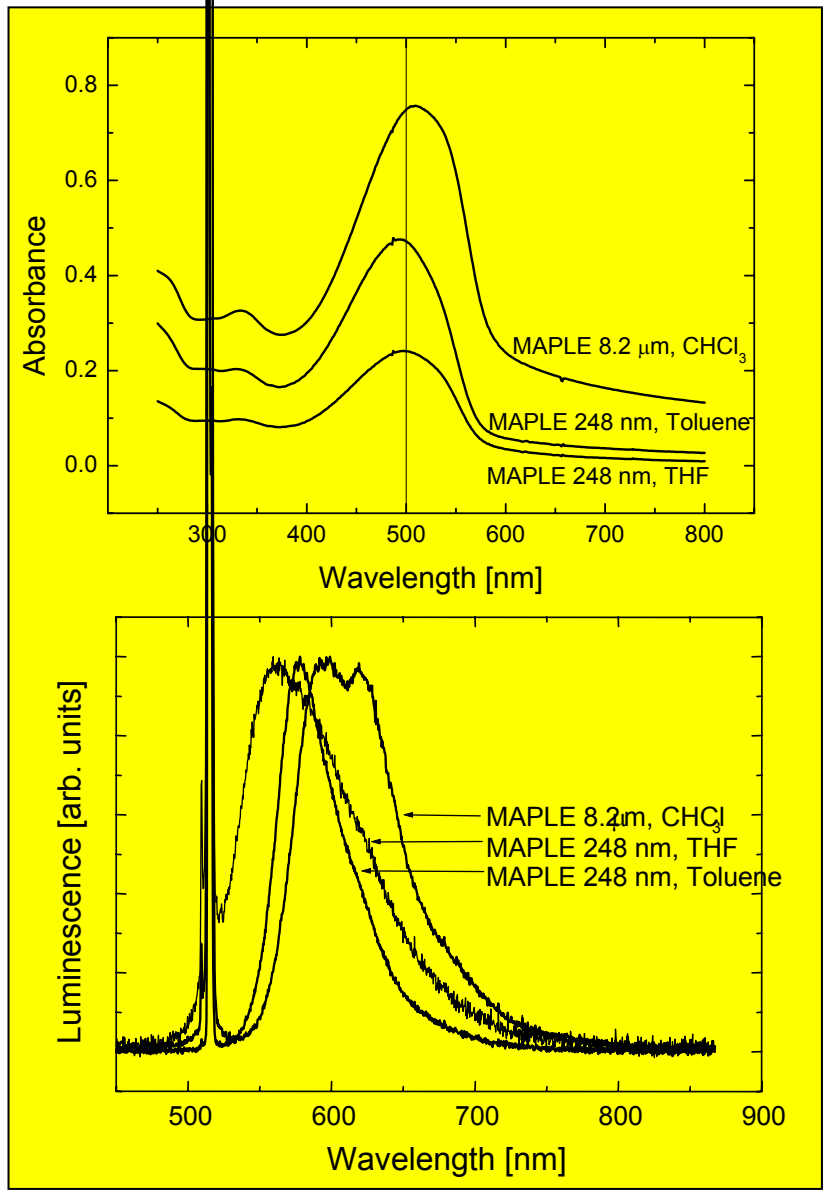
- Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene
- MEH-PPV to physicists!
- Organic light emitter (flat-panel and mobile device displays).
- Spin-coating and drop-casting not optimal.



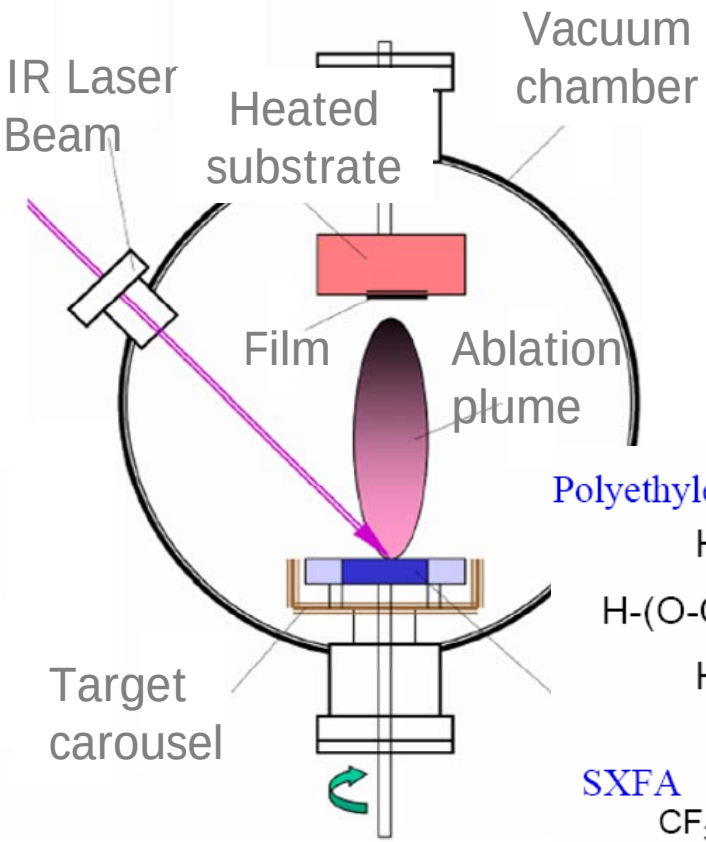
Reference: Toftmann *et al.*, *Thin Solid Films* (EMRS-2003)

Optical response of MAPLE-MEH-PPV

- Photoluminescence (pump at 514 nm), peaks normalized to maximum above that wavelength.
- Little to no shift in uv-vis absorbance, but …
- Substantial changes in luminescence spectrum with wavelength and solvent.
- Other researchers observed correlations between peak shifts and solvent, as well as film morphology.
- Smooth films grown at 193 nm and by RIR-PLD, but UV-PLD films are too thin.

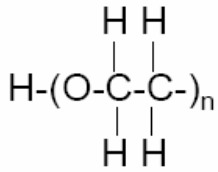


RIR-PLD demonstrated on …



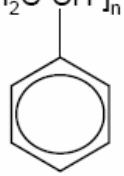
RIR-PLD collaboration (Bubb, Haglund et al., Horwitz) at the Vanderbilt FEL has demonstrated low-temperature IR-laser deposition of large, thermally labile thermoplastic and thermoset polymers for a wide variety of applications.

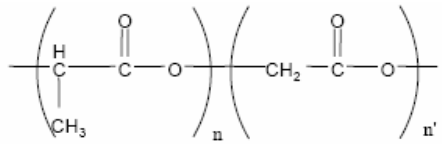
Polyethylene Glycol



Teflon $-(CF_2)_n-$

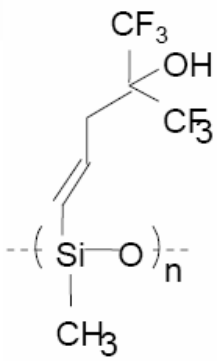
Polystyrene $-[H_2C\text{-}CH\text{-}]_n-$

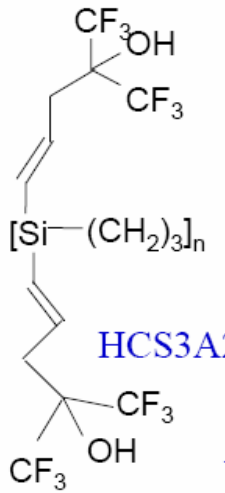




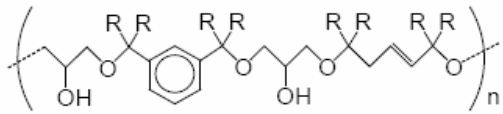
poly(DL-lactide-co-glycolide) (PLGA)

SXFA

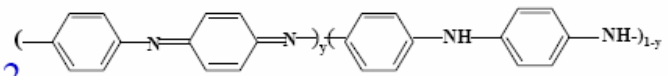




Fluoropolyol



$R = CF_3$ Polyaniline



HCS3A2

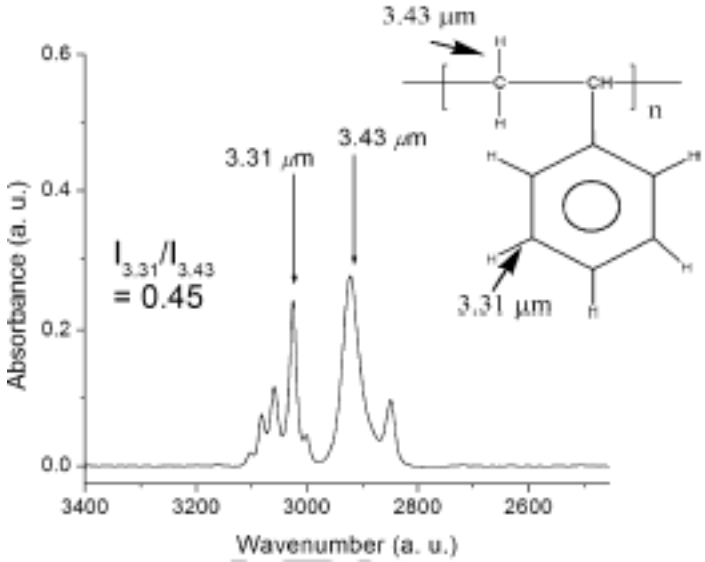
Versatile technique which preserves chemical structure and function

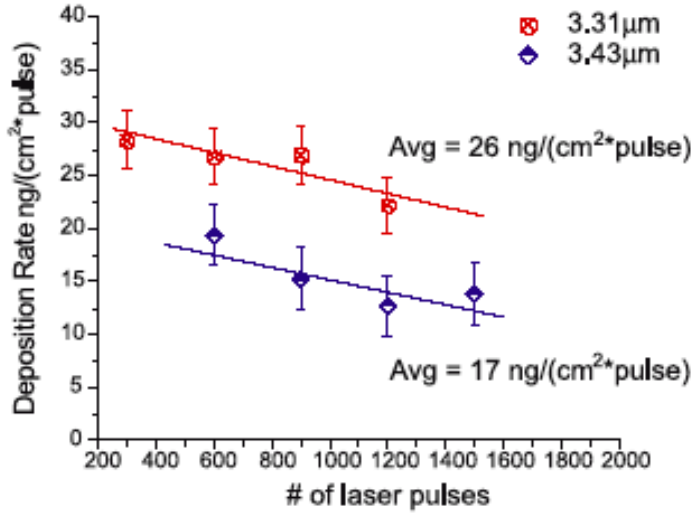
Electroluminescent polymers for OLEDs

So what have we learned?

- A new paradigm: resonant infrared pulsed laser deposition (RIR-PLD) of polymers
- Some case studies …
  - Biomedical applications: PEG, PLGA, Teflon
  - Sensors: fluoropolyol, SXFA
  - Electronic applications: Polyimide
  - Opto-electronic applications: MEH-PPV
- Evidence for low-temperature, non-thermal character of RIR-PLD … and some thoughts about a substitute for the FEL

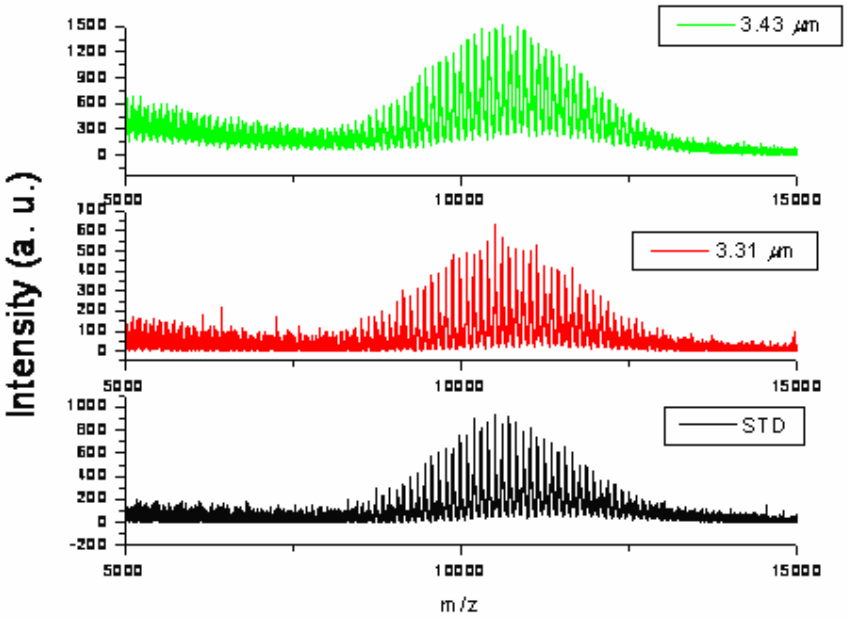
Ablation of poly(styrene)





- FEL macropulse ablation, fluence ~ 5 J/cm^2
- Molecular weight ~10 kDa
- Chain length ~100 monomer chain
- τ(3.31)~450 fs, τ(3.43)~150 fs
- *Applied Physics A* **83**, 147 (2006)

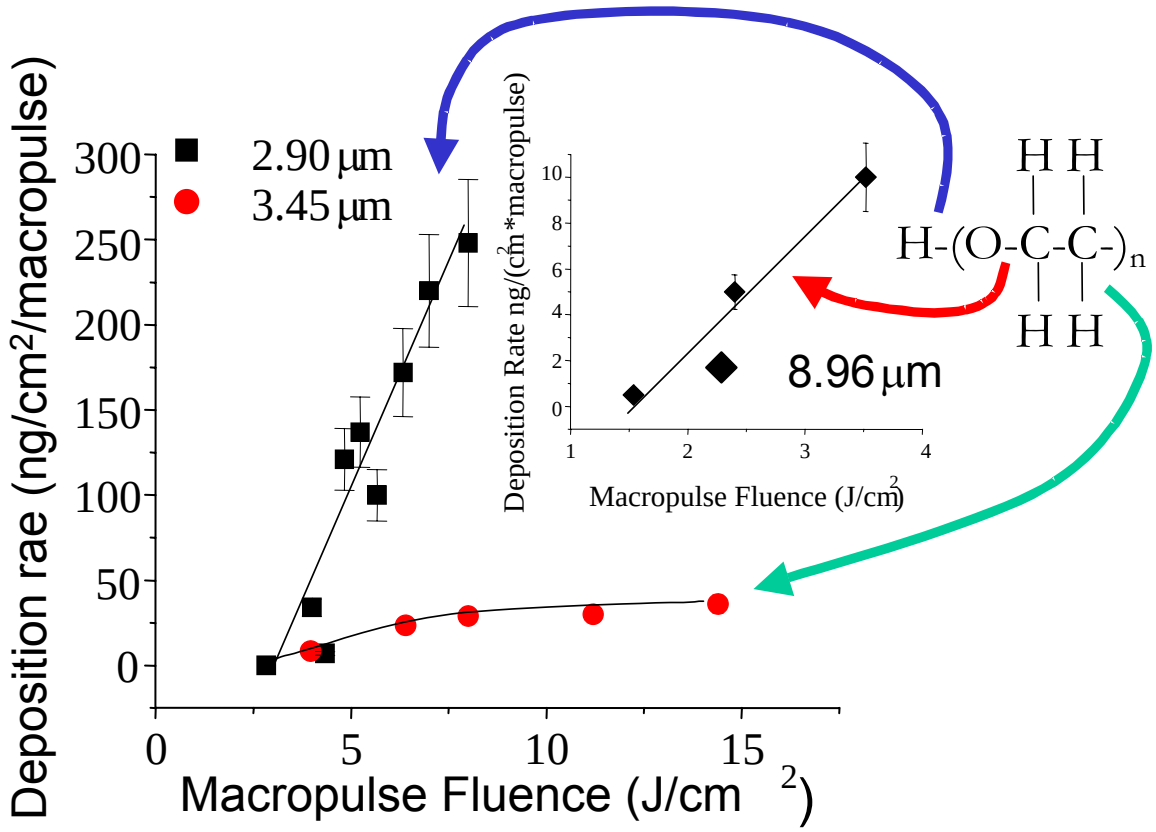
What's happening?



	3.31 μm	3.43 μm
α (cm^{-1})	1280	1450
L_p (μm)	7.8	6.9
$D_{thermal}$ (cm^2/s)	10^{-4}	10^{-4}
c_{sound} (m/s)	2200	2200
$\tau_{thermal}=(L_p)^2$ (ms)	5.7	4.5
$\tau_{pressure}=L_p/c_s$ (ns)	3.5	3.1
η/η_0	10^{-2}	10^{-2}

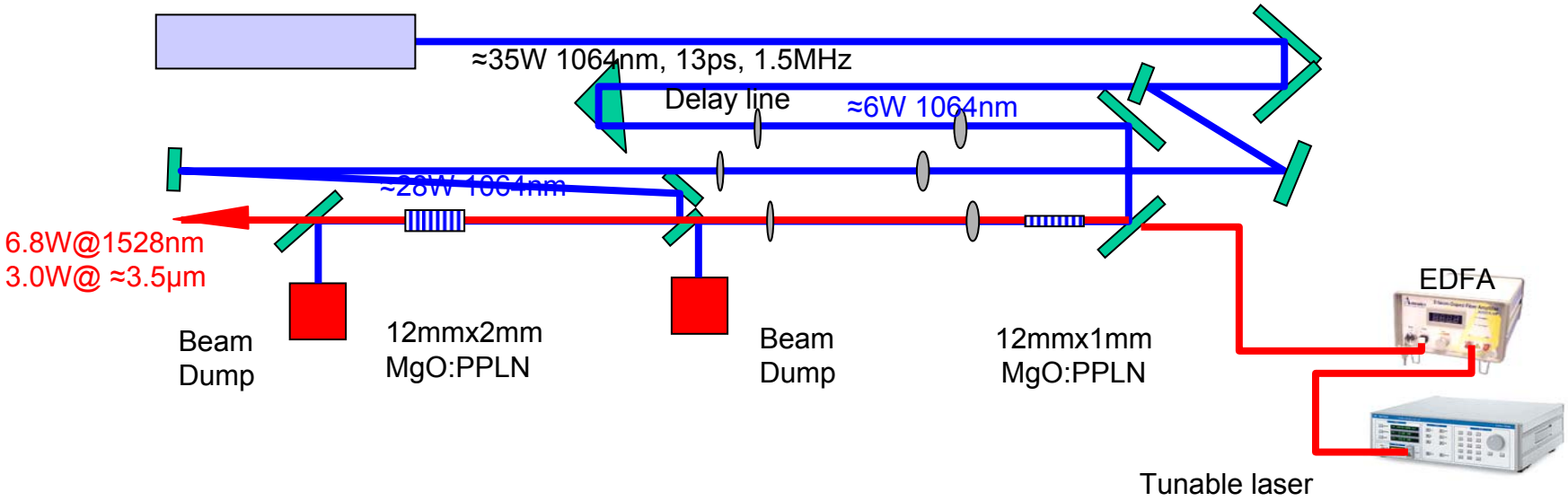
- Fragmentation usually from backbone modes
- Gentle bond-breaking from side-chain stretch
- Thermally, but not pressure, confined
- Dramatic decrease in viscosity (Vogler-Fulcher)
- Hydrogen bond-breaking between polymers

Evidence for mode-specific response



J Appl Phys **91**, 9809 (2002)

- Ablation efficiency not correlated with IR absorption strength
- Ablation efficiency correlates with inter-molecular bond (O-H)
- Weak absorption also correlates with least bond scission



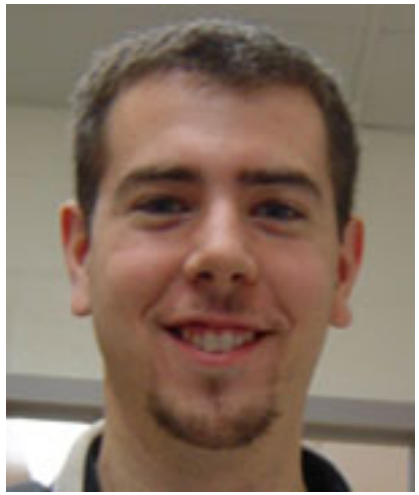
- All commercial components, all solid-state turnkey system, tunable, high average power
- In operation for over a year at Australian National University (Barry Luther-Davies)
- The challenge: to get beyond 4 μm!

- A new paradigm for pulsed laser deposition
  - Use tunable IR light to control penetration depth
  - Use high-intensity, low-energy, high pulse-repetition rate laser
  - Gives low-temperature, solvent-free, conformal deposition
- Applications potential demonstrated for
  - Many technologies (MEMS, biotechnology, sensors, OLEDs …)
  - Thermoplastic and thermosetting polymers
  - Polymers that cannot be deposited in liquid phase (*e.g.*,Teflon®)
- RIR-PLD is intrinsically a low-temperature process
  - Poly(amic acid) does not cure during ablation
  - Modest temperature rise, but large viscosity change
  - Mode selection influences ablation yield and fragmentation
- Next steps: photoacoustic measurements, more detailed characterization of transport properties, ellipsometry, hardness, patterning, integrating with plasmonics … above all, performance verification

Thanks to the heavy lifters …


Nicole Dygert


Stephen Johnson


Ron Belmont


Ken Schriver

$$upported by the Naval Research Laboratory, the Medical Free-Electron Laser Program administered by the Air Force Office of Scientific Research and the National Science Foundation (IGERT)

And about the Doorknob Principle: "It warn't so much what I didn't know what hurt me, but what I knowed that warn't so."

(Huck Finn)