Four-wave mixing with coherent x-rays:

The Whole Brillouin Zone

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OUTLINE

- Coherent x-ray four-wave mixing: Motivations
  - Dynamical events on short length scales
  - Association of correlation times and correlation lengths
  - Acoustic & structural responses
- Experimental approach & results to date
  - High harmonic generation
  - Soft x-ray gratings, interferometer
  - Soft coherent x-ray lithography
  - time-resolved measurements under way
- Complementary measurements
  - 100-GHz acoustic wave transduction

Coherent x-ray FWM: Motivations

Collective events have associated time <u>and length</u> scales

- e.g. polymer relaxation dynamics
- Are faster, intermediate, & slower dynamics associated w/ shorter, intermediate, & longer chain elements?
- What about molecular liquids? Glasses, partially disordered solids?

Are ***correlation times*** associated with ***correlation lengths***?

Unlike molecular case, we don't already know length scales

Coherent x-ray FWM permits direct measurement of both *time and length scales*

Currently available: HHG soft x-rays

Anticipated: X-ray FEL hard x-rays

NANOMETER CORRELATION LENGTHS RULE!

CONDENSED-MATTER CHEMISTRY, PHYSICS, TECHNOLOGY

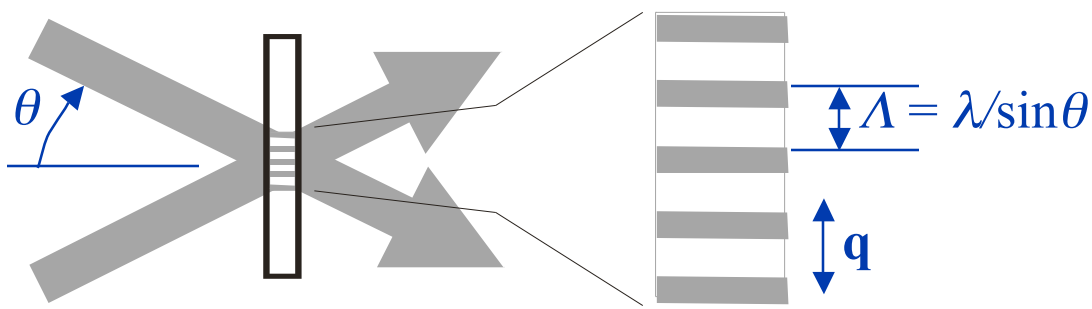
- Liquid-state molecular dynamics
  - Water structure, liquid molecular orientational & other fluctuations
- Structural relaxation in polymers, supercooled liquids
  - Viscous liquid shear & density fluctuations, structural relaxation, polymer persistence length
- Collective structural change in solids
  - Phase transitions; domain formation, growth, switching; ferromagnetic, ferroelectric, other order parameter fluctuations
- Electron, exciton migration & correlation lengths
- Events utilized in device applications
  - Domain switching in relaxor ferroelectric DRAMS, advanced piezoelectrics, ferromagnetic materials
  - Electron migration, electronic excitation in semiconductors, organic electronics, hybrid structures

X-rays provide access to well defined "mesoscopic" distance scales

Optical measurements can define distance scales on the order of the light wavelength λ

- Light scattering wavevectors q cover 0.1% of the Brillouin zone
- Corresponding wavelengths $\Lambda = 2\pi/q$ are in the micron range
- But most of chemistry, physics, and technology involves much smaller distance scales!

Four-wave mixing ("transient grating") measurement



Optical wavelengths

Λ in micron range

X-ray wavelengths

Λ in nanometer range

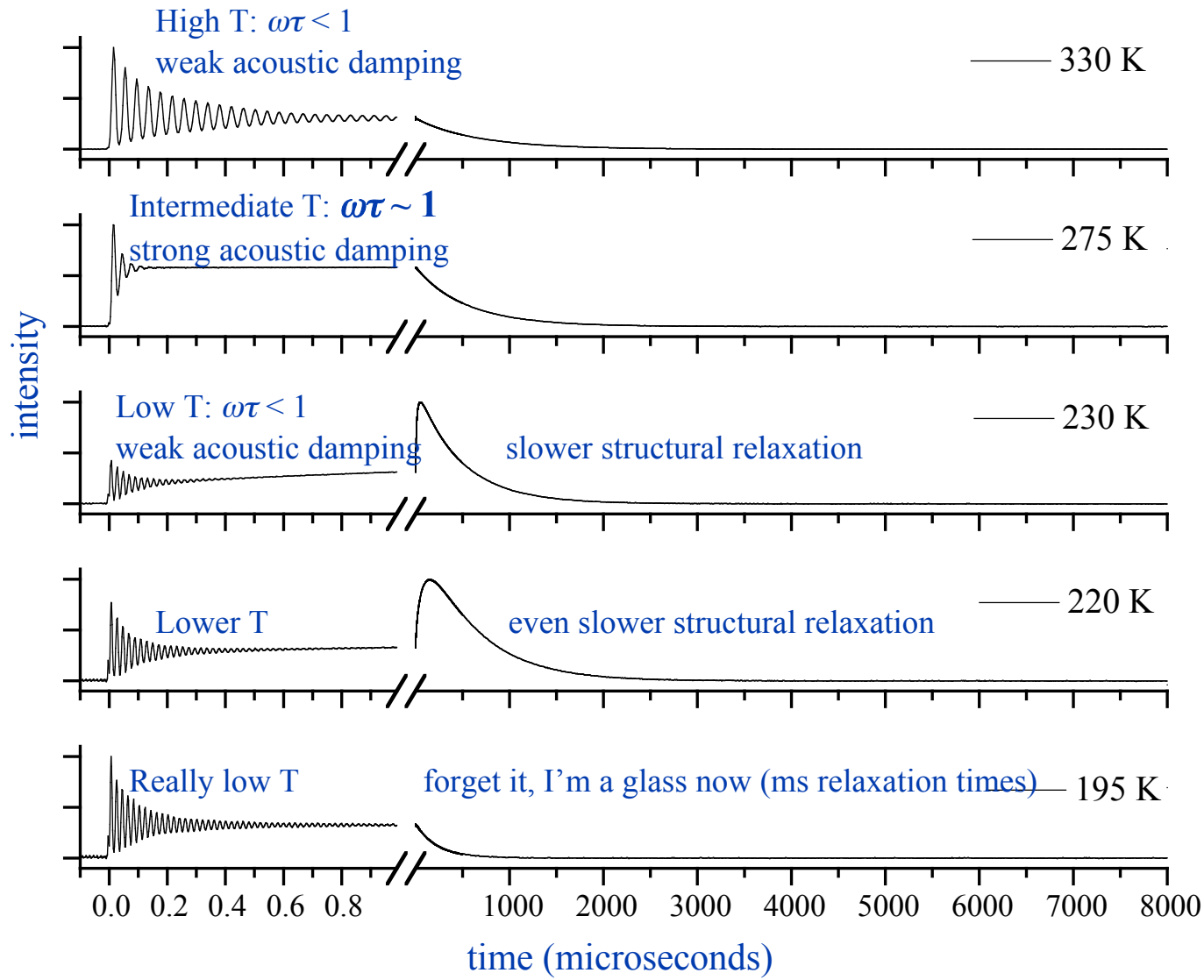
Current 4WM limitations

- Studies of crystalline & amorphous solids, glass-forming liquids, polymers
  - Hydrodynamic responses observed
    - Acoustic waves, thermal diffusion
    - Dynamics depend on wavevector – e.g. high acoustic frequency requires high q
    - *General questions:*
    - *At what q range does acoustic propagation start & localization begin?*
    - *At what q range does thermal transport become diffusive?*
  - Nonhydrodynamic responses observed
    - Structural relaxation dynamics in liquids – limited by acoustic frequency & q
    - Optic phonons in crystalline solids – limited to Brillouin zone center
- Studies of thin films
  - Surface & planar waveguide acoustic modes yield film thickness, mechanical properties, delamination from substrates
  - Depth profiling possible, but can't characterize layers much smaller than surface acoustic wavelength – limited by q

Visible wavelengths: FWM data from glycerol

$q = 0.086\ \mu m^{-1}$, $\Lambda = 73\ \mu m$ = transient grating fringe spacing

Acoustic & slower density dynamics $\langle\rho(q,0)\ \rho(q,t)\rangle$ **at low *q***



Time scales:

$0.2\ ns < \tau < 1\ ms$

Misses lots of faster dynamics

Need higher q ⇒ $\omega_{ac}\tau \sim 1$ for $1\ ps < \tau < 100\ ps$

Length scales:

No info at all!

Need higher q ⇒ ***Need qd ~ 1*** *for $1\ nm < d < 100\ nm$*

What do FWM experiments measure?

High-wavevector responses to high-wavevector excitation

Correlation function $\langle A(\mathbf{q}_1,t_1)\, B(\mathbf{q}_2,t_2)\rangle$

- A is the quantity perturbed by *x-ray grating excitation*
- $\mathbf{q}_1$ is the (large) x-ray excitation grating wavevector
- B is the quantity probed with *x-ray coherent scattering*
- $\mathbf{q}_2 = \mathbf{q}_1$ if phase matched
- t_2-t_1 is the delay time

e.g. Infer density-density correlation function $\langle \rho(q,0)\, \rho(q,t)\rangle$

- Density dynamics **at high** $\boldsymbol{q}$ depend on correlation length d and correlation time τ
- Dynamical response changes when $\boldsymbol{\omega\tau \approx 1}$ **or** $\boldsymbol{qd \approx 1}$
- Information provided on correlation length and its relation to correlation time

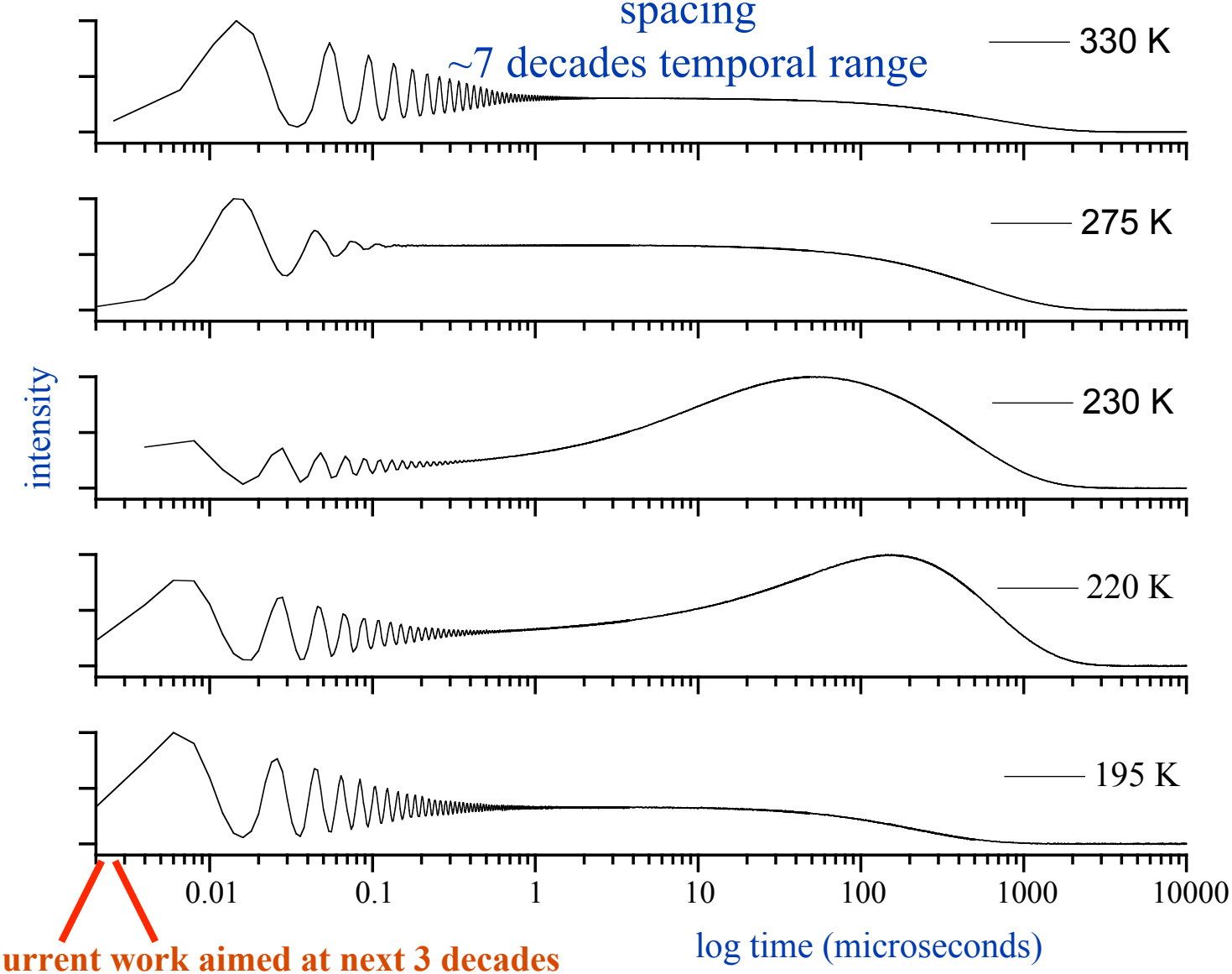
Similar for electron, exciton correlation lengths d

- Dynamical response changes dramatically when $qd > 1$

Visible wavelengths: FWM data from glycerol

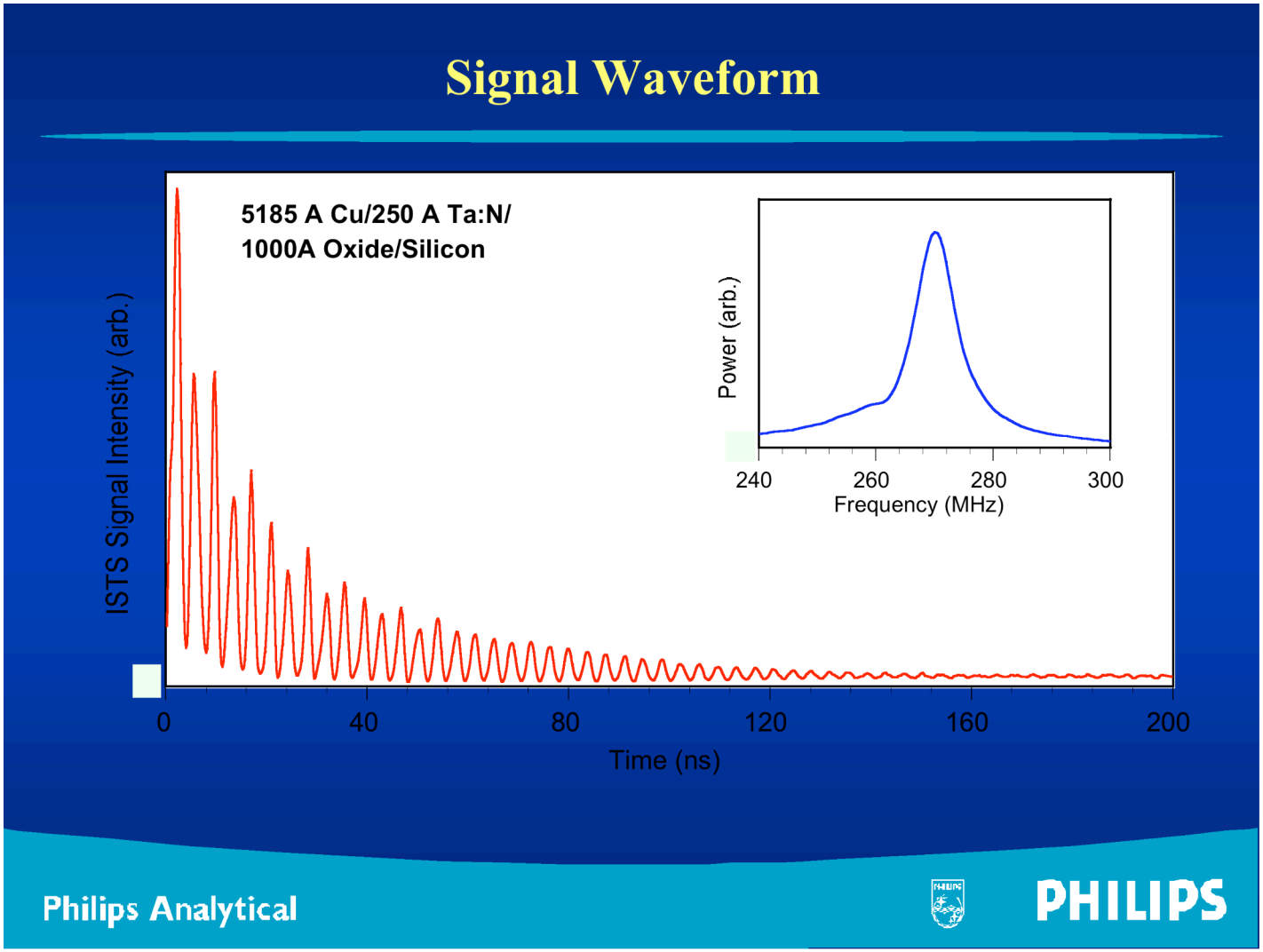
q = 0.086 μm^{-1}, Λ = 73 μm = transient grating fringe spacing

~7 decades temporal range



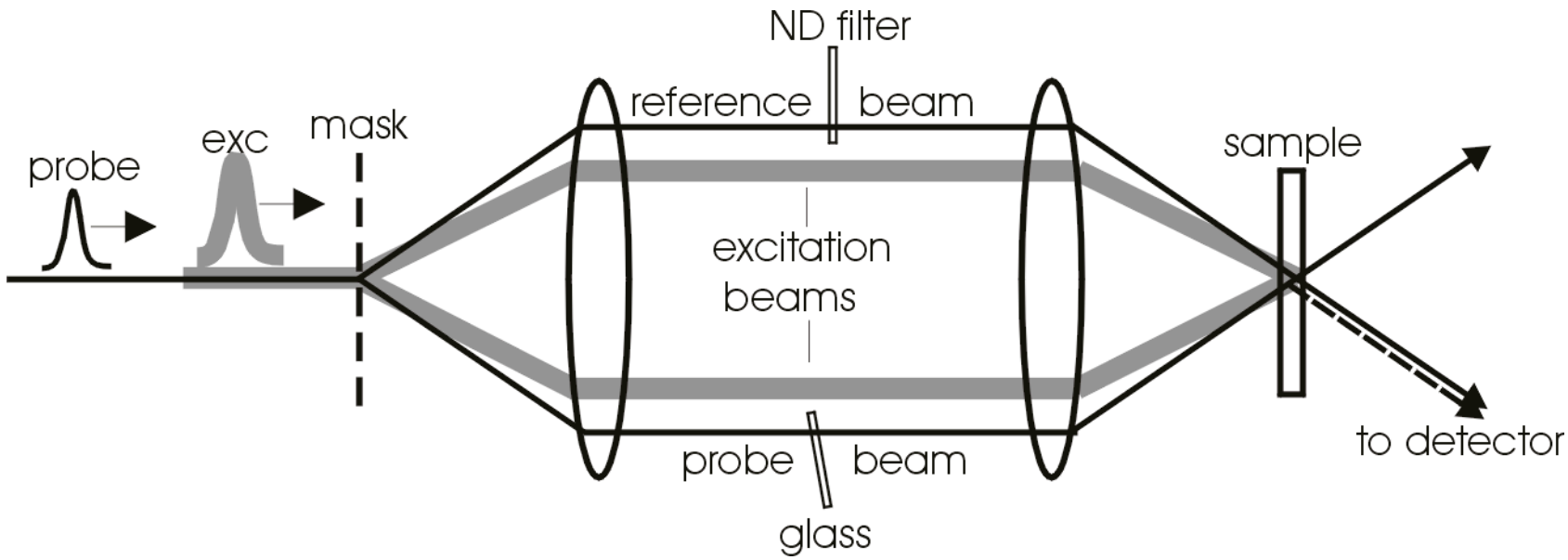
Current work aimed at next 3 decades
> 100 GHz frequencies, < 50 nm wavelengths

Visible wavelengths: FWM data from thin films
Commercialized metrology for microelectronics fabrication



Higher $q \Rightarrow$ thinner film mechanical, dimensional, **adhesion** properties

4-wave mixing at optical wavelengths



Routine experiment with diffractive optics

- Generation & delivery of beams to sample
- Optical heterodyne detection
- Changing of transient grating fringe spacing

Sufficiently robust for commercial use

X-ray FWM through high harmonic generation

- High harmonic generation
  - Spatial coherence demonstrated - needed for transient grating formation
  - Compact HHG beamline – ready for spectroscopic applations
  - High pulse energy, high harmonics through quasi-phase matching
  - High excitation energy through dual fiber pumping
  - Tight focusing for high excitation intensity
- Beam delivery to sample
  - Reflective optics
  - Diffractive optics
- Demonstration of coherent x-ray lithography, diffraction

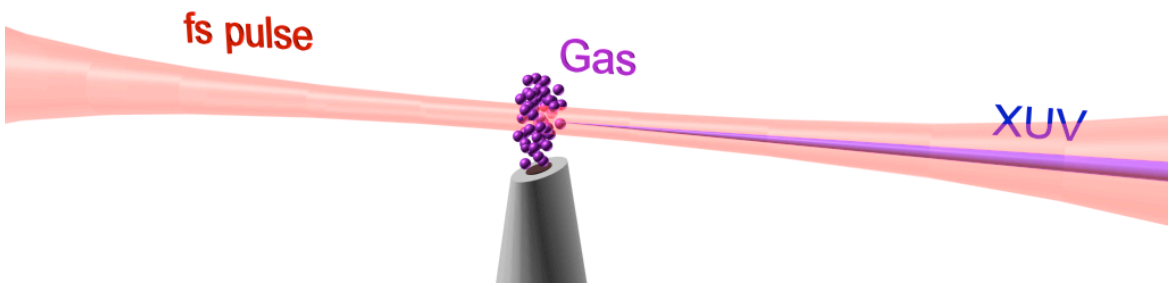
Extreme nonlinear optics: Coherent x-ray generation

Coherent x-rays are generated by focusing an intense laser onto atoms

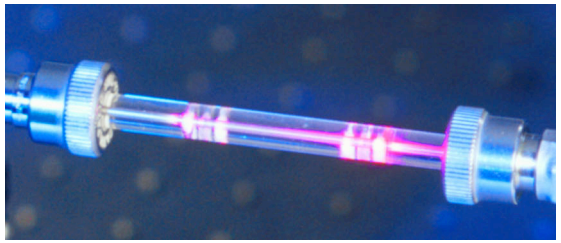
Broad range of energies generated simultaneously from 4.5 - 600 eV

"Laser-like" coherent beams in EUV

- full spatial coherence
- adjustable temporal coherence



Gas jet

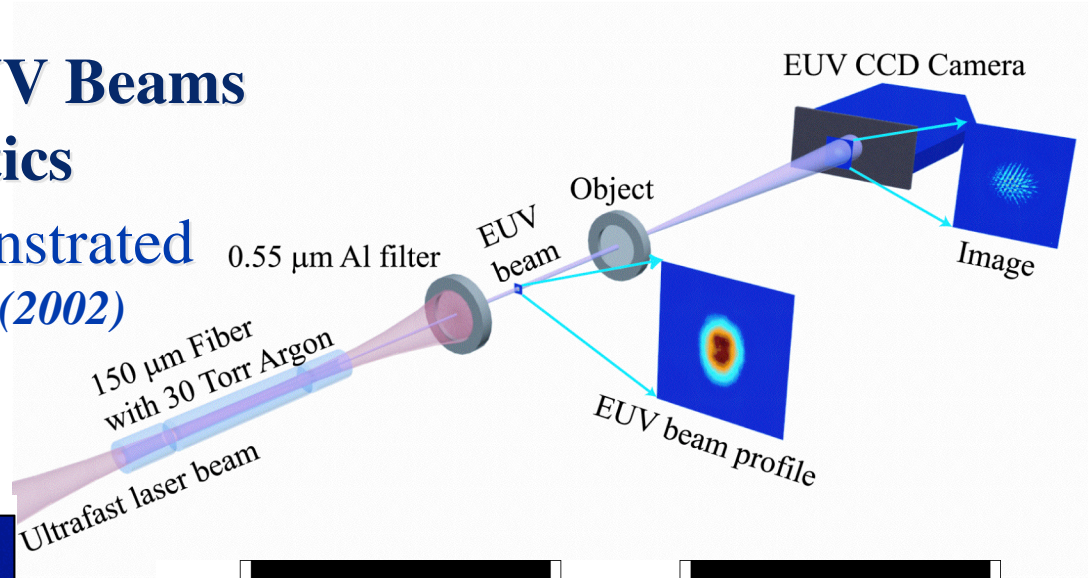


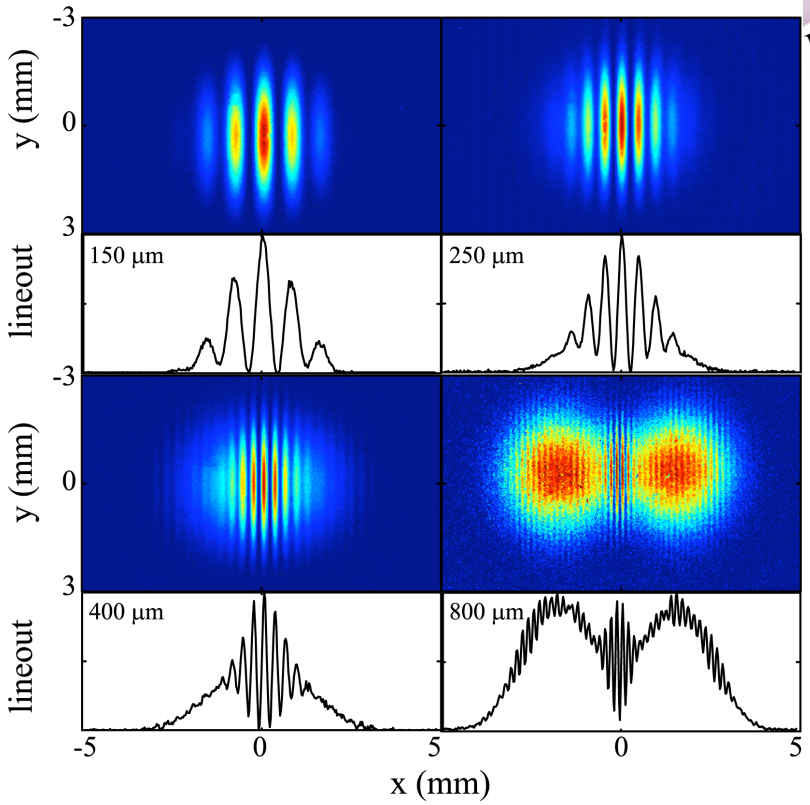
Fiber

Generation of Laser-Like EUV Beams using X-Ray Fiber Optics

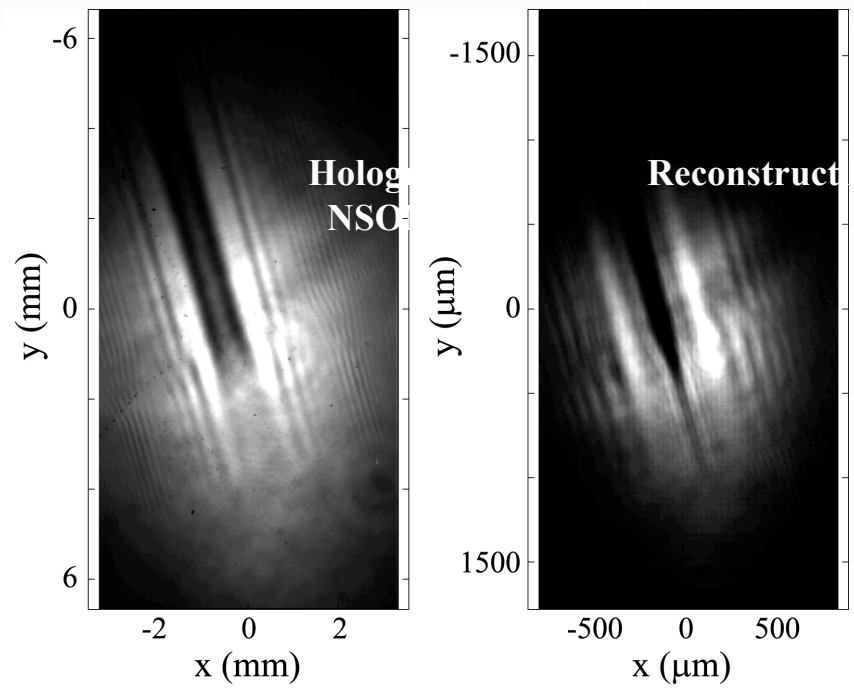
High spatial coherence demonstrated

R. Bartels et al., Science 297, 376 (2002)



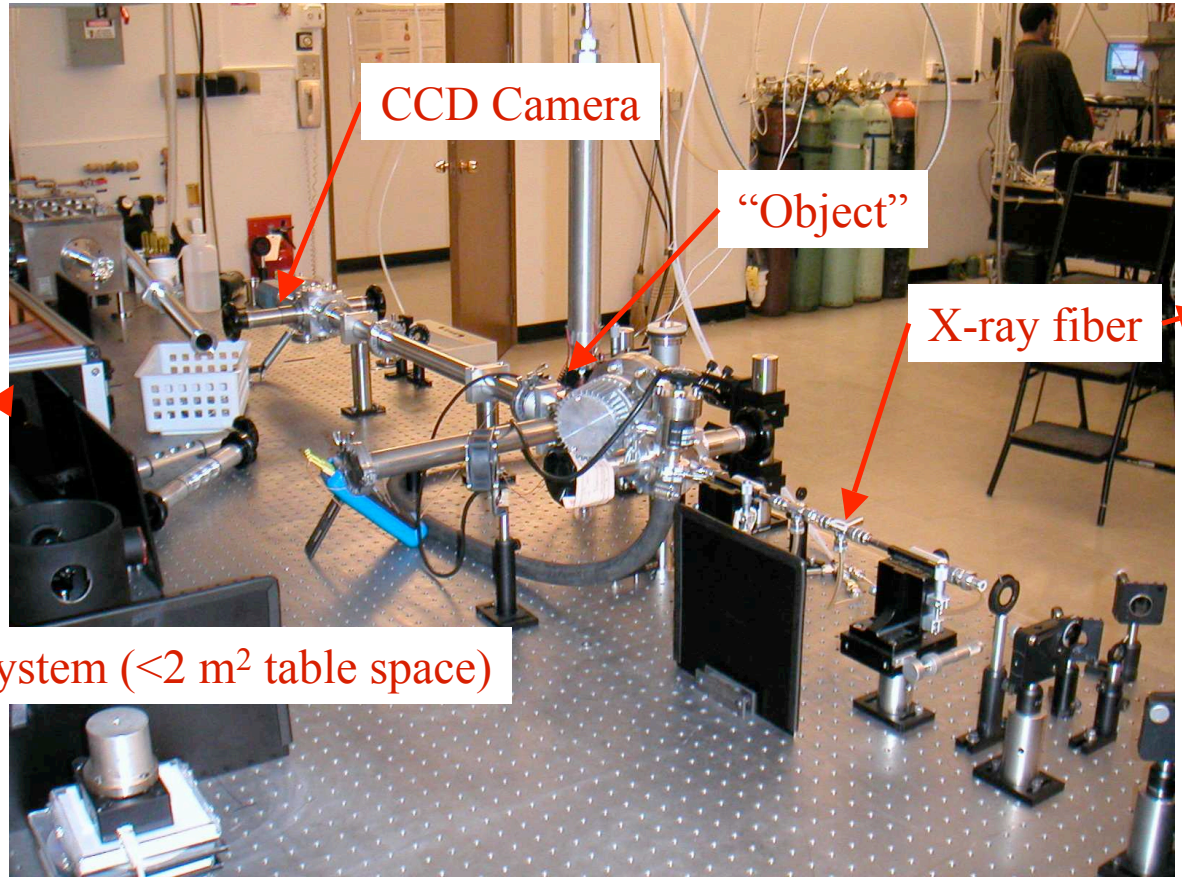


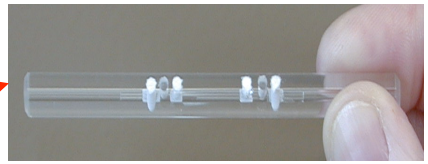
Laser-like EUV beams exhibit high-quality interference patterns



First demonstration of holography at EUV wavelengths using a compact EUV source

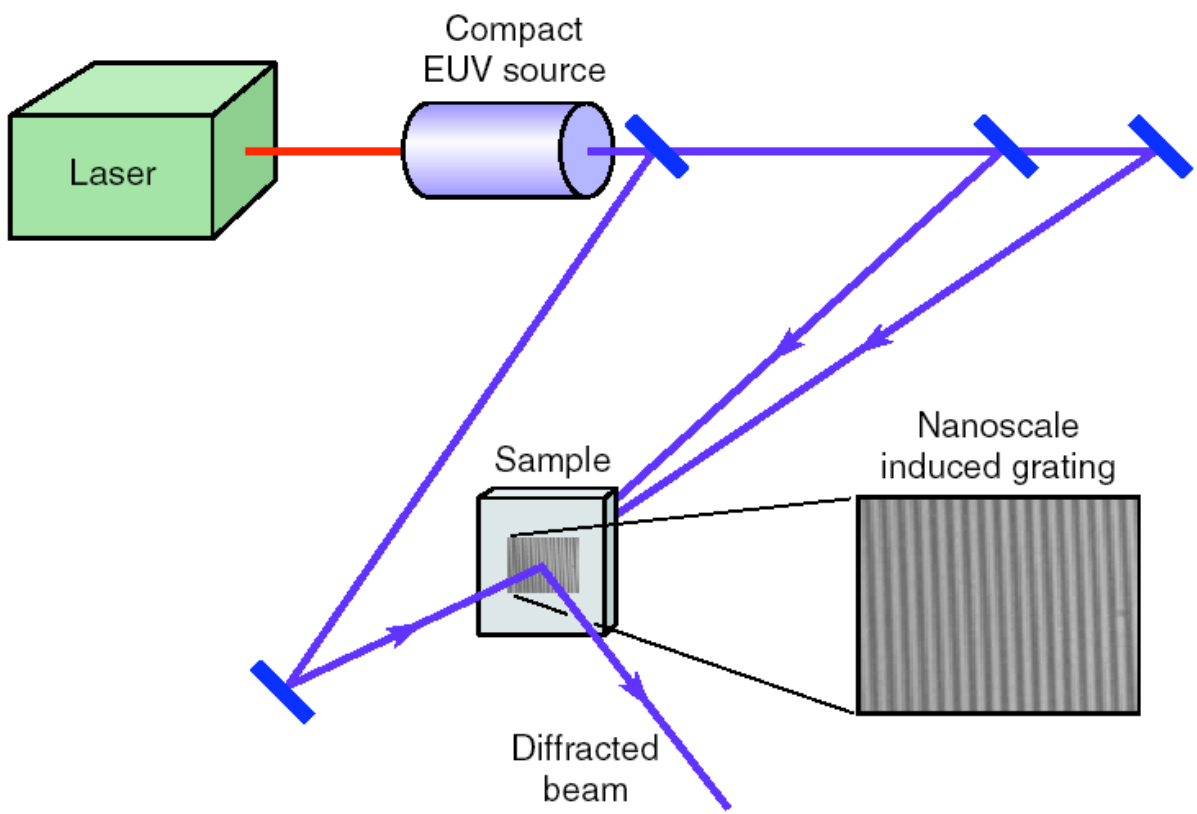
Compact EUV Beamline using X-Ray Fiber Optics

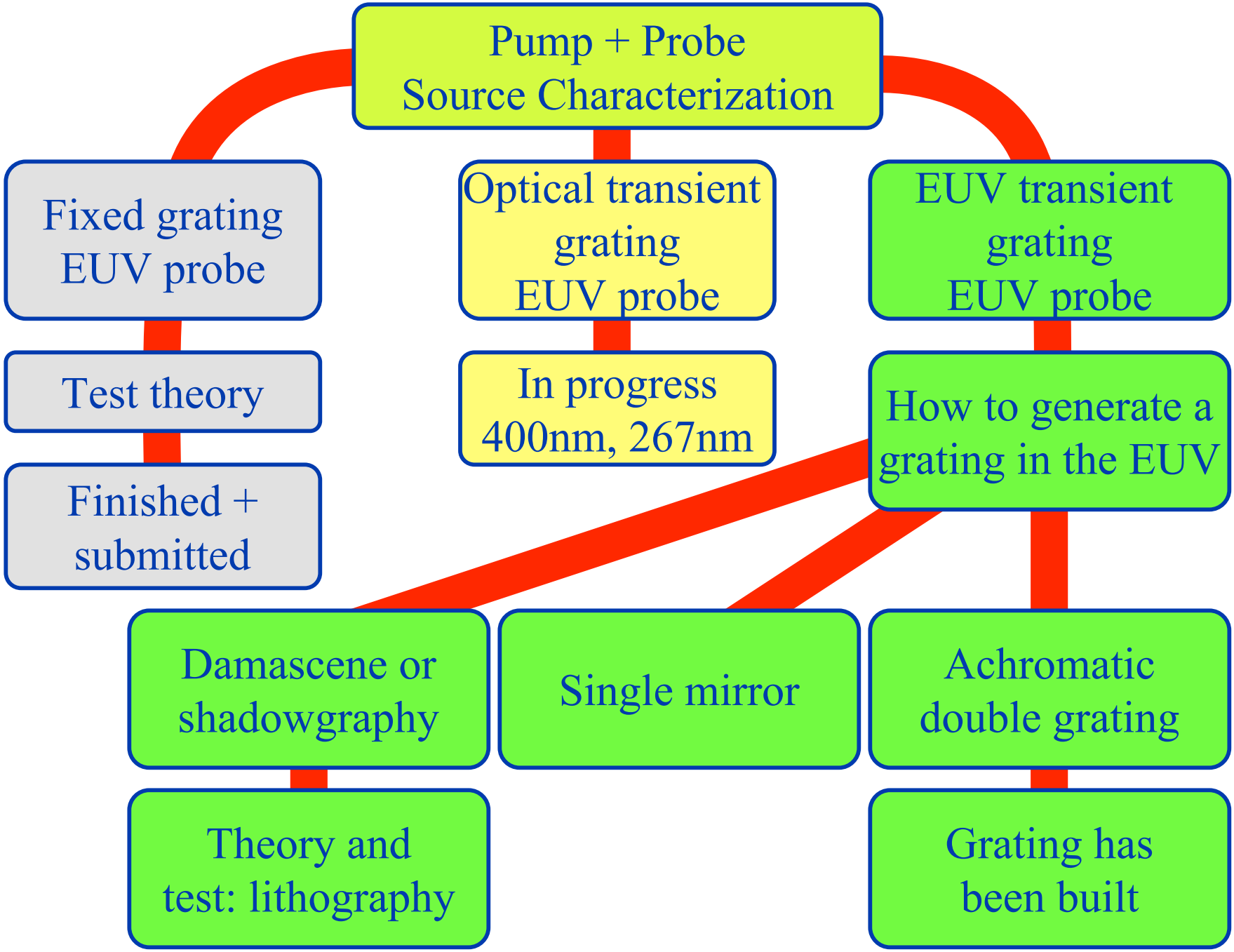




EUV Nonlinear spectroscopies (Colo-MIT collaboration)

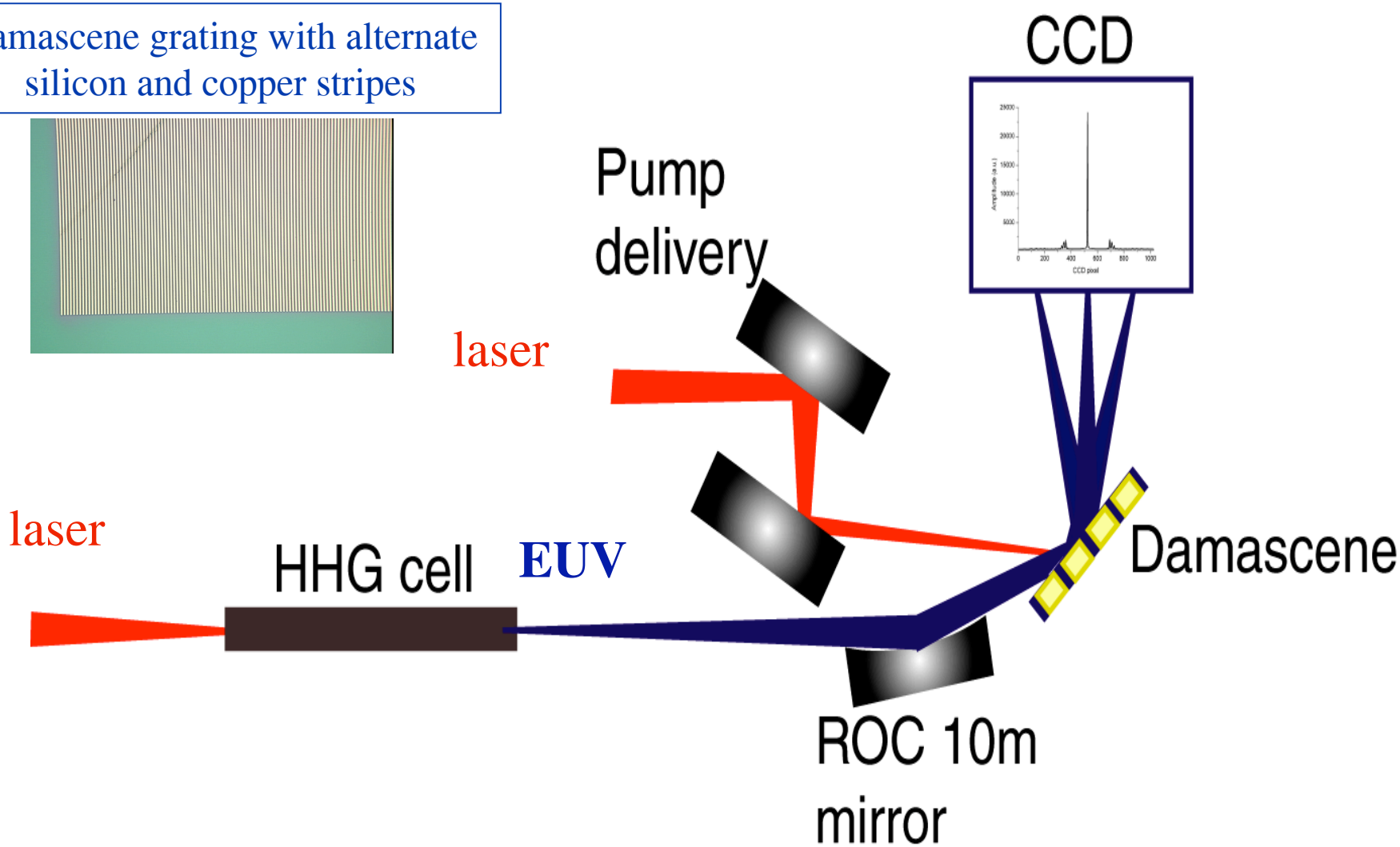
Objective: All-EUV time-resolved FWM measurements



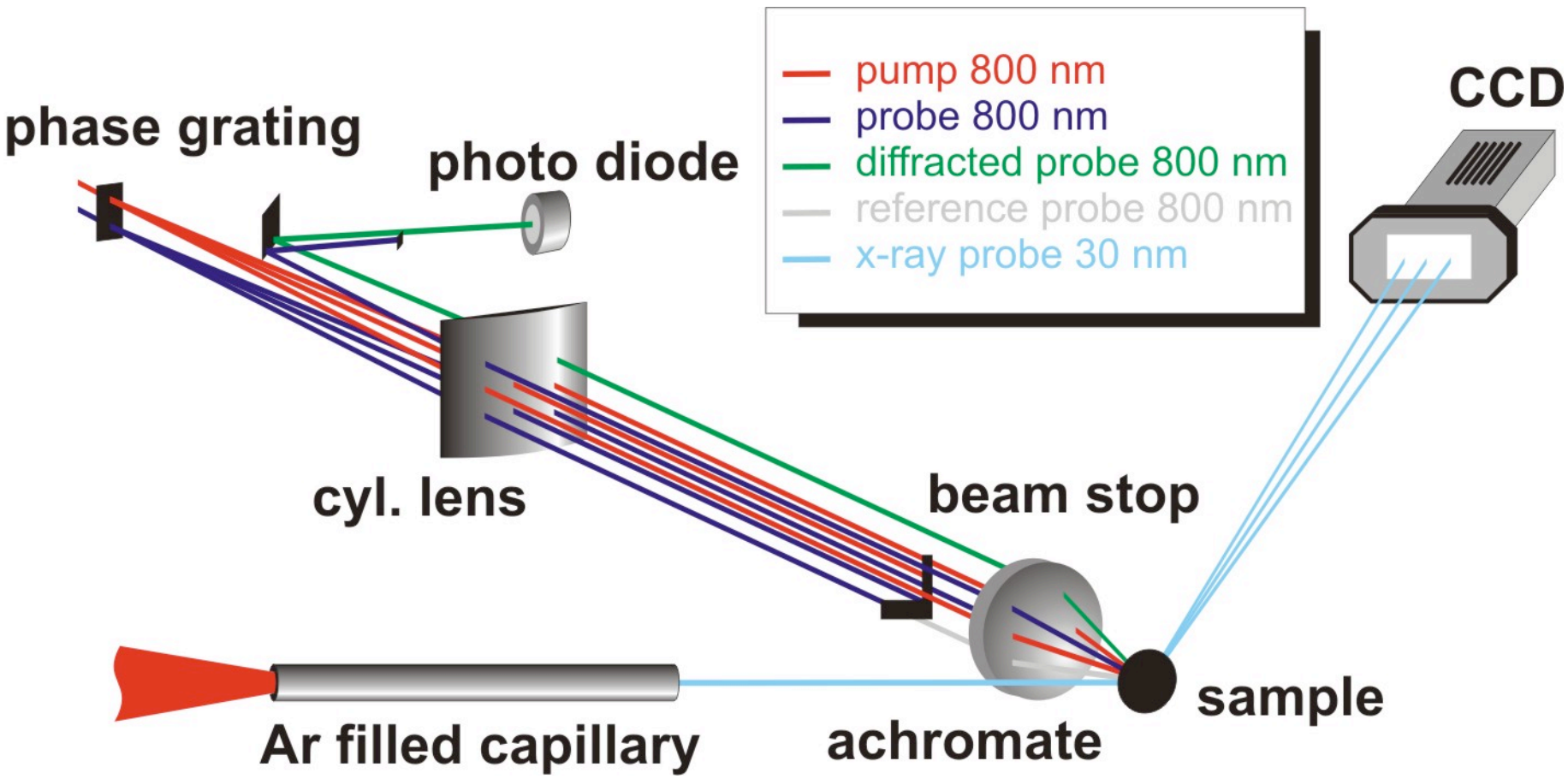

Pump + Probe
Source Characterization
Fixed grating
EUV probe
Optical transient
grating
EUV probe
EUV transient
grating
EUV probe
Test theory
In progress
400nm, 267nm
How to generate a
grating in the EUV
Finished +
submitted
Damascene or
shadowgraphy
Single mirror
Achromatic
double grating
Theory and
test: lithography
Grating has
been built

Experimental Setup
Visible excitation, EUV probe
"Damascene" grating sample

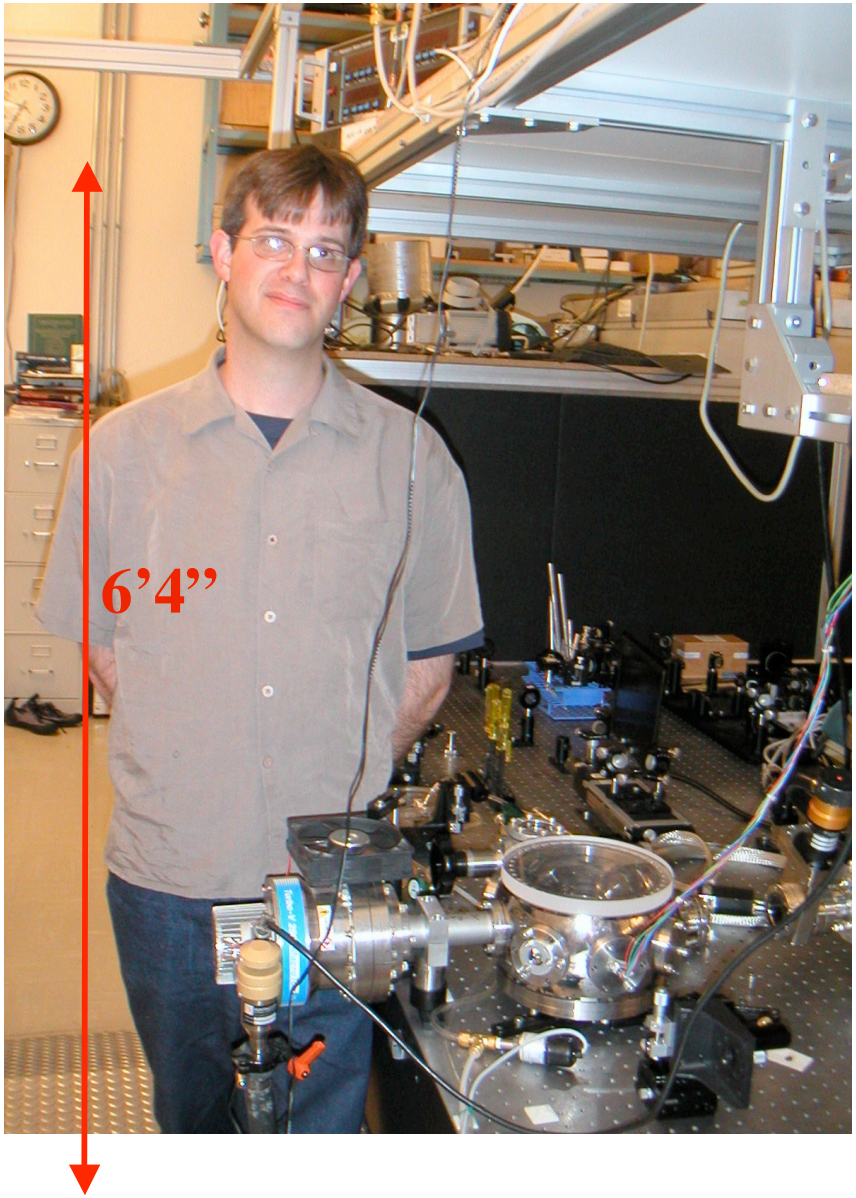
Damascene grating with alternate silicon and copper stripes



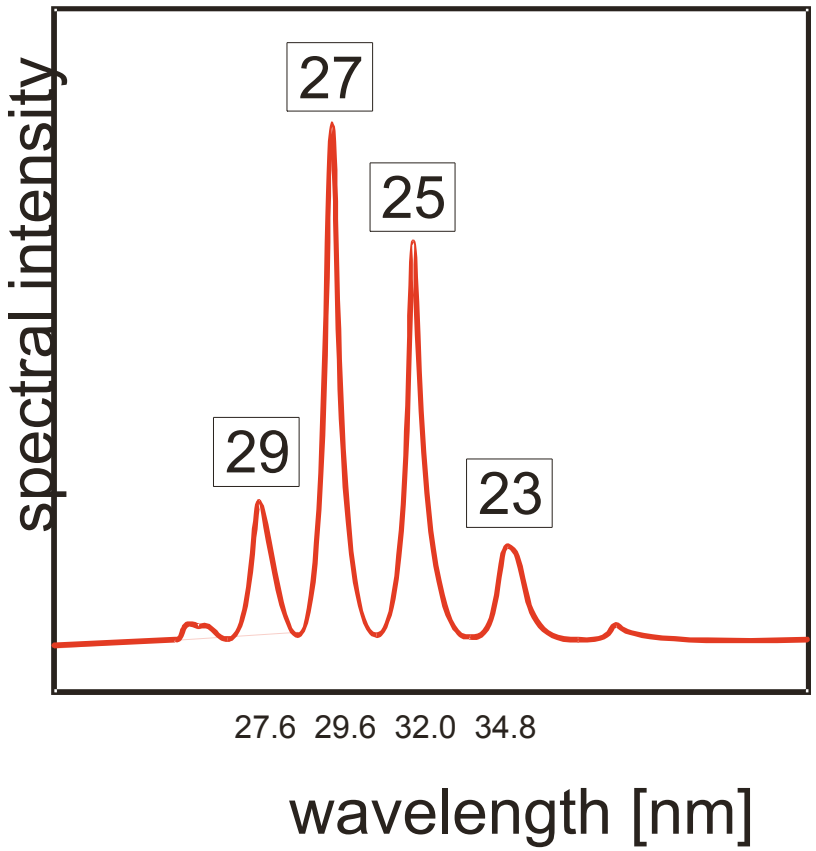
Experimental Setup
Visible excitation, visible & EUV probe

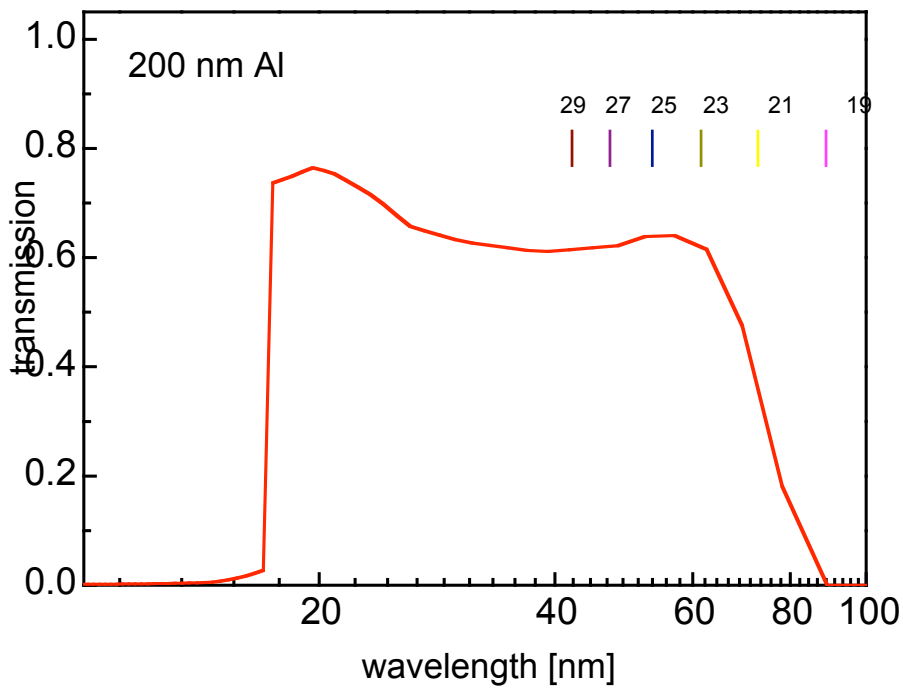


Experimental Setup



Experimental Setup
EUV wavelengths used





Experimental Setup

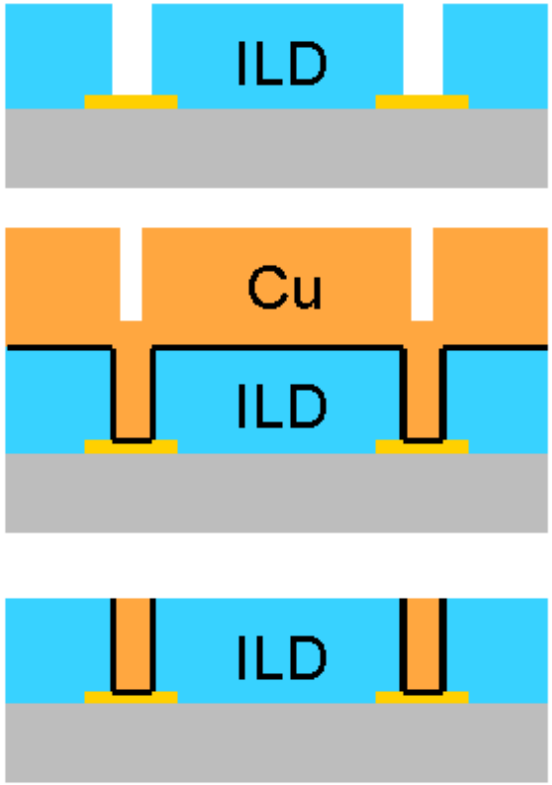
EUV wavelengths used

beam diameter @ capillary	**150 μm**
beam divergence	**1 mrad**
most intense harmonics	**25, 27**
'center wavelength'	**32.0 nm, 29.6 nm**
bandwidth of each harmonic	**~ 0.7 nm**
photons per pulse	**4.5 _ 10^8**
energy per pulse	**2.7 nJ**
average power	**2.7 μW**
pulse width	**< 5 fs**
peak power	**> 500 kW**

General CMP Topics

PENNSTATE

Damascene Process

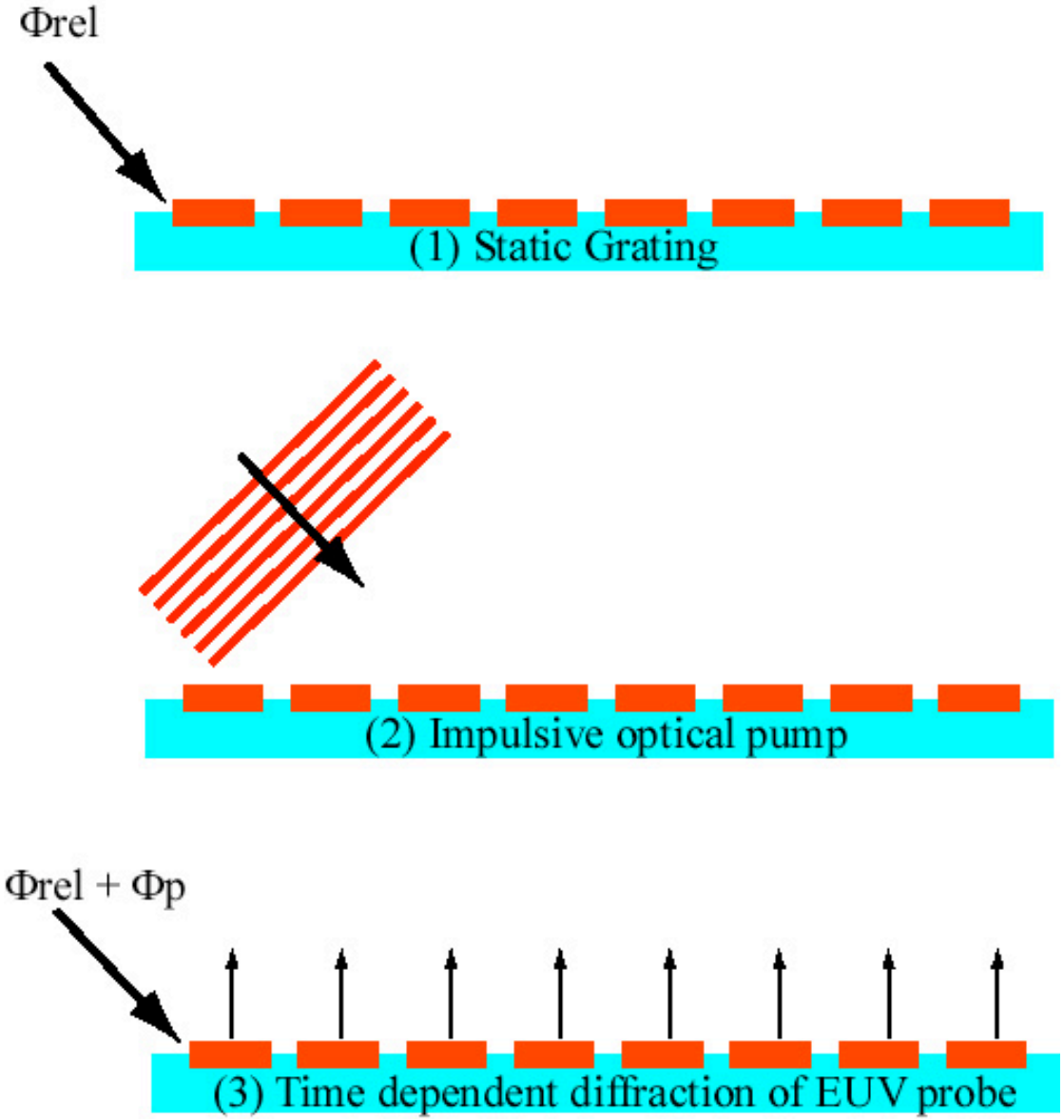


- Deposit ILD
- Pattern ILD
- Deposit Barrier Metal
- Deposit Copper
- Polish Down to ILD or…
  - Polish Down to Barrier
  - Etch Barrier Metal

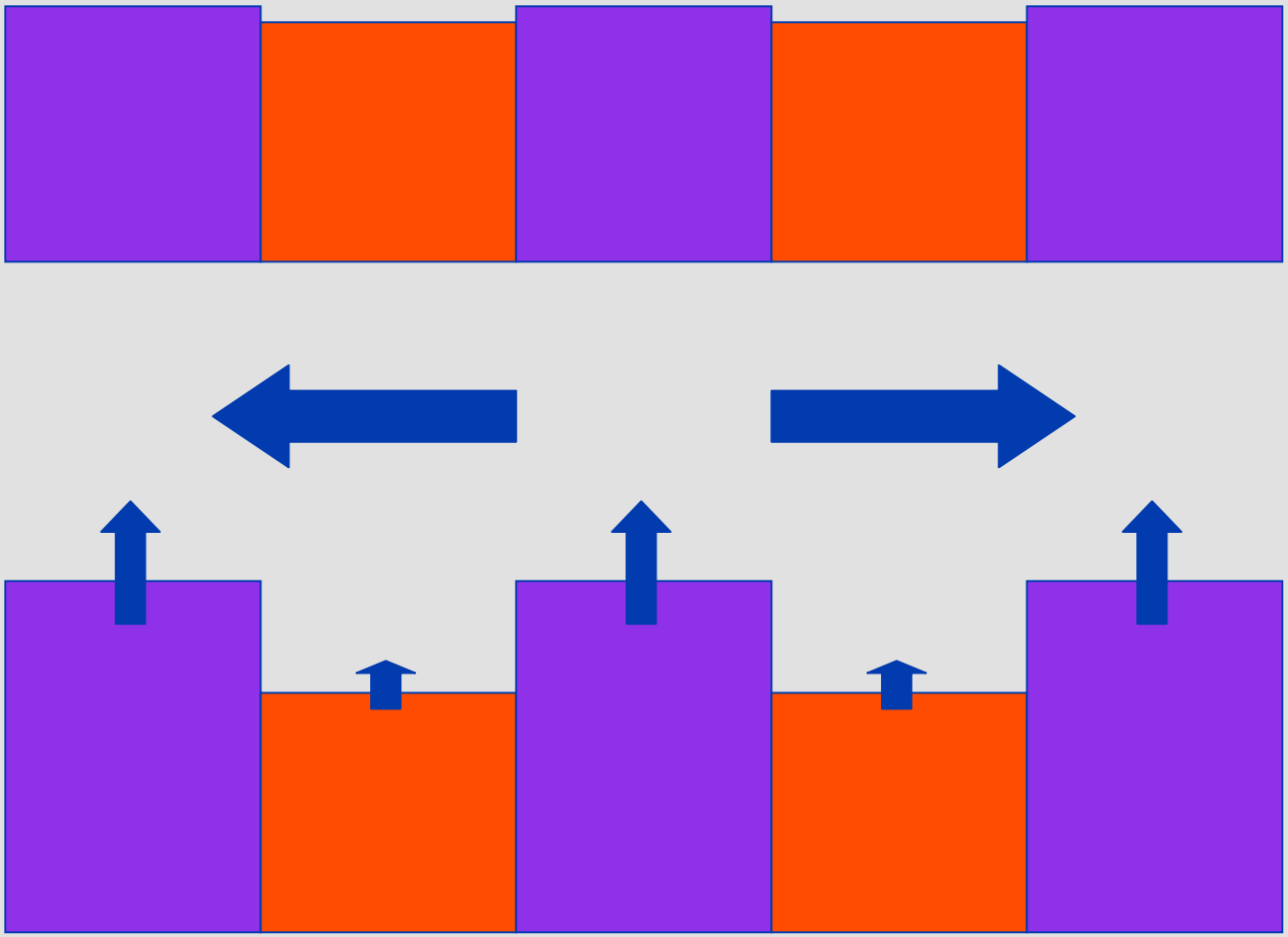
Easier said than done

http://jerg.ee.psu.edu/alumni/vince_baiocco/relatedPages/EE597A

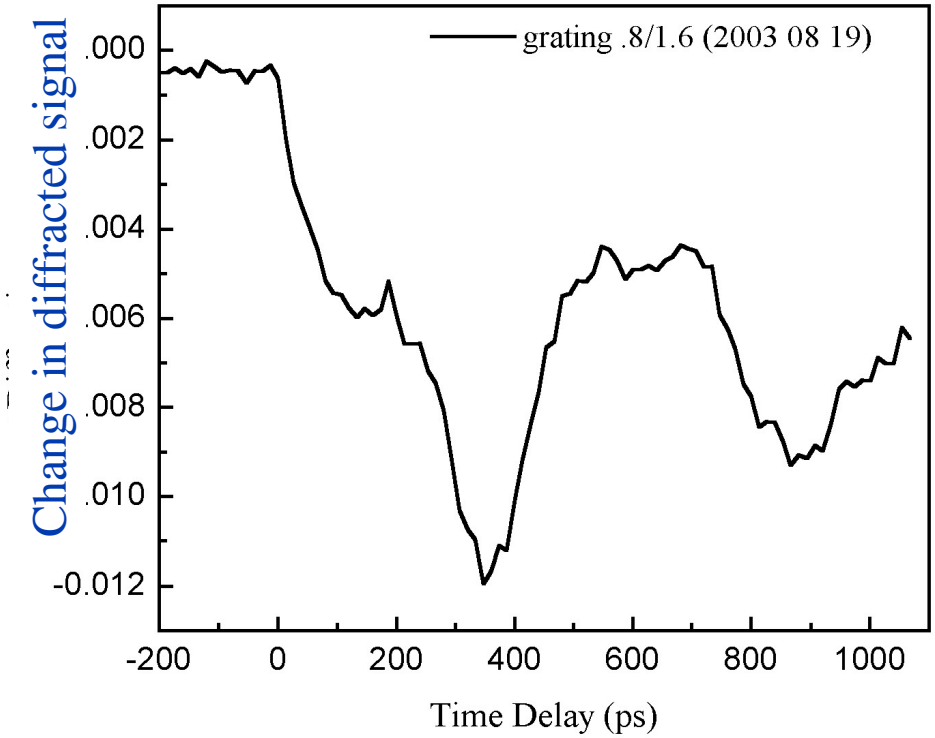
Impulsive Stimulated Thermal Scattering



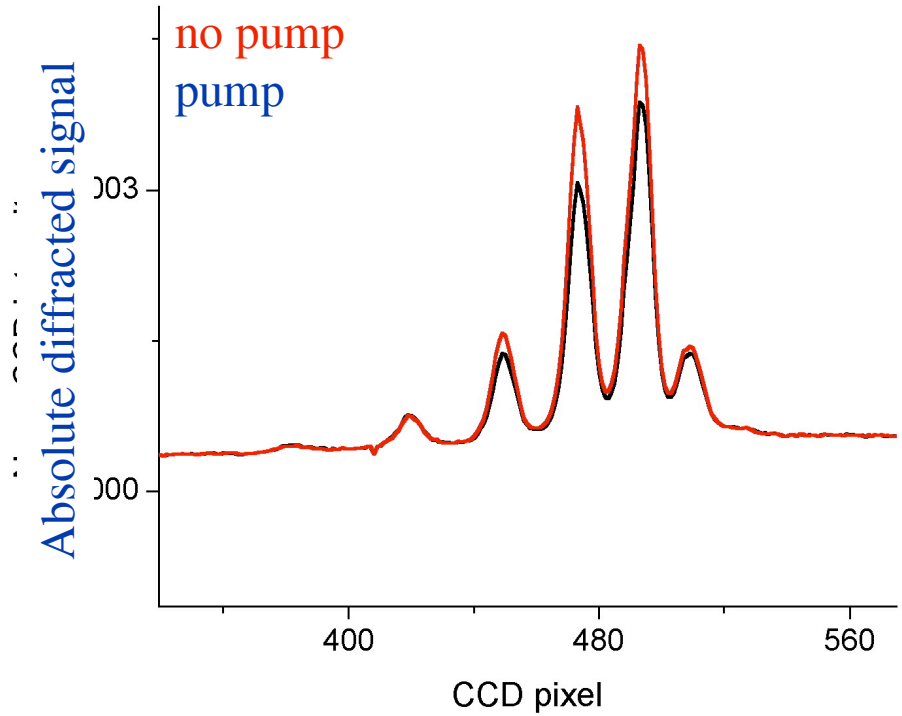
Time-dependent acoustic response in damascene



Observe strong experimental EUV modulated signal from damascene samples

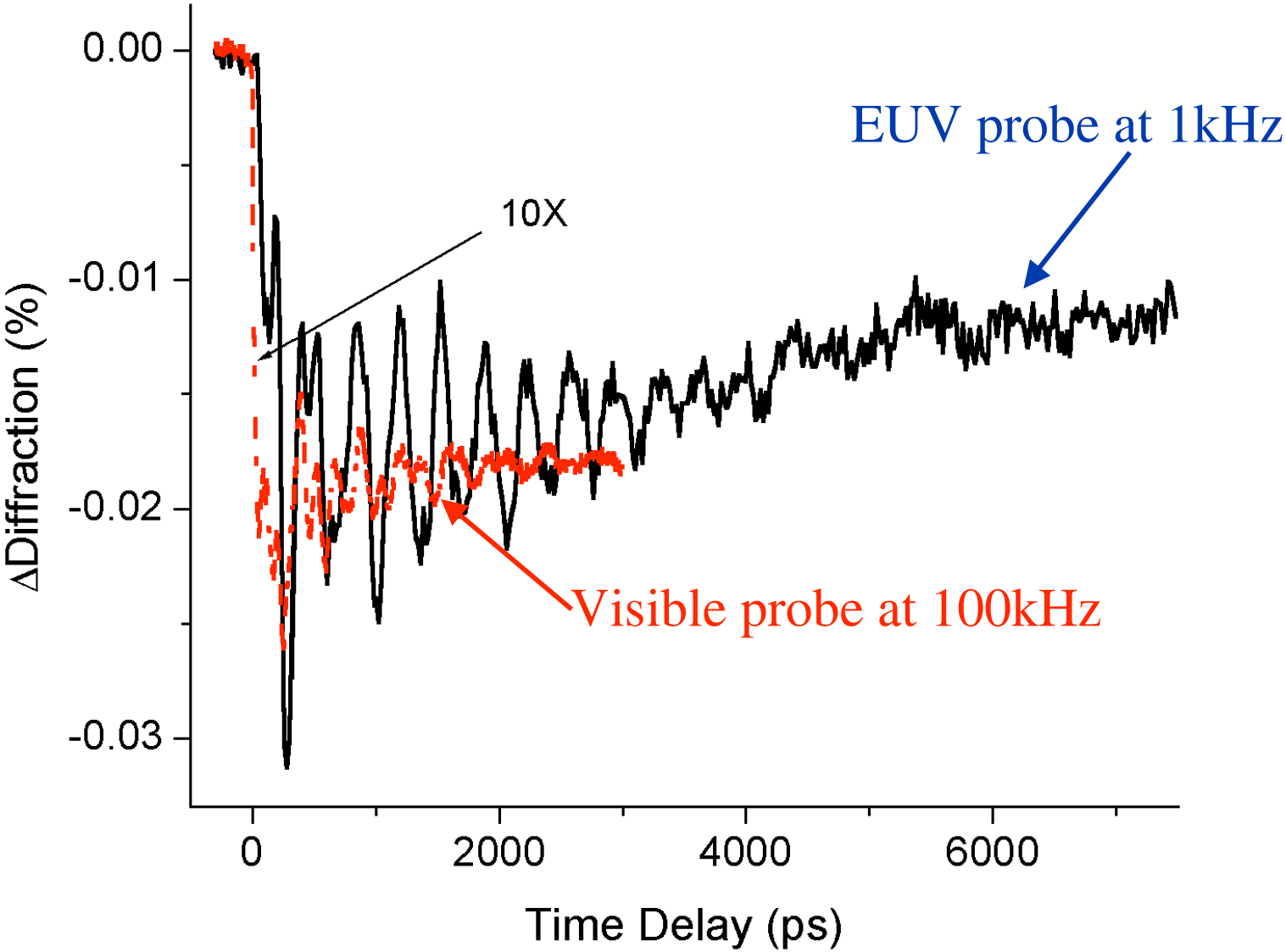


- Several percent change in reflectivity is easily observed

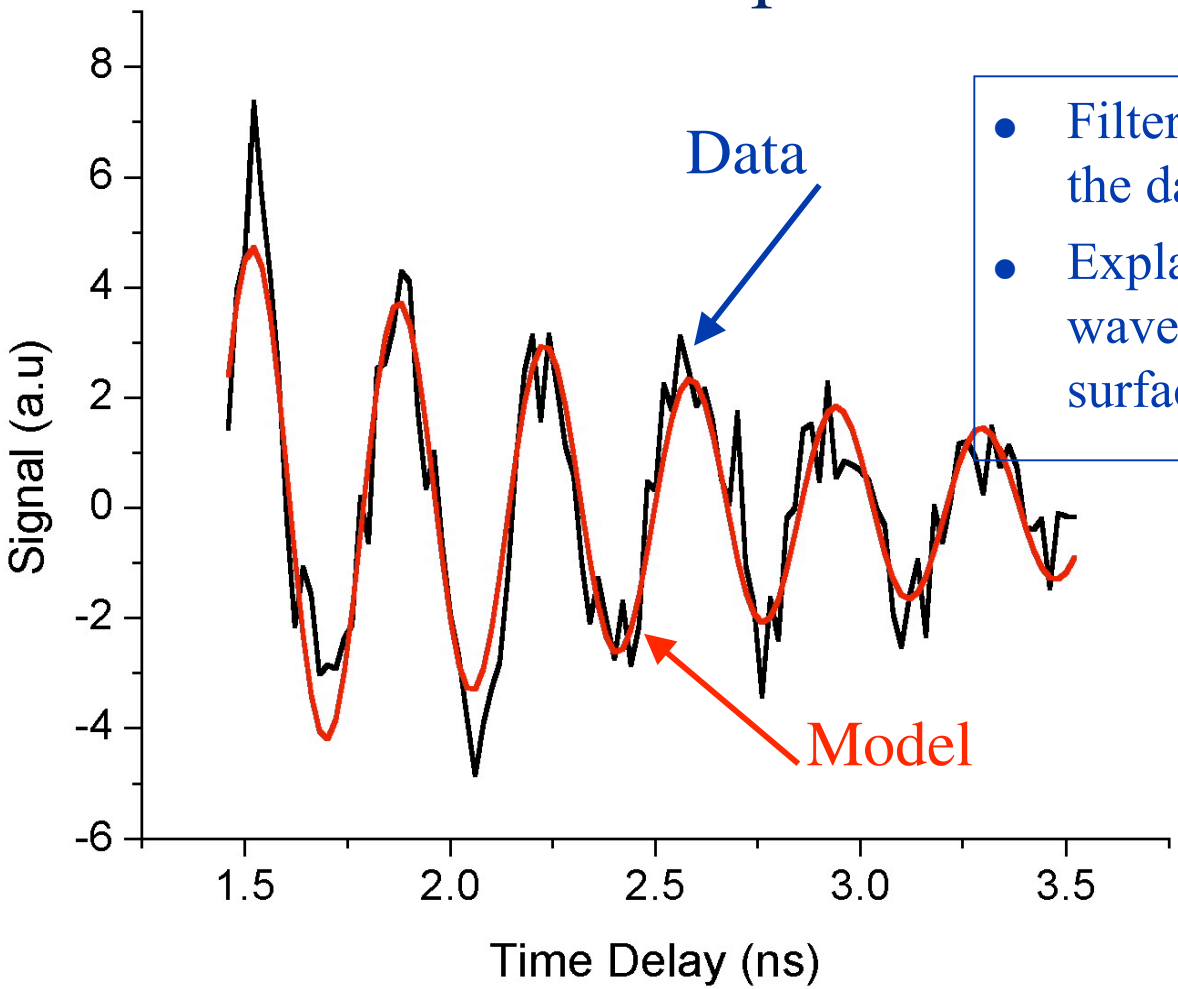


Sensitivity in EUV far higher than visible probe

Phase shift for EUV is proportionally higher



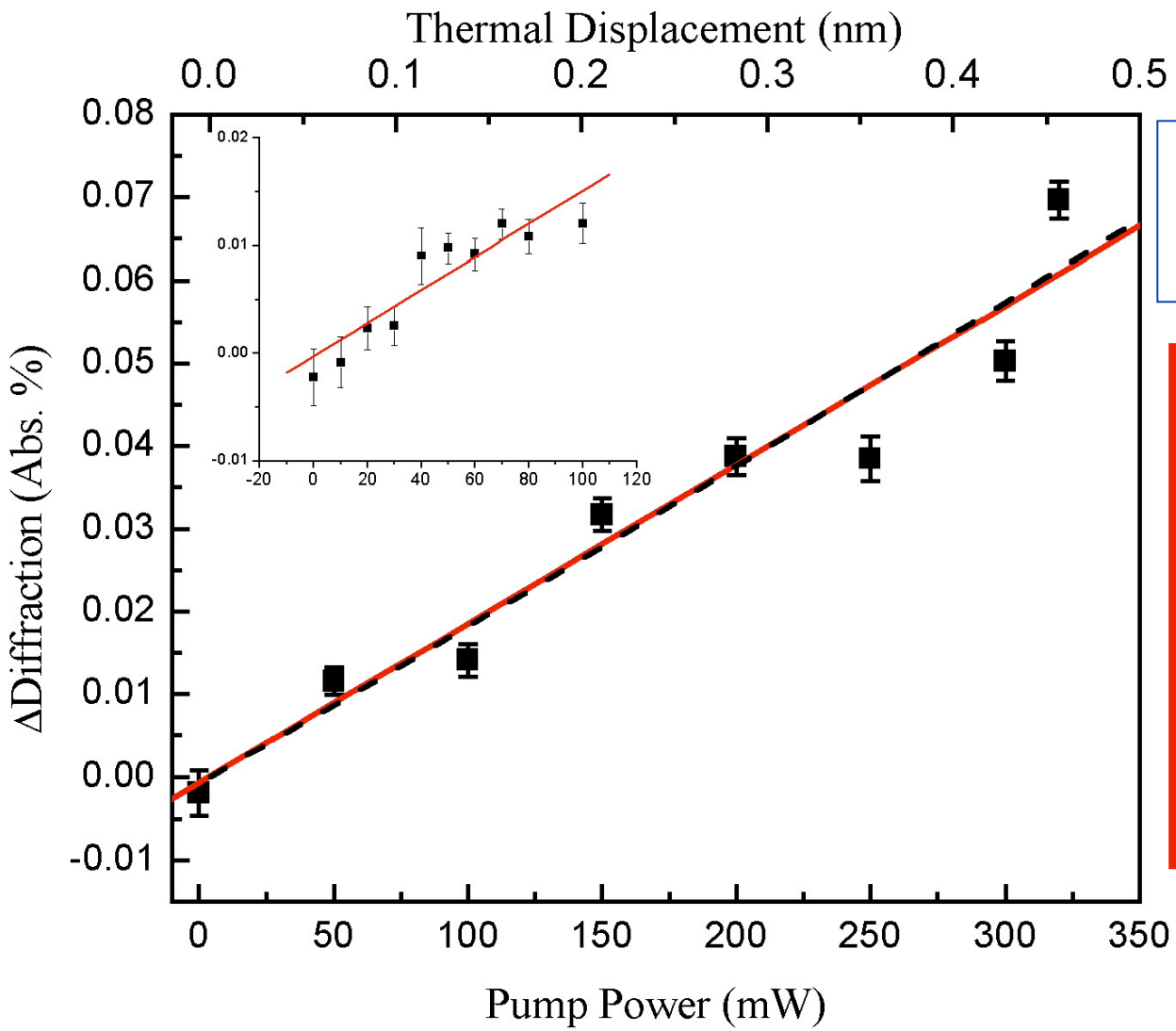
Measured frequencies agree with theoretical predictions



- Filter diagonalization fit to the data yields 2.86GHz
- Explained by surface acoustic wave propagating along the surface of the grating

$$\frac{1}{frequency} = \frac{w_{Cu}}{v_{Cu}} + \frac{w_{Si}}{v_{Si}}$$

Very sensitive measurement of dynamic displacements



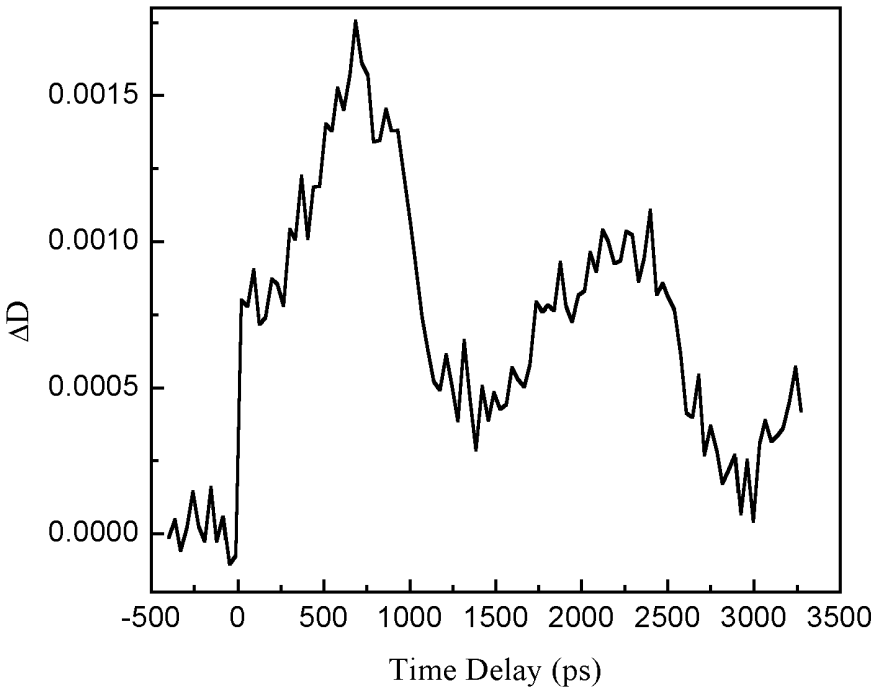
- Measure ≈ 0.02 nm or λ/1500 at 30 nm!

Current/future work:

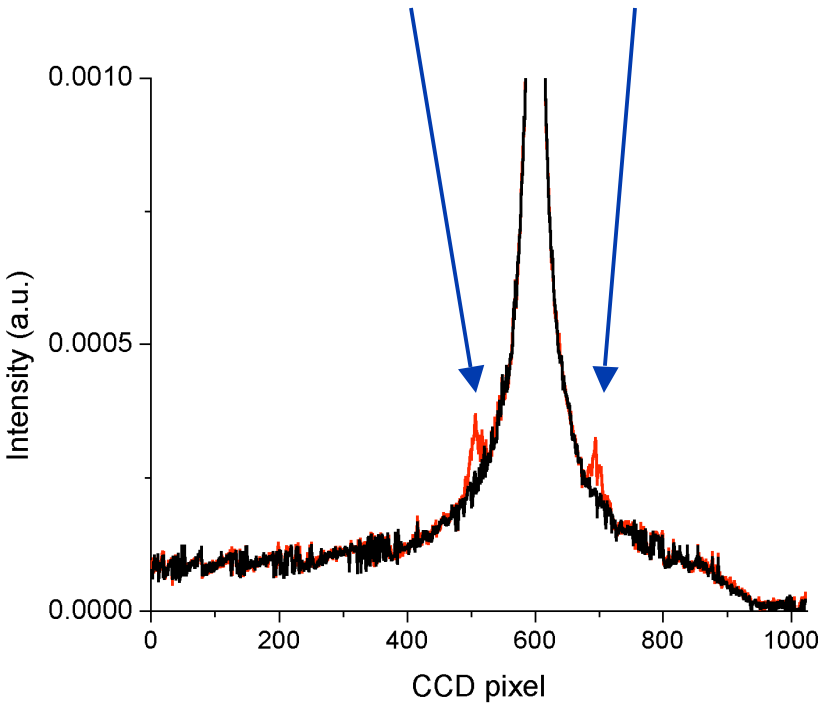
- Use smaller scale structures
- Examine different overcoated materials
- Perform transient grating expt. using multiple beams

Transient Grating Spectroscopy
Crossed 800 nm pump pulses, 30 nm probe pulse

- Flat Al mirror sample
- 5micron spatial period



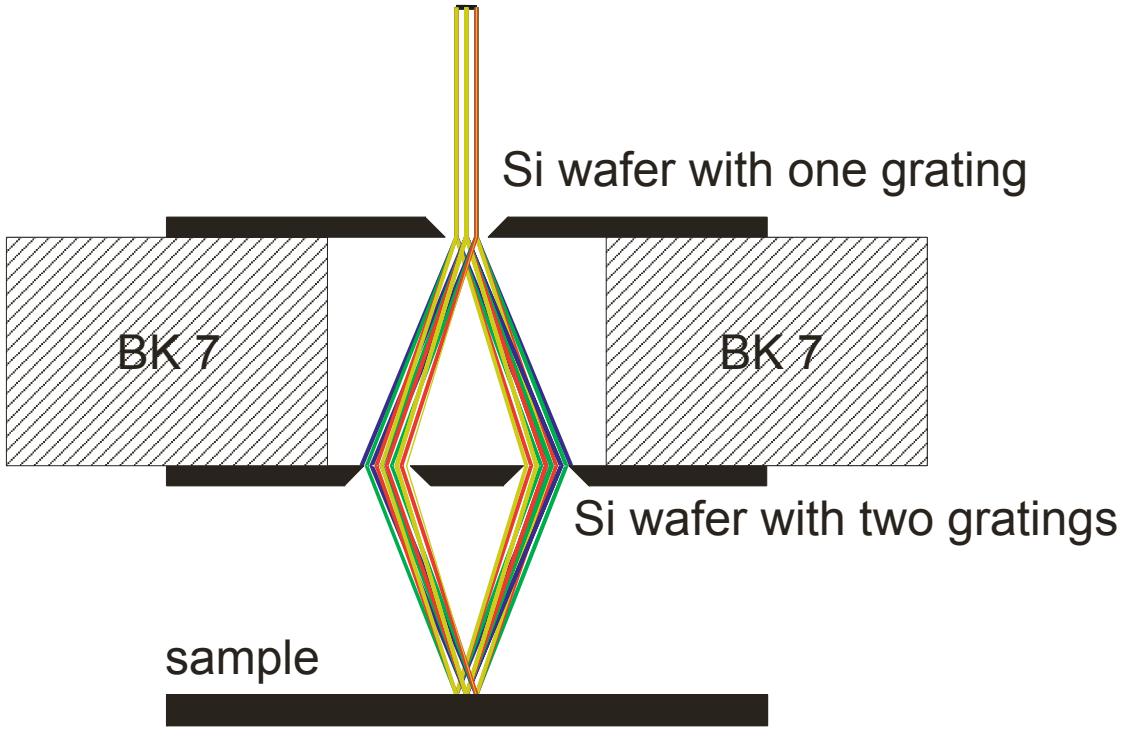
- Signal at these pixels



EUV Excitation Pulses/Nano Fabrication

Diffractive optics with unsupported SiN gratings

Made by T. Savas & H.I. Smith, MIT EECS

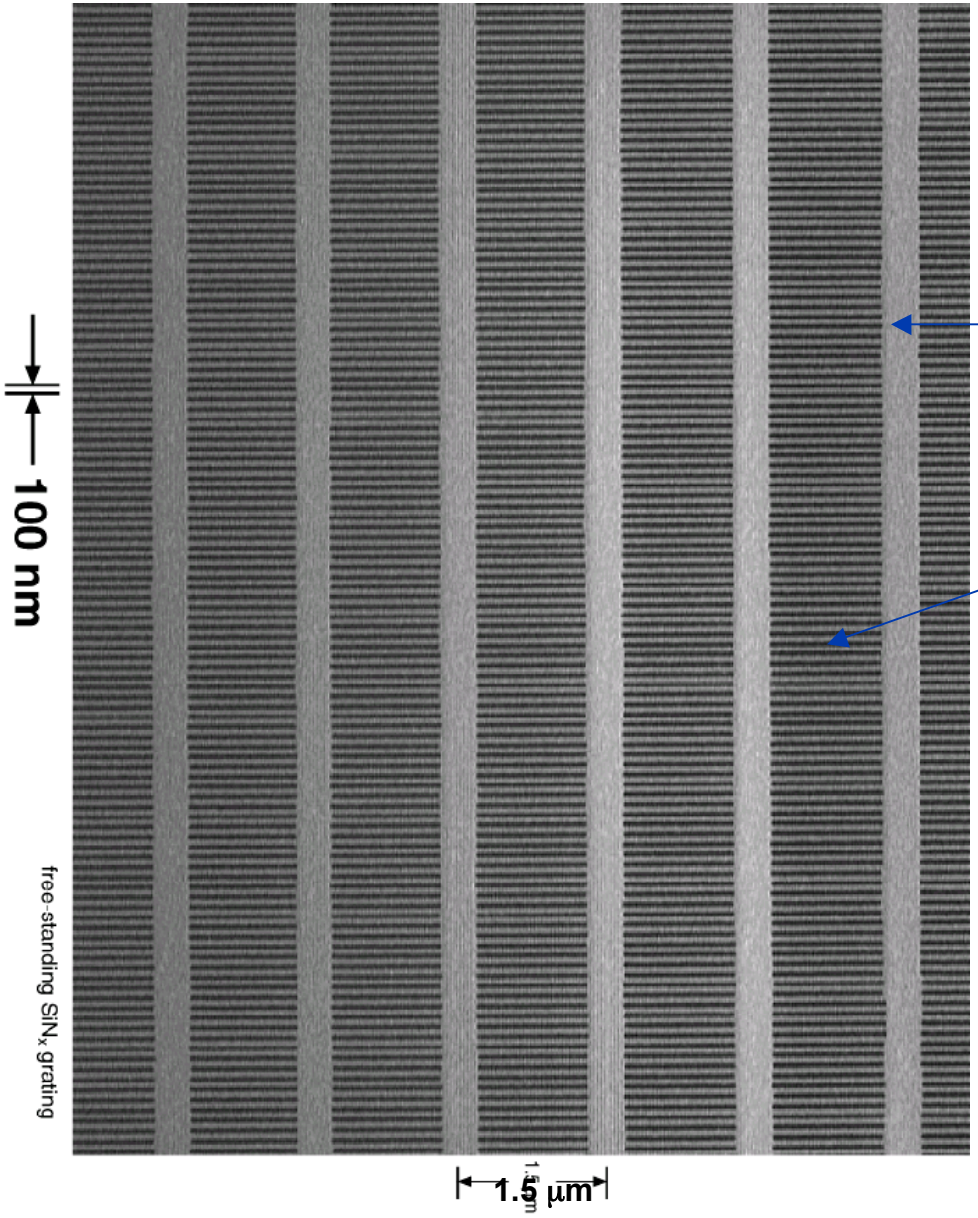


Heterodyned detection possible in x-ray FWM

But total efficiency with supported gratings ~ 0.1%

Stand-alone unsupported grating

Electron microscope image



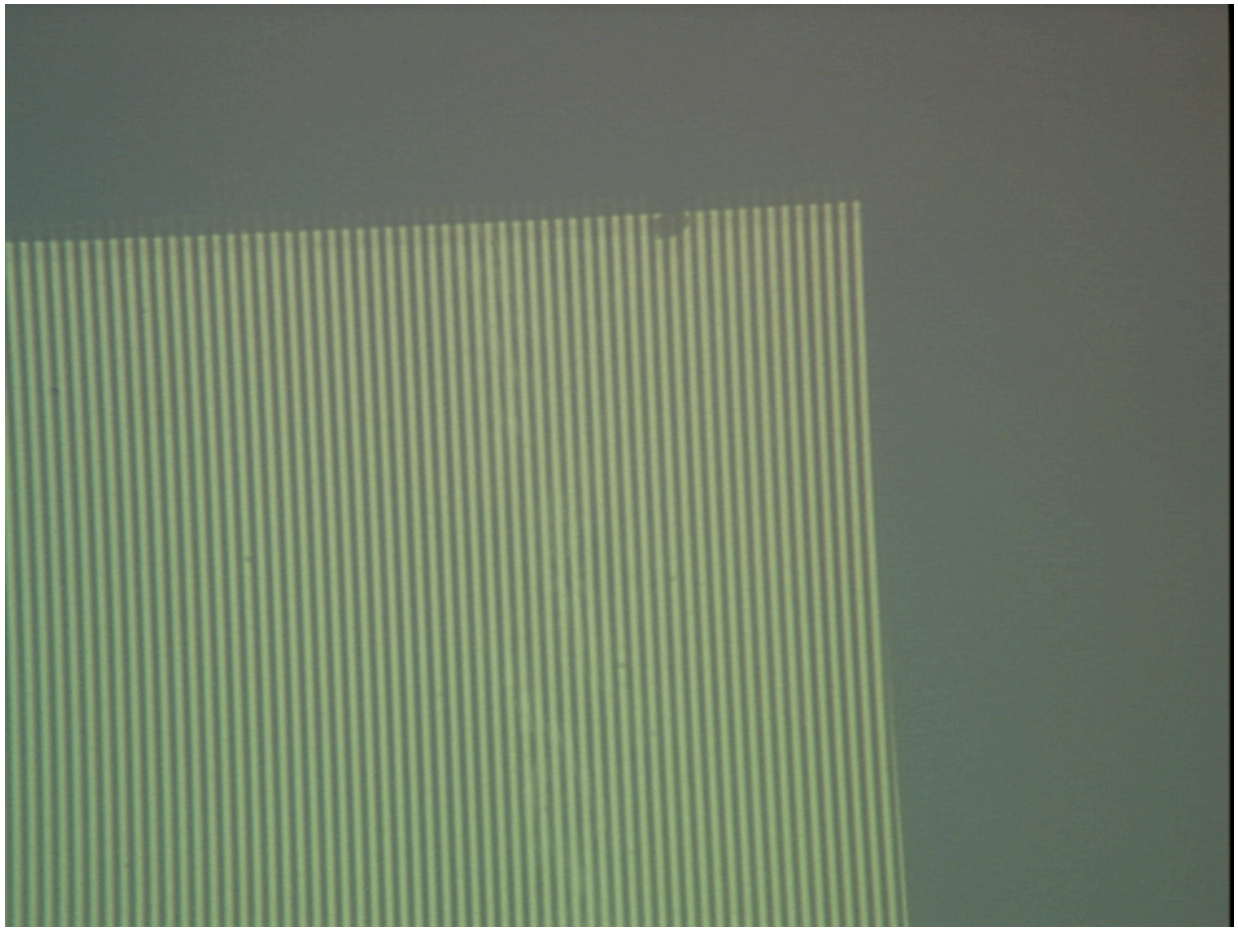
support structure

free standing grating

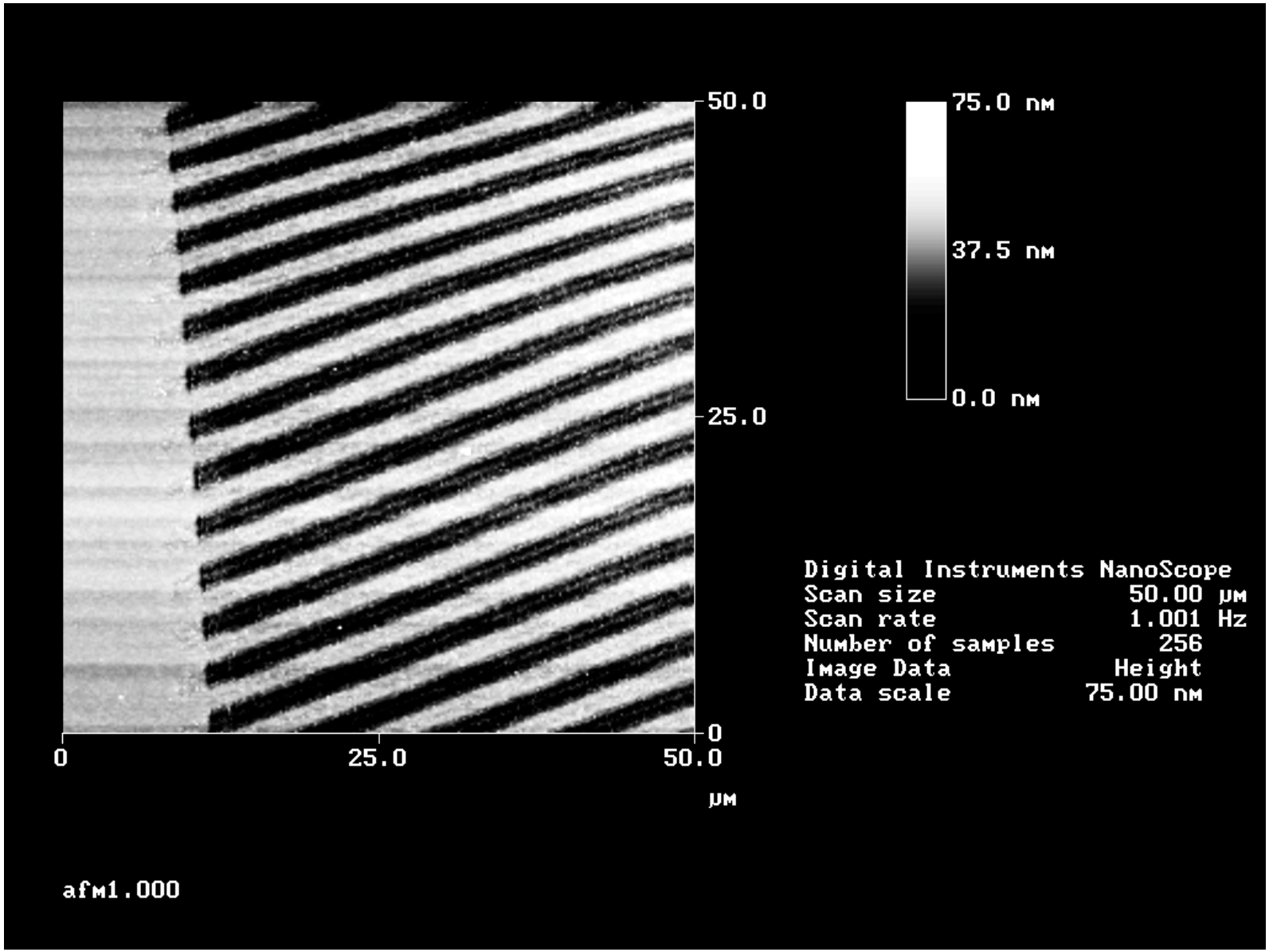
Shadow-masking with 100 nm grating

Coherent x-ray lithography of PMMA

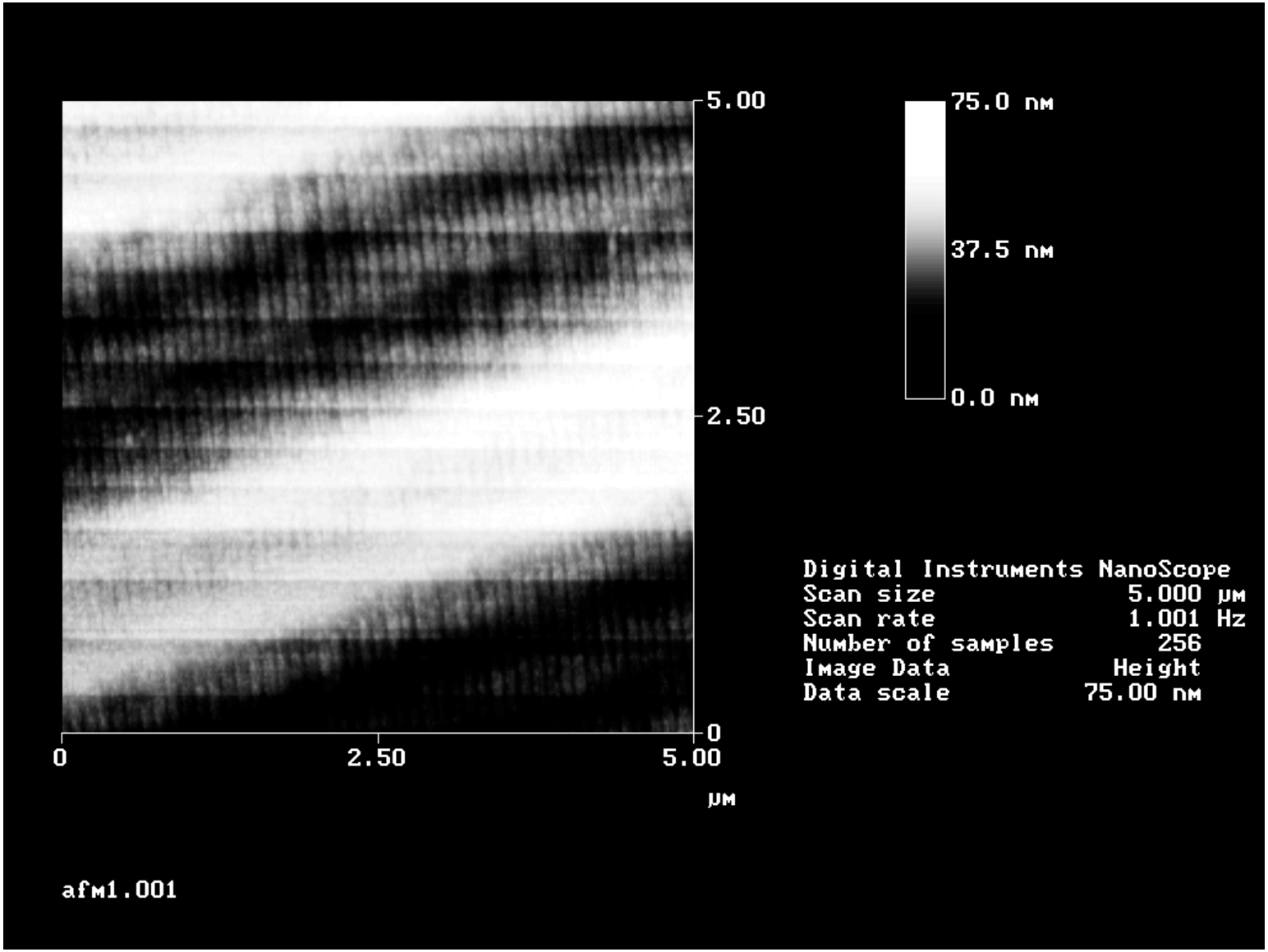
1000x optical microscope image



Closer…..


50.0
25.0
0
0
25.0
50.0
µm
75.0 nm
37.5 nm
0.0 nm
Digital Instruments NanoScope
Scan size 50.00 µm
Scan rate 1.001 Hz
Number of samples 256
Image Data Height
Data scale 75.00 nm
afm1.000

Closer…..


5.00
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Digital Instruments NanoScope
Scan size 5.000 µm
Scan rate 1.001 Hz
Number of samples 256
Image Data Height
Data scale 75.00 nm
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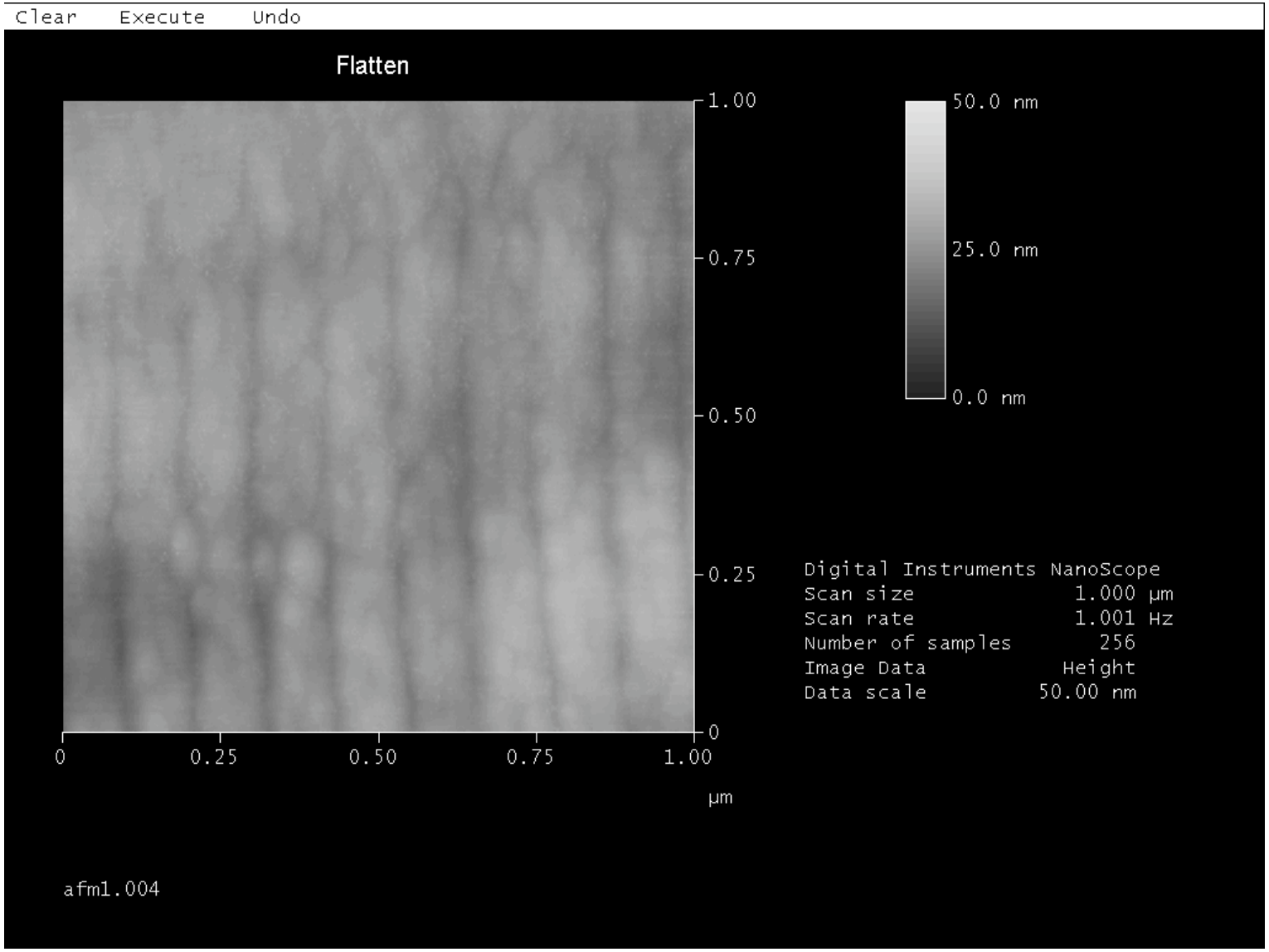
Closer…



100-nm pattern clearly revealed

Diffraction effects show grating too far from sample

Shadow-masking with 100 nm grating

Coherent x-ray lithography of PMMA

90 nm PMMA on Si

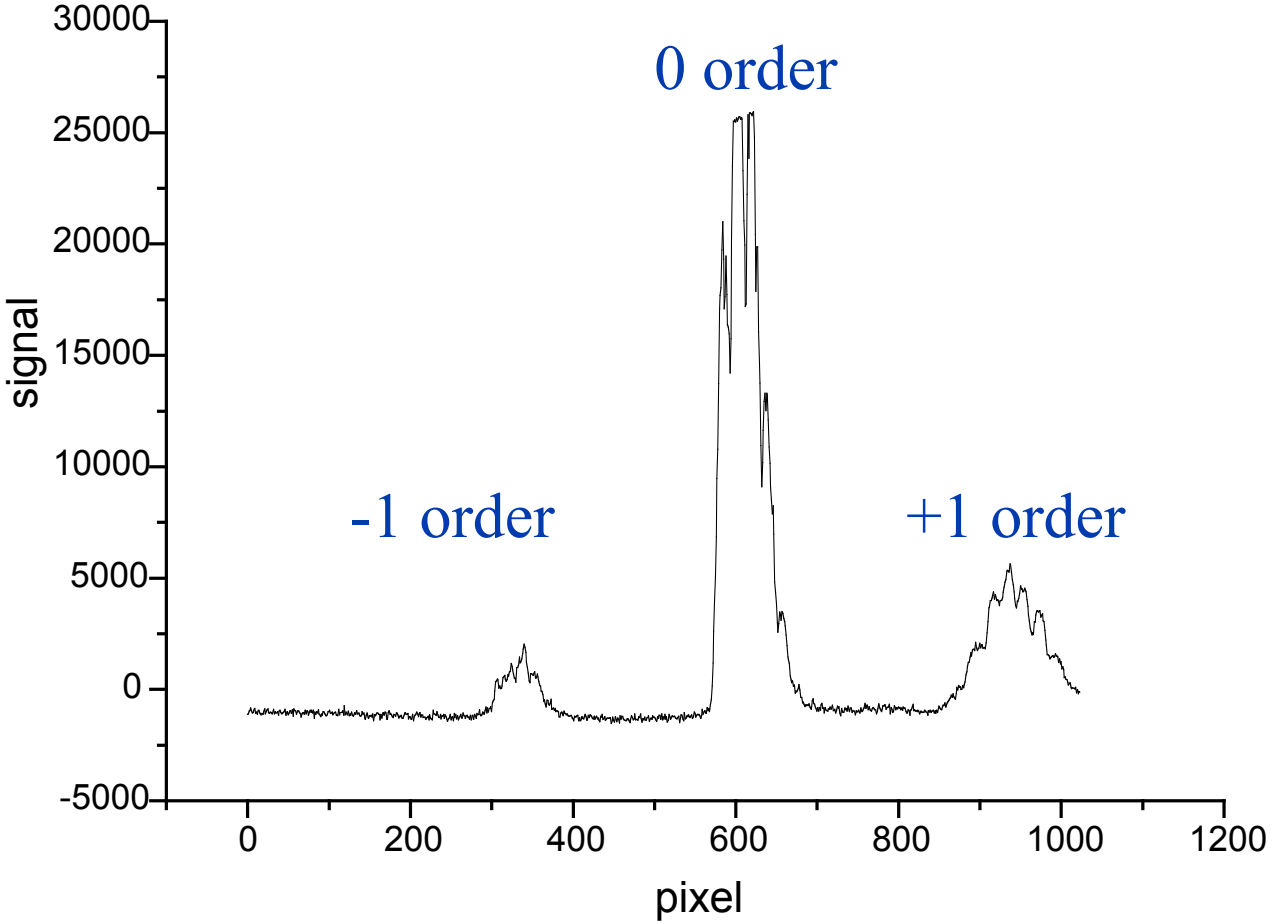
Threshold dose 2kJ/cm^3

Laser energy per shot	750 μJ	
Approximate wavelength	30 nm (41 eV)	
Laser repetition rate	2 kHz	
Ar pressure	40 torr	
Current reading Al diode (10% efficiency)	500 pA	2 nA
x-ray beam diameter	1 mm	
x-ray photons	1.6×10^7	6.2×10^7
Energy [pJ]	103	410
Fluence [nJ/cm^2]	13	52
Energy density [mJ/cm^3]	3.3	13.1
Exposure time [sec]	153	38

~ 1 minute exposure times were adequate, as expected

Coherent x-ray diffraction from a permanent grating

1.5 μm SiN grating support structure used



15-20% diffraction efficiency

2nd order diffraction also seen

Progress Report:
Visible transient grating excitation, EUV probe

800 nm pump excitation pulses
30 nm probe can diffract at small angle

Ultimate objective:
X-ray transient grating excitation, X-ray probe

Two fibers or split beam for excitation pulses

Separate fiber possible for pump and probe beams

Higher efficiency interferometer possible,
especially for hard x-rays

Summary

Visible pump EUV probe FWM now demonstrated
EUV grating excitation demonstrated

All-EUV FWM anticipated
All-Hard-X-ray FWM anticipated!
Entire Brillouin zone available
Measurements in bulk materials possible

Direct determination of structural correlation times and lengths
Exciton, electronic correlation lengths also accessible

AND SOMEDAY...

Femtosecond PULSE SHAPING techniques now used in the optical regime....

will be used for coherent x-rays…

to permit coherent control over short distance scales…

to induce nonlinear collective responses, including shock formation, with small characteristic length scales

Coherent control on specified time and length scales will be possible!

CREDITS

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DOE NSF