Alphabet Soup
An Overview of Diagnostic Techniques

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http://www.bnl.gov/cfn/

http://www.bnl.gov/ps/

What we want to know

Crystalline cathodes (Diamond, GaAs, metals)

- Surface orientation, texture, grain size, defect density and type, strain, multilayer spacing and properties
- Surface chemistry, contamination, termination
- Bulk impurities, doping levels
- Surface morphology, spatial variation
- Electronic and emission characteristics: energy/momentum spread, QE, temporal response, carrier velocity, trapping, carrier lifetime/escape depth, scattering, density of states

Grown Cathodes (Cs_2Te, Cs_3Sb, CsK_2Sb)

- As above, plus film thickness and uniformity
- In situ diagnostics during growth

Diffraction

X ray diffraction (XRD) provides information on crystal structure, grain size and texture, strain

Grazing Incidence (GID) improves surface sensitivity

Topography provides strain and defect image

(Jean's talk)

Electron diffraction (LEED, RHEED) provides surface orientation, including reconstruction

Electron Backscattered Diffraction (EBSD) provides spatially resolved grain maps

Photoemission Spectroscopy

Ultraviolet Photoemission Spectroscopy (UPS)

- Angle Resolved (ARPES) – valence band structure, momentum band structure, emission characteristics, electron/phonon coupling, scattering
- Photoemission electron microscope (PEEM) - Spatially resolved electron emission

X-ray Photoemission Spectroscopy (XPS)

- Surface chemical composition, contamination

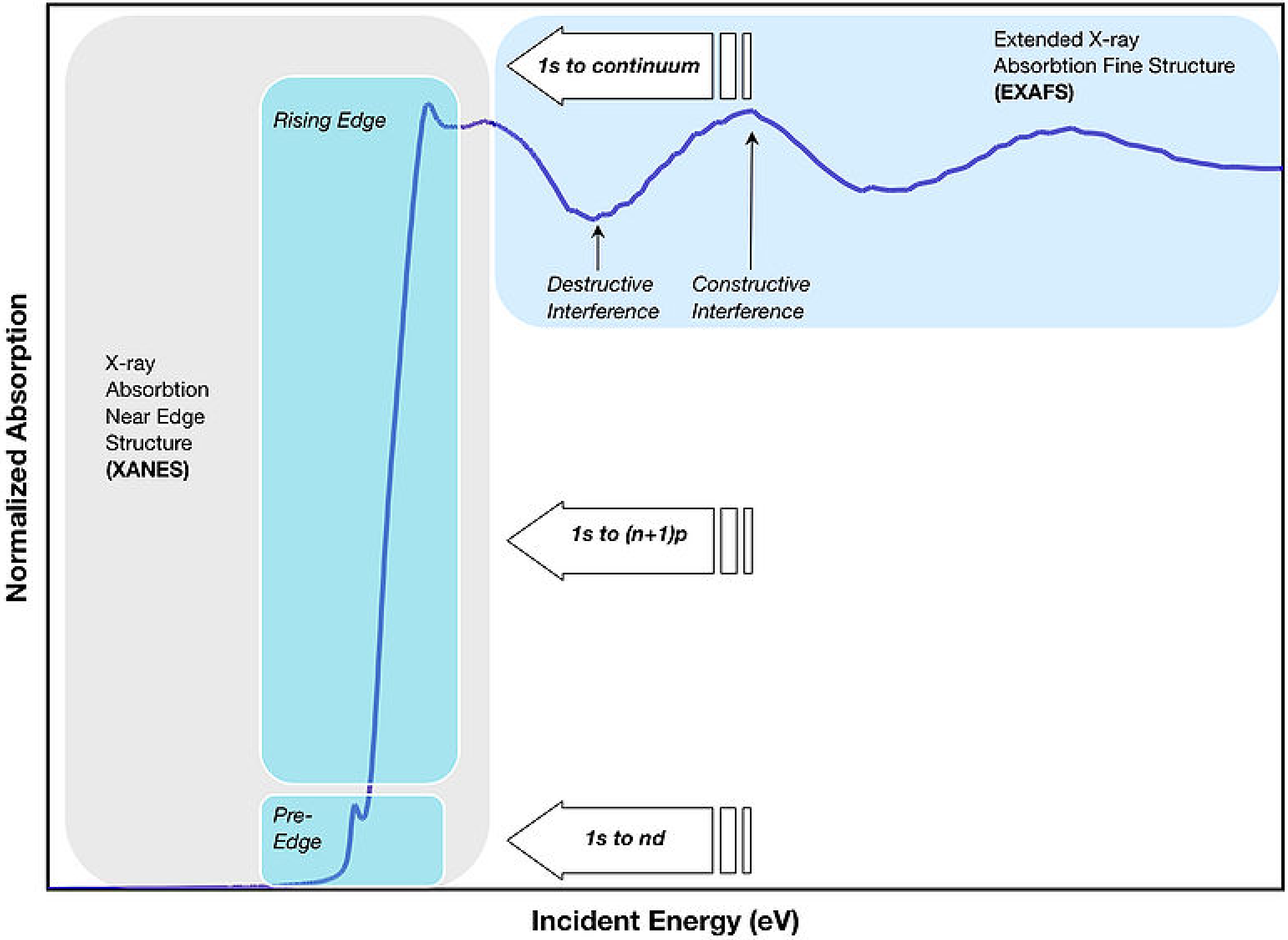
Absorption/Fluorescent Spectroscopy

X-ray Fluorescence (XRF) provides elemental analysis

- Can be stimulated with X-ray or Electron beams
- Energy Dispersive X-ray Spectroscopy (EDS) provides spatial resolved elemental composition

X-ray Absorption Spectroscopy (XAS)

- Measure electron yield or fluorescent yield for near edge analysis (NEXAFS/XANES) – provides surface or bulk chemical information, joint density of states
- Measure absorption or fluorescence for “extended” structure (>100 eV above edge, EXAFS) – provides information on local atomic environment due to photoelectron scattering


Extended X-ray
Absorbtion Fine Structure
(EXAFS)
1s to continuum
Rising Edge
Destructive
Interference
Constructive
Interference
X-ray
Absorbtion
Near Edge
Structure
(XANES)
1s to (n+1)p
Pre-
Edge
1s to nd
Normalized Absorption
Incident Energy (eV)

Other Spectroscopy

Infrared Spectroscopy (FTIR) – Vibrational modes, Impurity content, doping level, typically spatially resolved

Raman Spectroscopy – phonon/vibration modes, material identification

Photoluminescence (PL) – Impurities, intra band states in semiconductors, electronic impact of crystalline defects

Total Yield Spectroscopy (TYS) – QE vs photon energy, indirect information on density of states and scattering mechanisms

Imaging

- Scanning Electron Microscopy (SEM)
- Surface scanning
  - Atomic Force Microscopy (AFM) and Profilometry
  - Kelvin Probe Force Microscopy (KPFM)
    - Local work function
  - Scanning Tunneling Microscope (STM)
    - Local density of states
- Combined w/ other techniques (PEEM, XBIC, Topography)

Induced Current

- Beam induced current (BIC) provides carrier dynamics (mobility, saturation velocity, lifetime, trapping sites, contact type) with spatial resolution determined by beam size and rastering capability
- Electron, X-ray and Ion beams are used (EBIC, XBIC, IBIC)
  - XBIC provides the ability to probe depth
  - EBIC provides SEM spatial resolution
  - IBIC provides “delta function” temporal response

Diamond Science at BNL

Imaging

SEM	Scanning Electron Microscopy	Surface morphology
LEEM	Low Energy Electron Microscopy	Imaging of hydrogenated surface, spatially localized LEED, work function mapping
AFM	Atomic Force Microscopy	Surface morphology

Diffraction

XRD	X-ray diffraction, time resolved	Characterization of metal contacts, including temperature of formation and crystalline texture
XRD	X-ray diffraction	Diamond crystal quality; evaluation of stress caused by laser shaping
Topography		Diamond crystal quality, localization and identification of defects
LEED	Low Energy Electron Diffraction	Surface crystal analysis, evaluation of hydrogenated surface

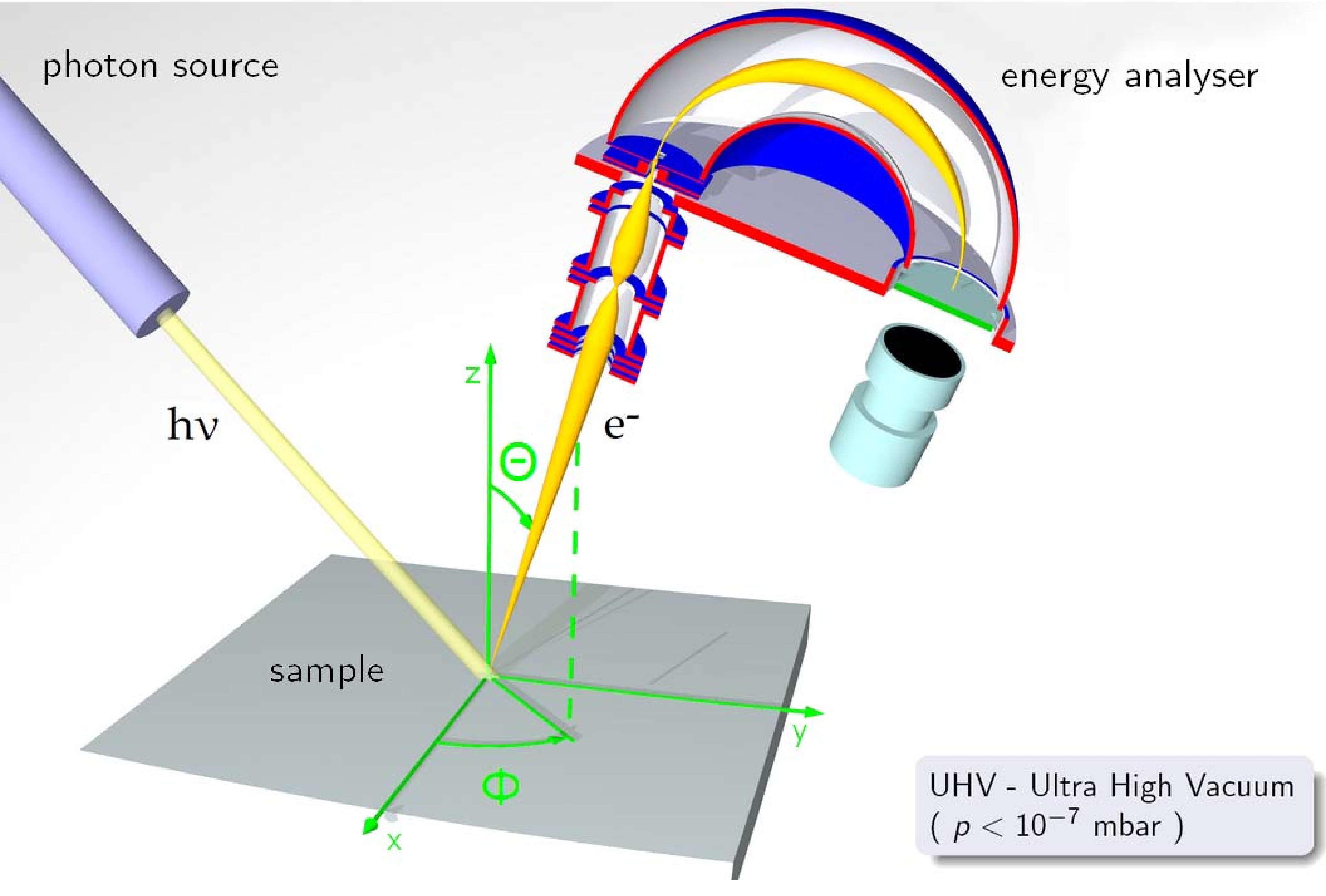
Spectroscopy

UPS/ARPES	Ultraviolet Photoemission Spectroscopy	Electron affinity, energy & angular distribution of emitted electrons, lifetime of NEA surface
TYS	Total Yield Spectroscopy	Evaluation of hydrogenated surface, lifetime
NEXAFS	Near Edge X-ray Absorption Fine Structure	Surface elemental analysis, characterization of surface bonding, carbon formation
XAFS	X-ray absorption fine structure	Titanium/diamond surface chemistry
EDS	Energy Dispersive X-ray Spectroscopy	Surface elemental analysis
FTIR	Fourier Transform Infrared Spectroscopy	Impurities in diamond
Photoluminescence & Raman Spectroscopy		Impurity analysis, identification of carbon chemistry, mapping

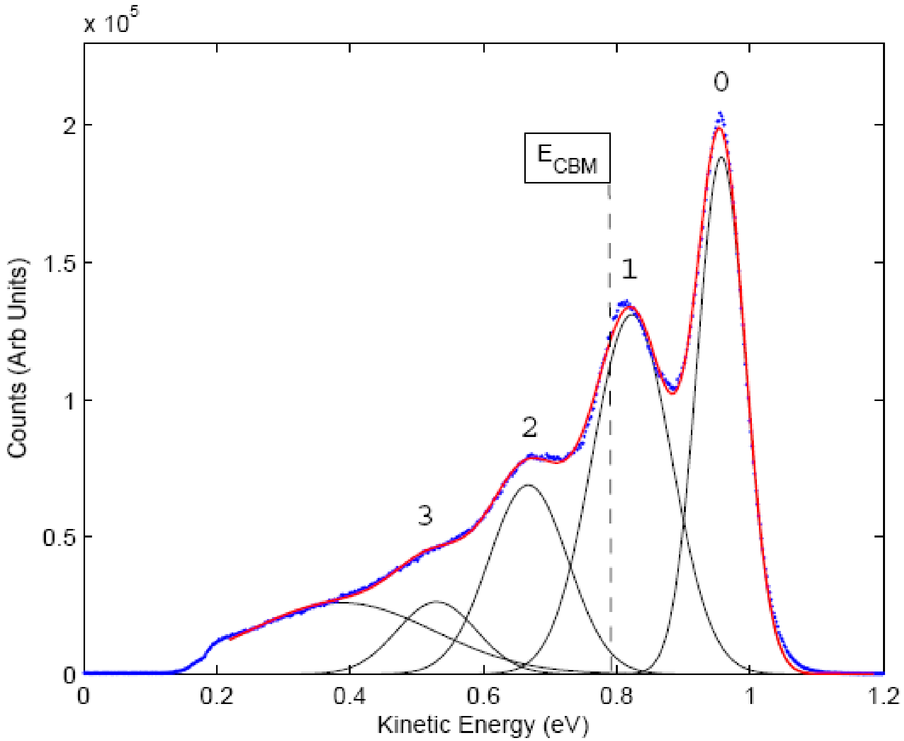
Carrier Transport and Emission

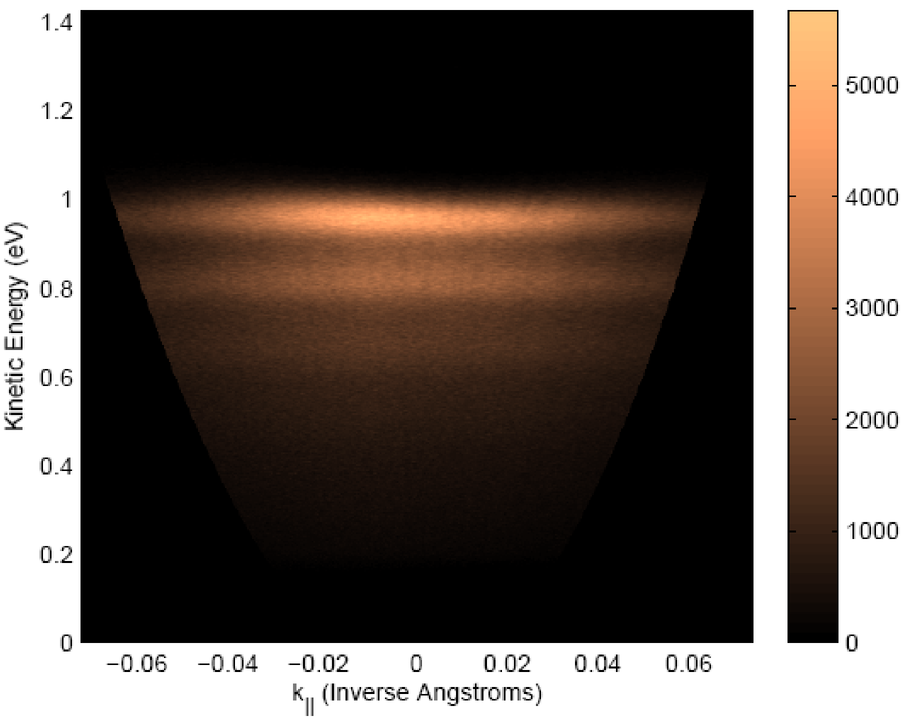
Electron Generated	Carrier Transport vs Field, Emission, Gain, Thermal Emittance
Photo-electron Generated	Gain, Timing
Soft X-ray, Monochromatic	Charge collection distance, Charge trapping/detrapping effects
Hard X-ray, Monochromatic	Measurement of mean ionization energy (gain)
High Flux White beam	Current Limits, Contact requirements, Heat management
Micro-beam Mapping	Localization of electrically active sites

Angle-Resolved Photoemission Spectroscopy



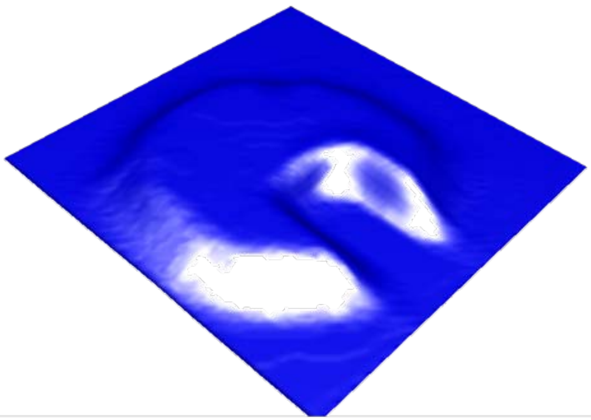
Laser ARPES
Boron Doped Diamond, H Terminated, [001]

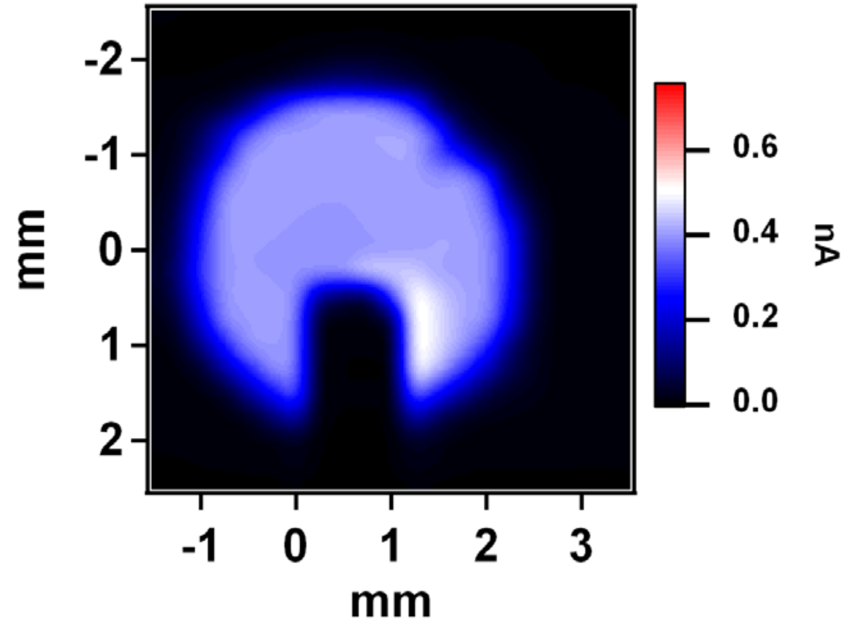




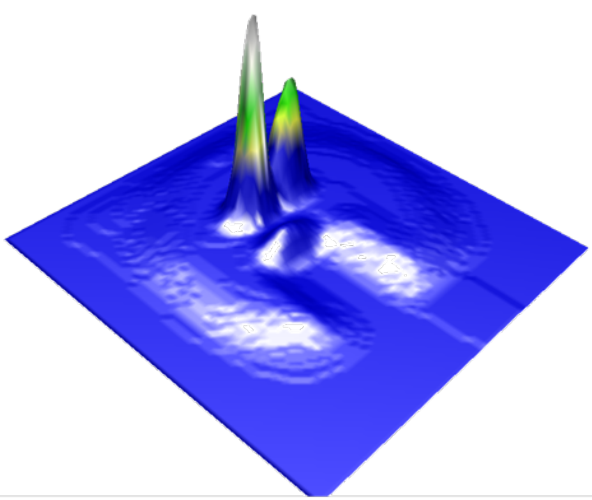
Used 6 eV photons – below direct transition band gap
(synchrotron ARPES gives direct PE behavior- no thermilization)
Max KE = NEA ~ 1 eV, as expected from theory
Spectrum is isotropic over at least 30 degrees from normal
Discrete peaks caused by phonon scattering – may depend on doping level

HID14 in X15
(80%, 100V, 1kHz, 19keV)

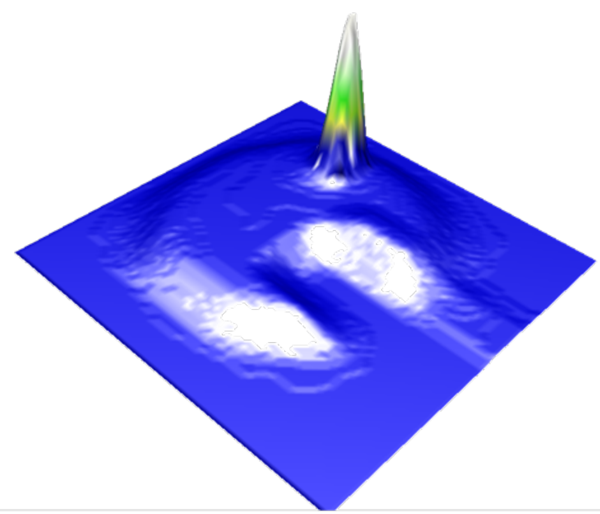




HID18 in X6B
(80% ,-100V, 1kHz, 19keV)

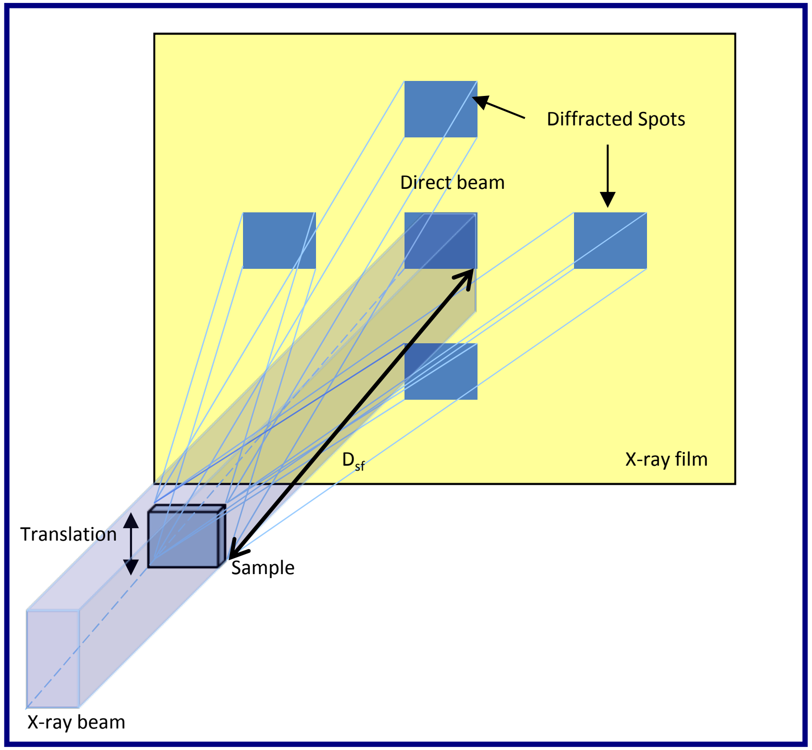


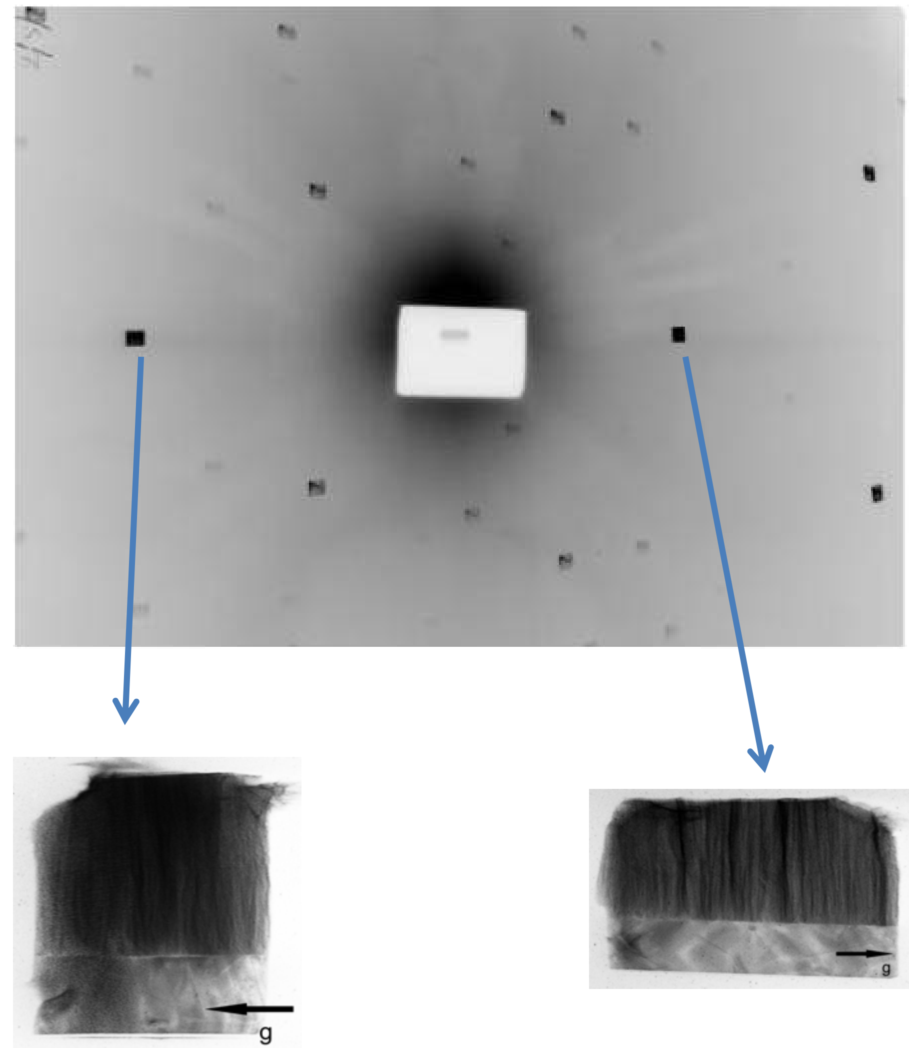
HID18 in X6B
(80% ,+100V, 1kHz, 19keV)



X-ray Topography

Transmission

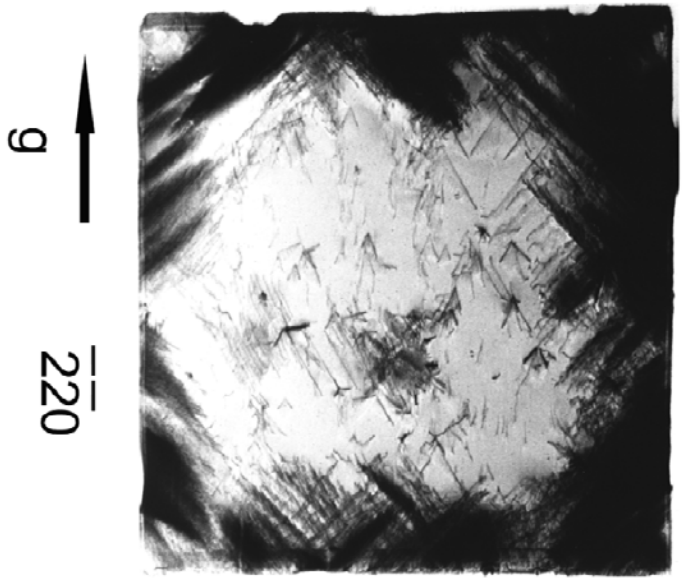




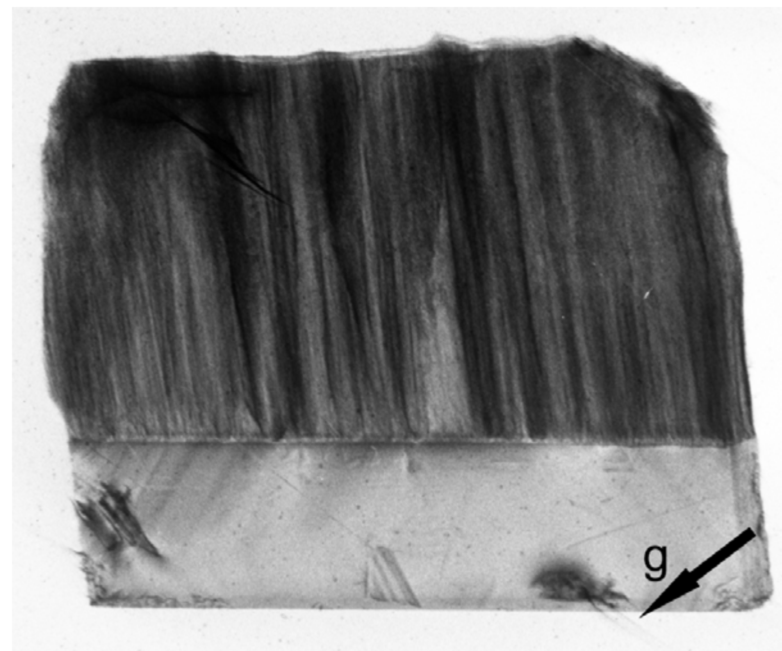
The diamond is placed on a stage that can be rotated to record various reflections like the {220}s , {400}s and {111}s below.

White Beam Topography

Single crystal CVD – slip bands near edges, threading dislocations throughout



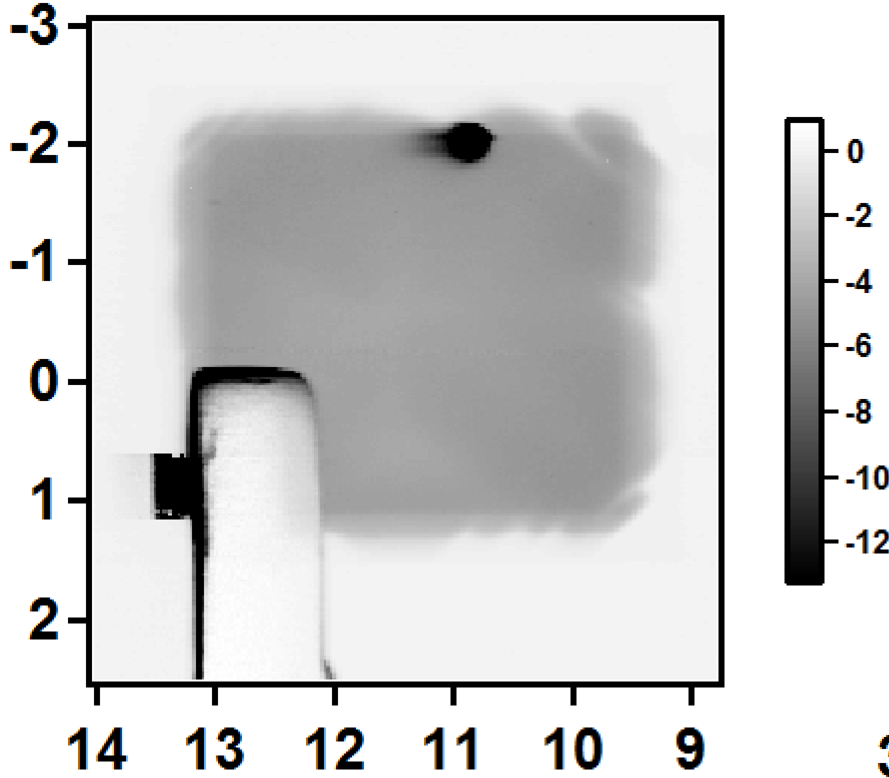
Vertically cut sample shows HPHT substrate which has significantly superior crystal quality but very poor charge transport. Most threading dislocations source at substrate.



-111

Thanks to B. Raghothamachar, M. Dudley (X19C), A. Lohstroh for vertical cut sample

X-ray Response Mapping, Revisited

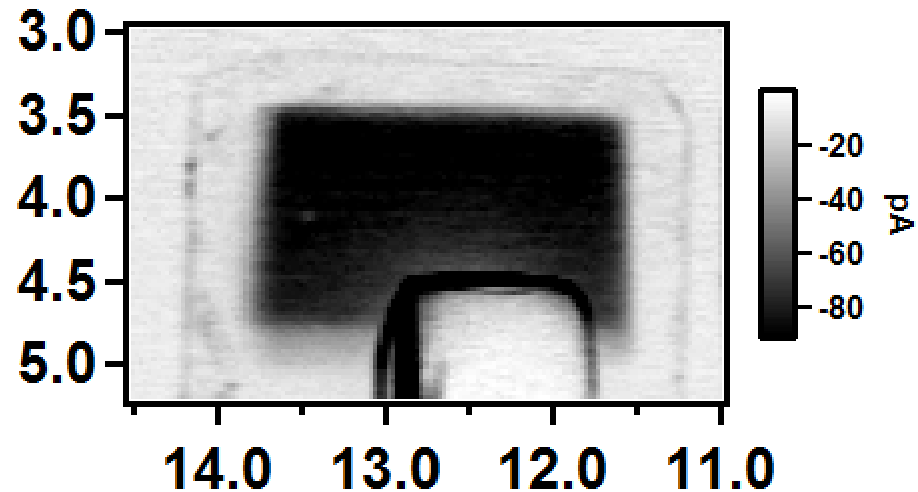


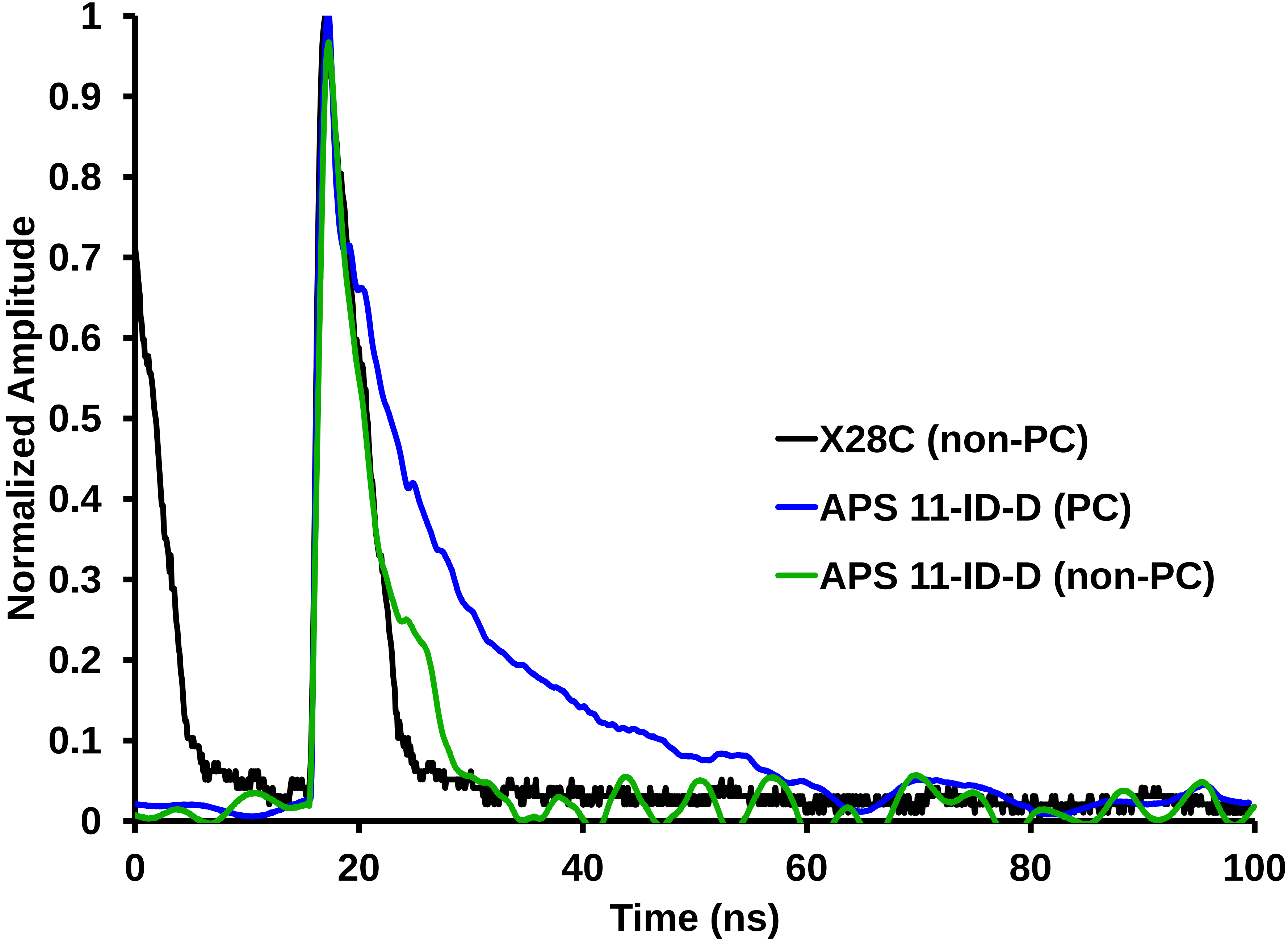
HID15 w/ annealed Pt contacts

- Single photoconductive region
- Slip bands reduce responsivity near edges for both polarities
- Center has expected "diode" response

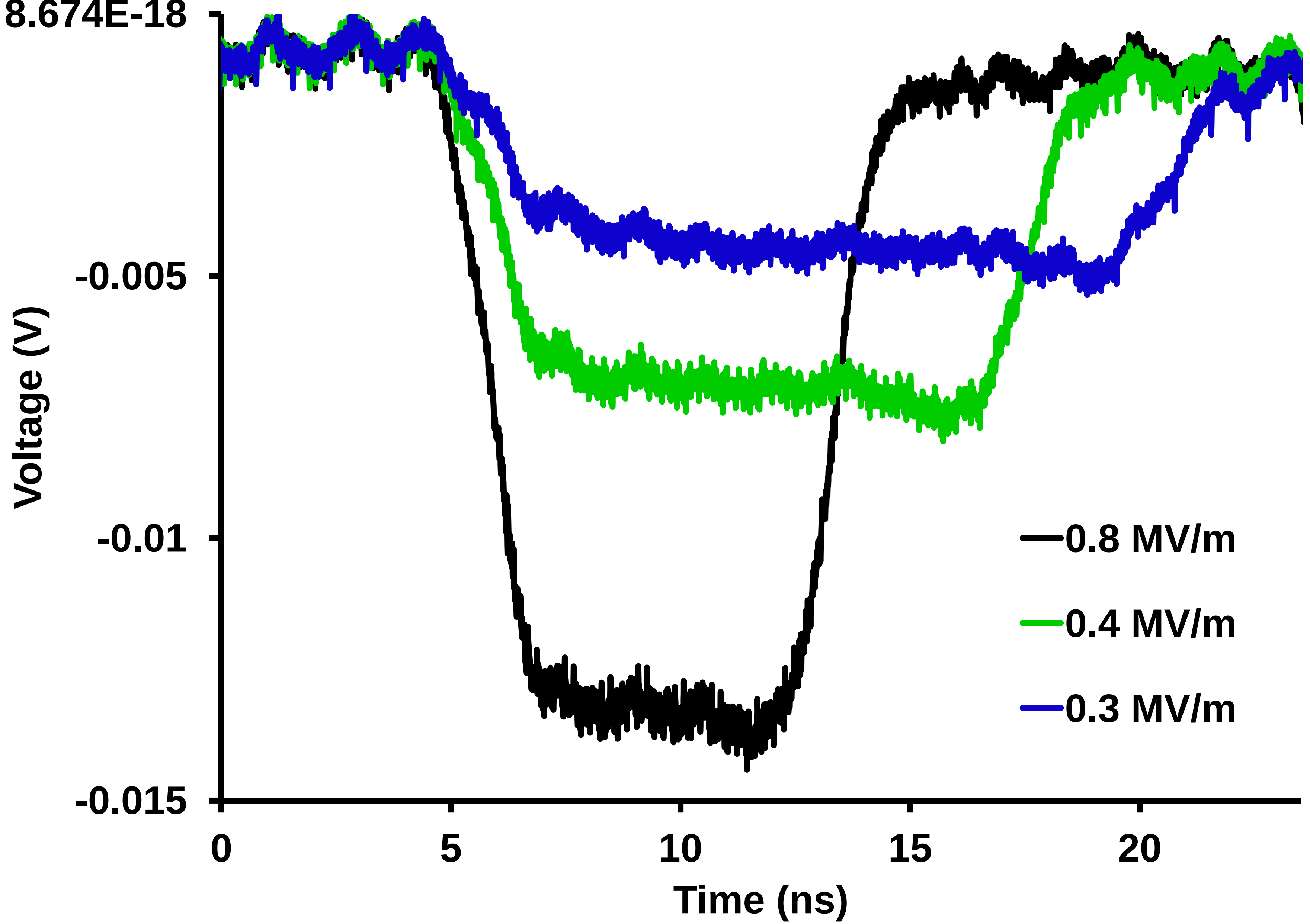
Vertical diamond

- Sub "diode" response
- Substrate has very low response

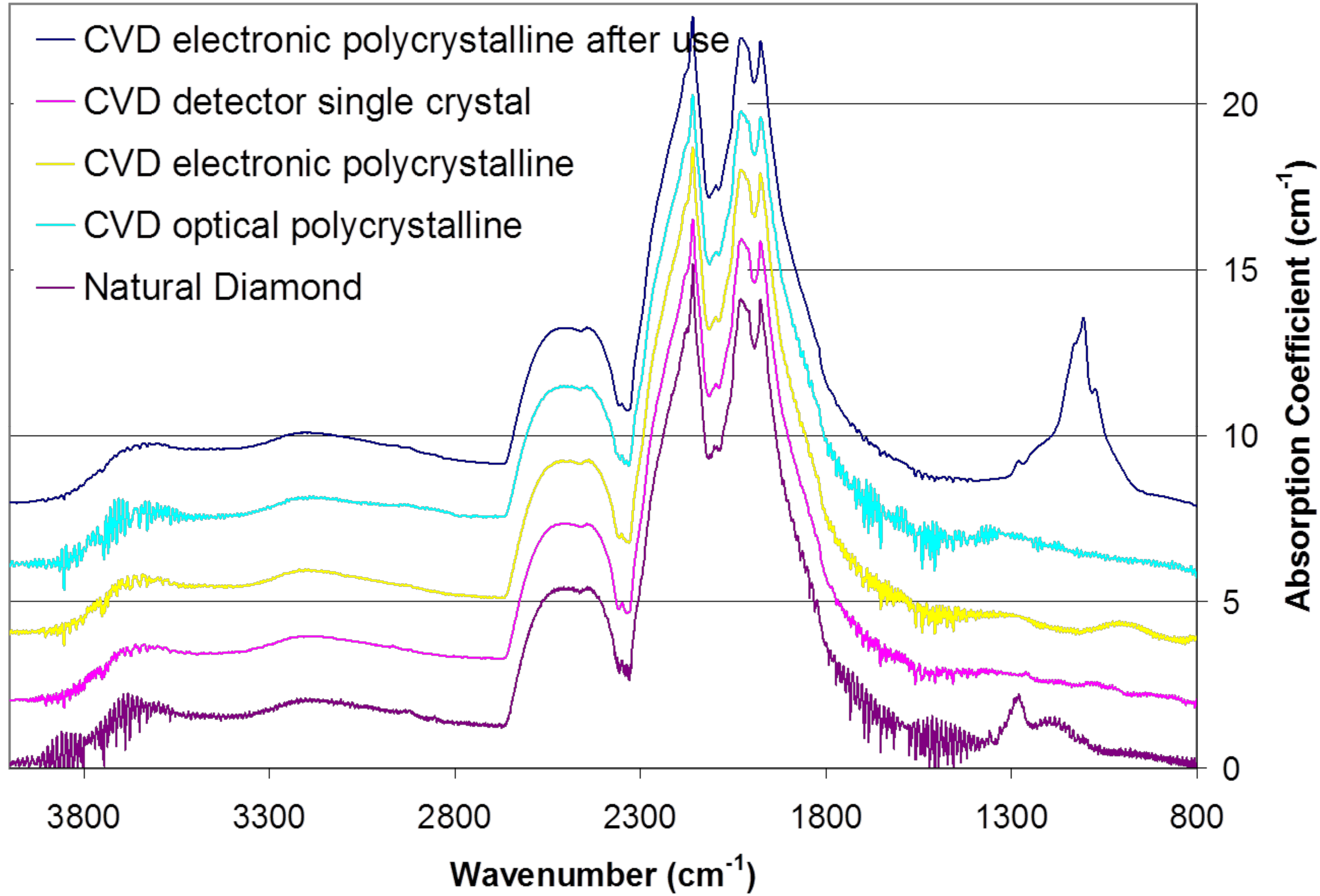



Normalized Amplitude
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
Time (ns)
X28C (non-PC)
APS 11-ID-D (PC)
APS 11-ID-D (non-PC)

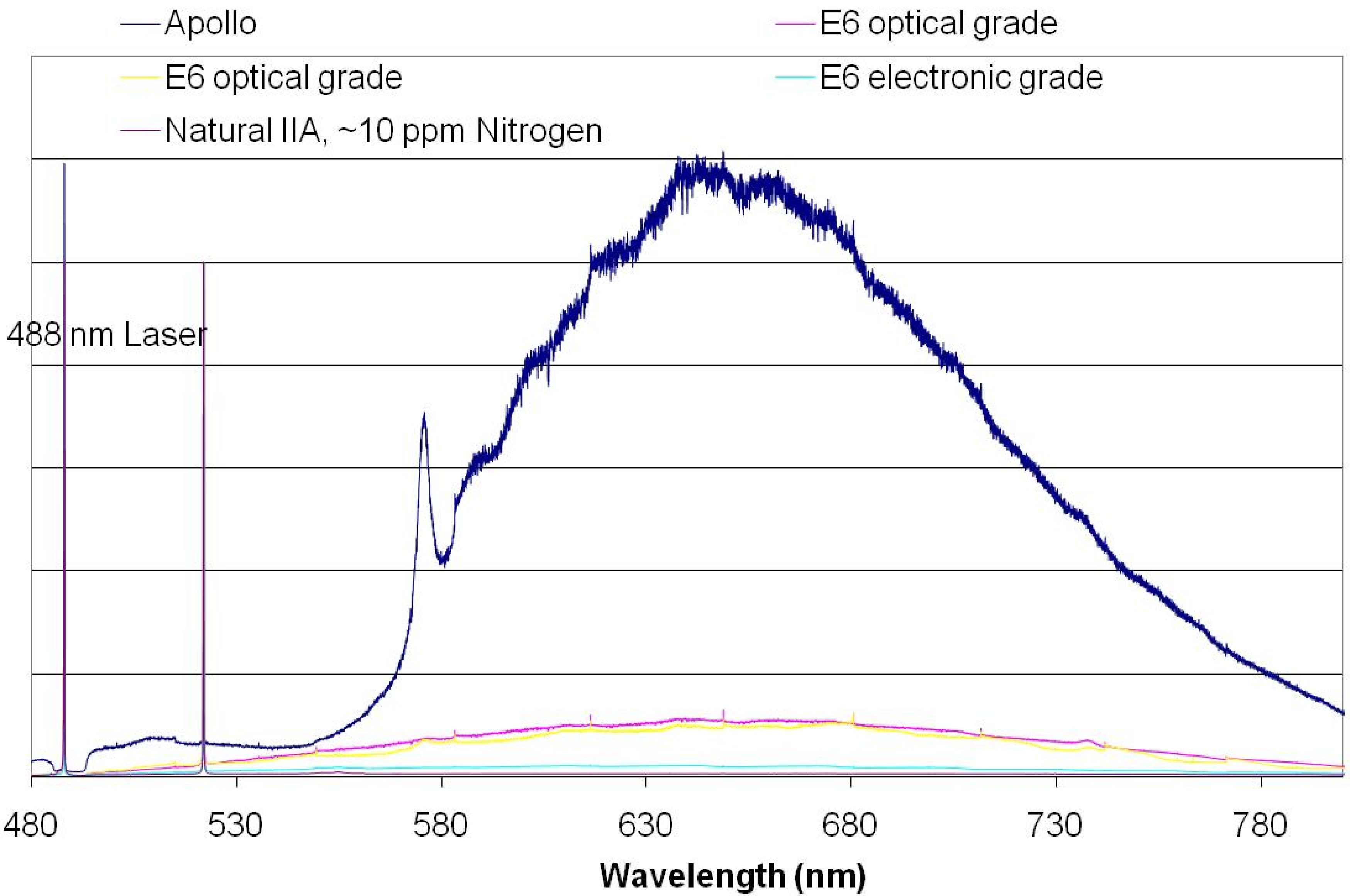
Temporal response, Soft X-rays



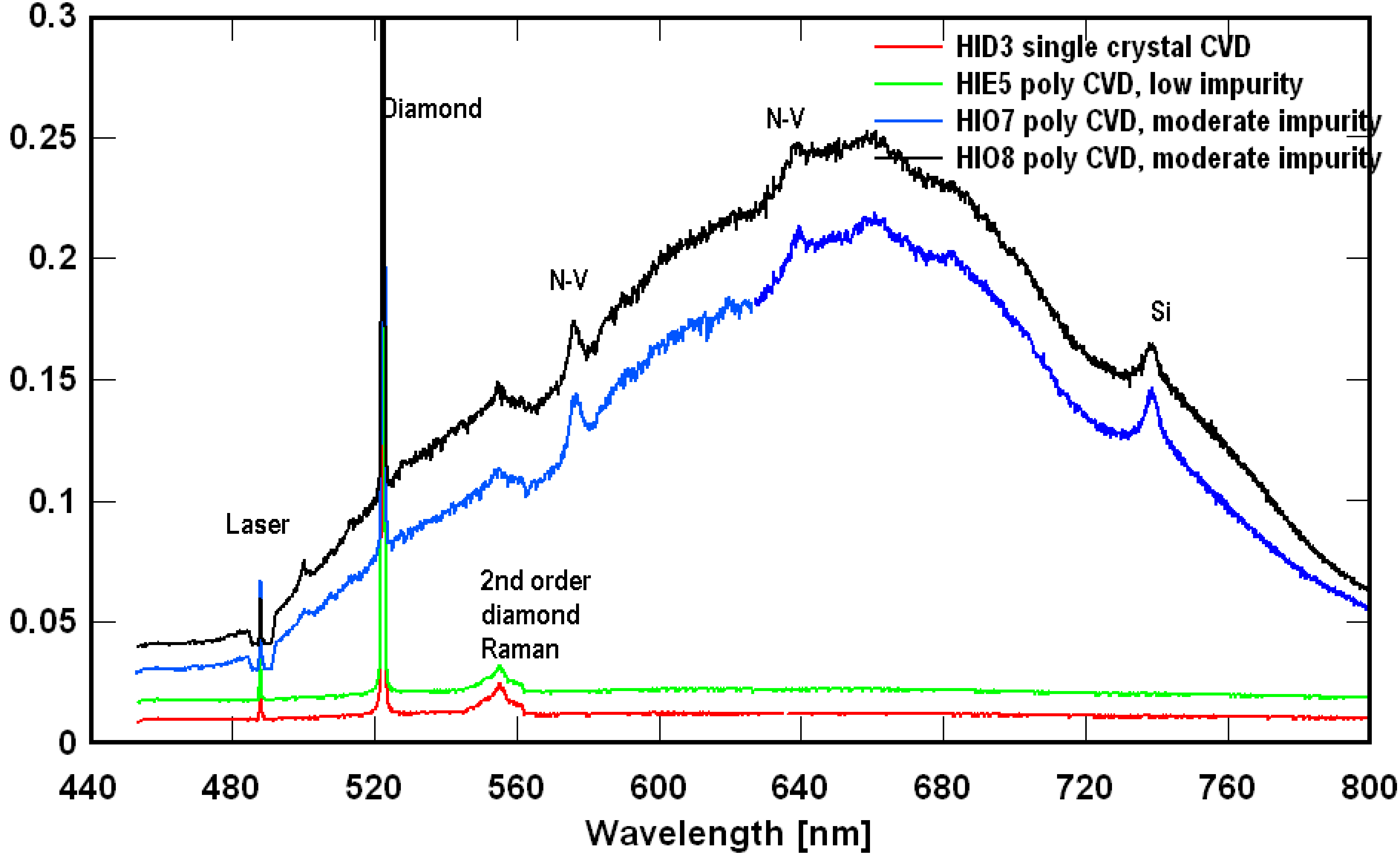
IR Spectroscopy (FTIR)



Photoluminescence

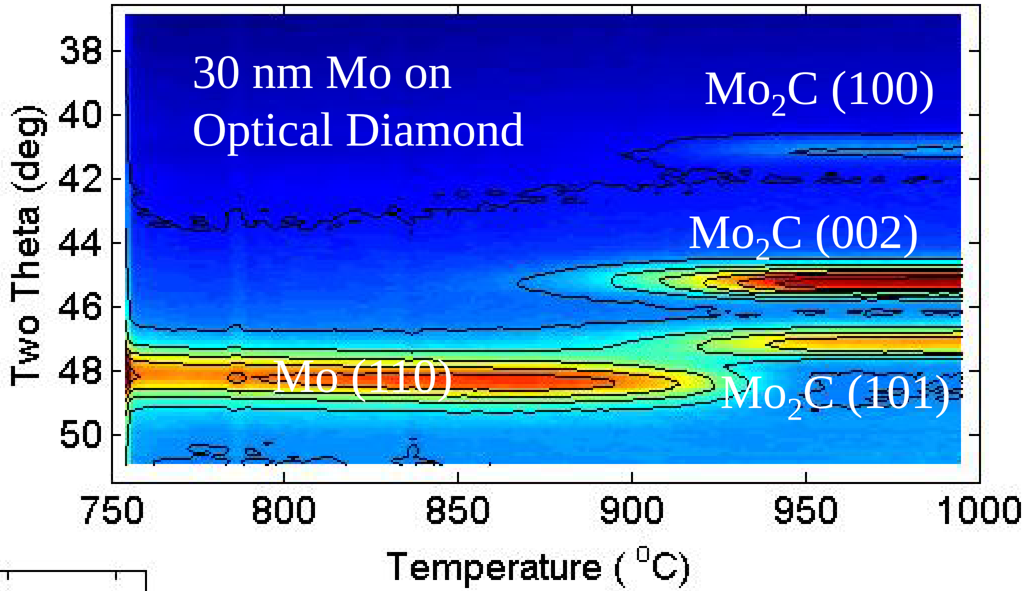


U2A

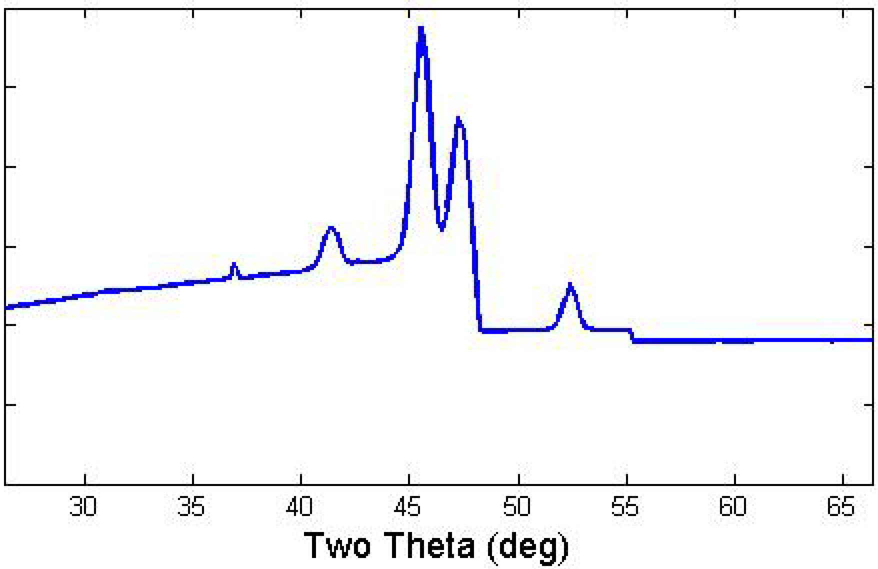


HID3 single crystal CVD
HIE5 poly CVD, low impurity
HIO7 poly CVD, moderate impurity
HIO8 poly CVD, moderate impurity
Diamond
N-V
N-V
Si
Laser
2nd order diamond Raman
0.3
0.25
0.2
0.15
0.1
0.05
0
440
480
520
560
600
640
680
720
760
800
Wavelength [nm]

Metallization & Carbide Formation



Investigate carbide forming metals (Ti, Nb Mo) via in-situ XRD



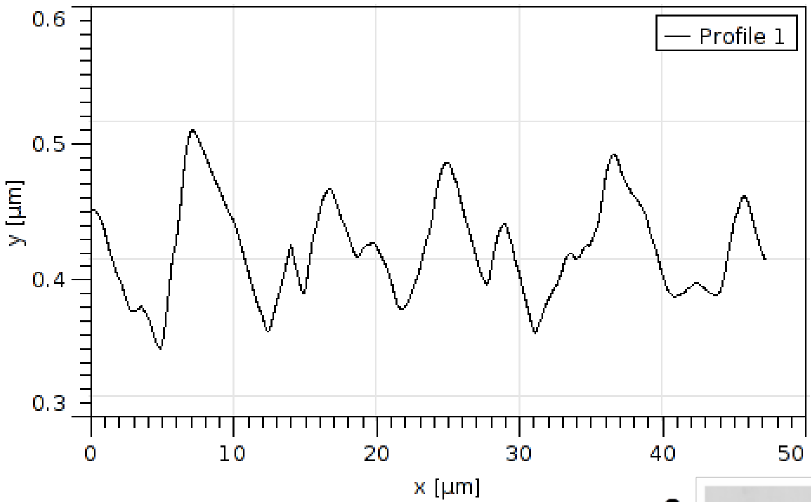
Molybdenum is attractive
- avoid capping Pt layer

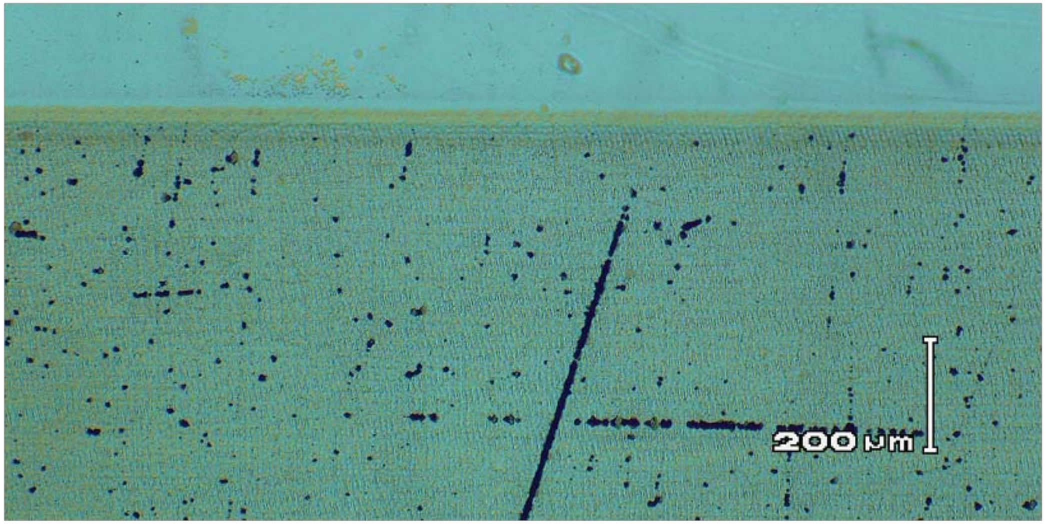
J. Appl. Phy. **99** 063740
J. Appl. Phy. **101** 053714

Diamond Thinning and Shaping

Laser Ablation

- Fast* (up to 0.3µm/s)
- Easy to Pattern

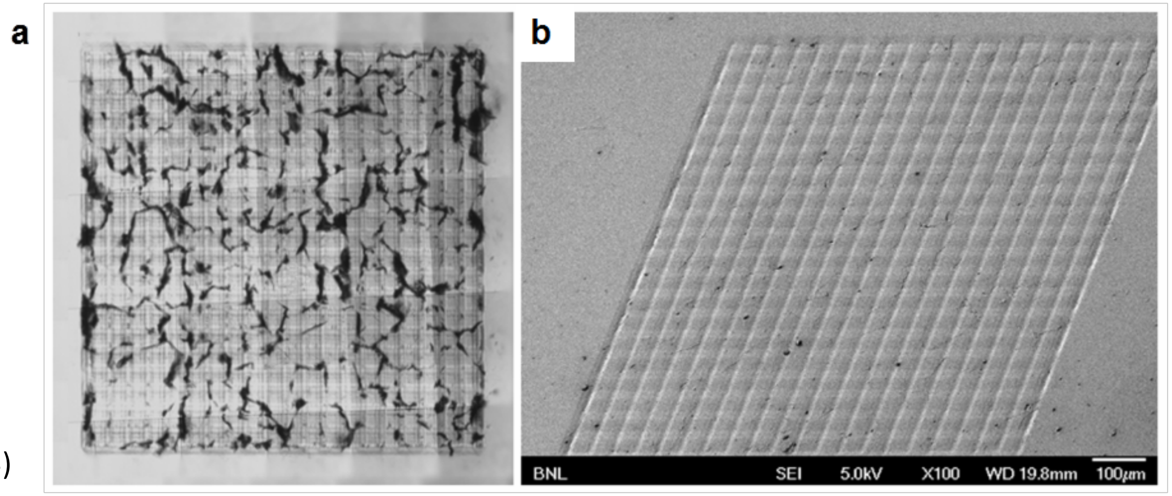




266nm, FWHM = 27µm, 30ps, 100 µJ, 10Hz
10µm interleaved raster, SC diamond, 2µm depth

But

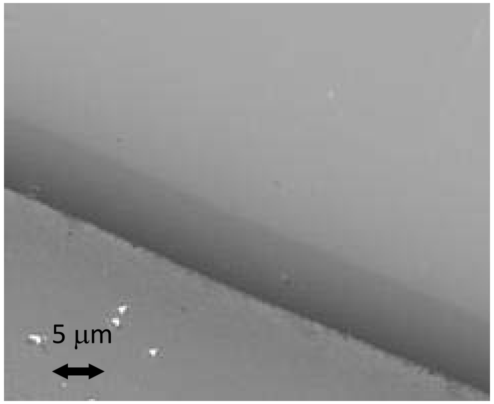
- Induces strain
- Non-diamond C

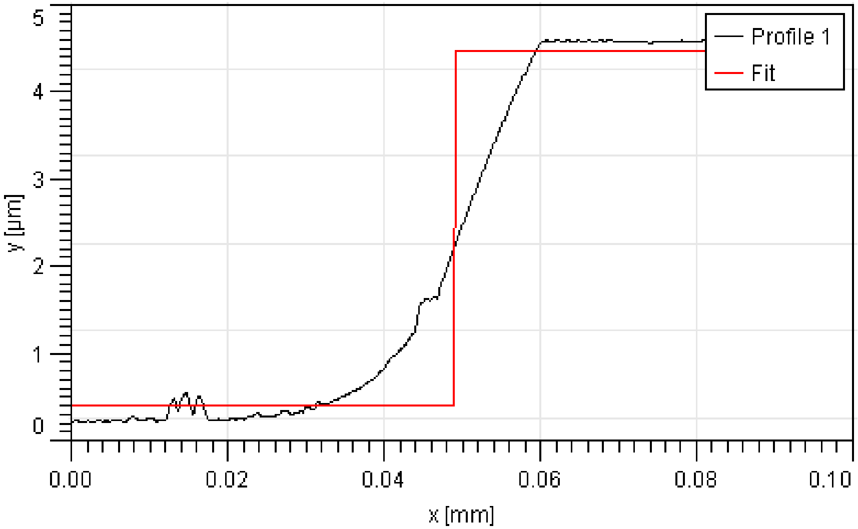


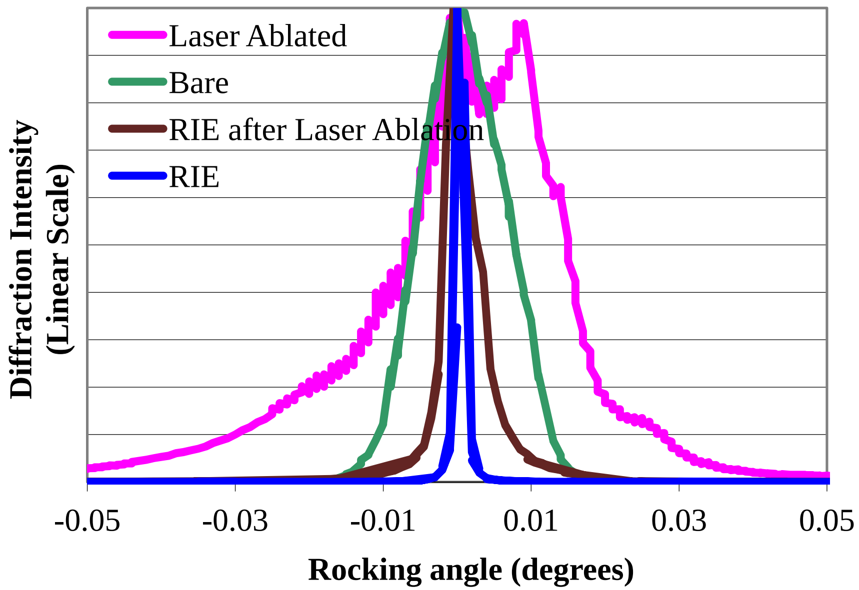
*George T., et al, Appl. Phys Lett. **62**, 2880 (1993)

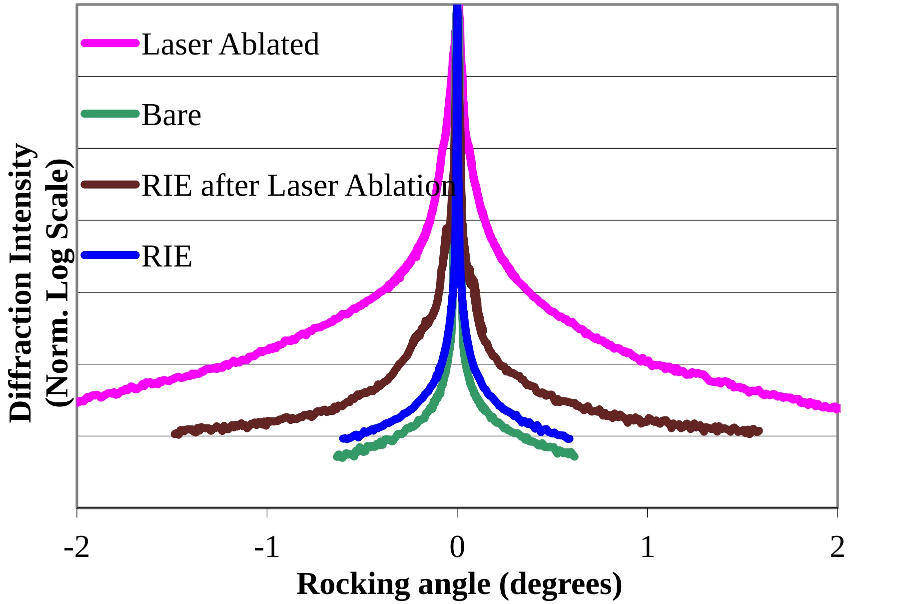
Reactive Ion Etching

ICP RIE
50 sccm O_2/ 8sccm Ar
850W P_{ICP}, 15W of P_{RF}
65–80nm/min.
Removes Strain Layer

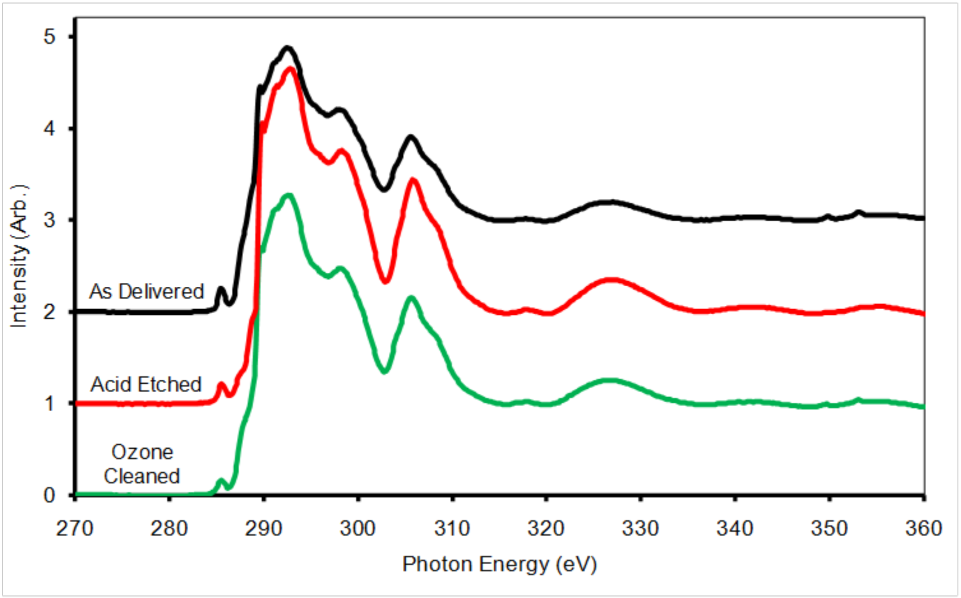






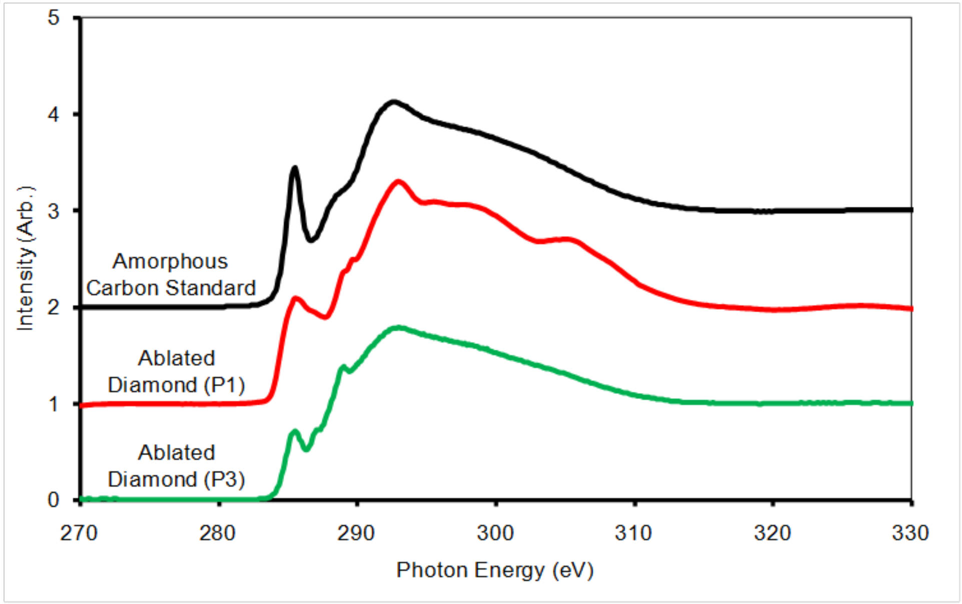


Non Diamond Carbon



Carbon edge NEXAFS shows small NDC contaminant on the surface of the diamonds, easily removed with acid etching or ozone cleaning

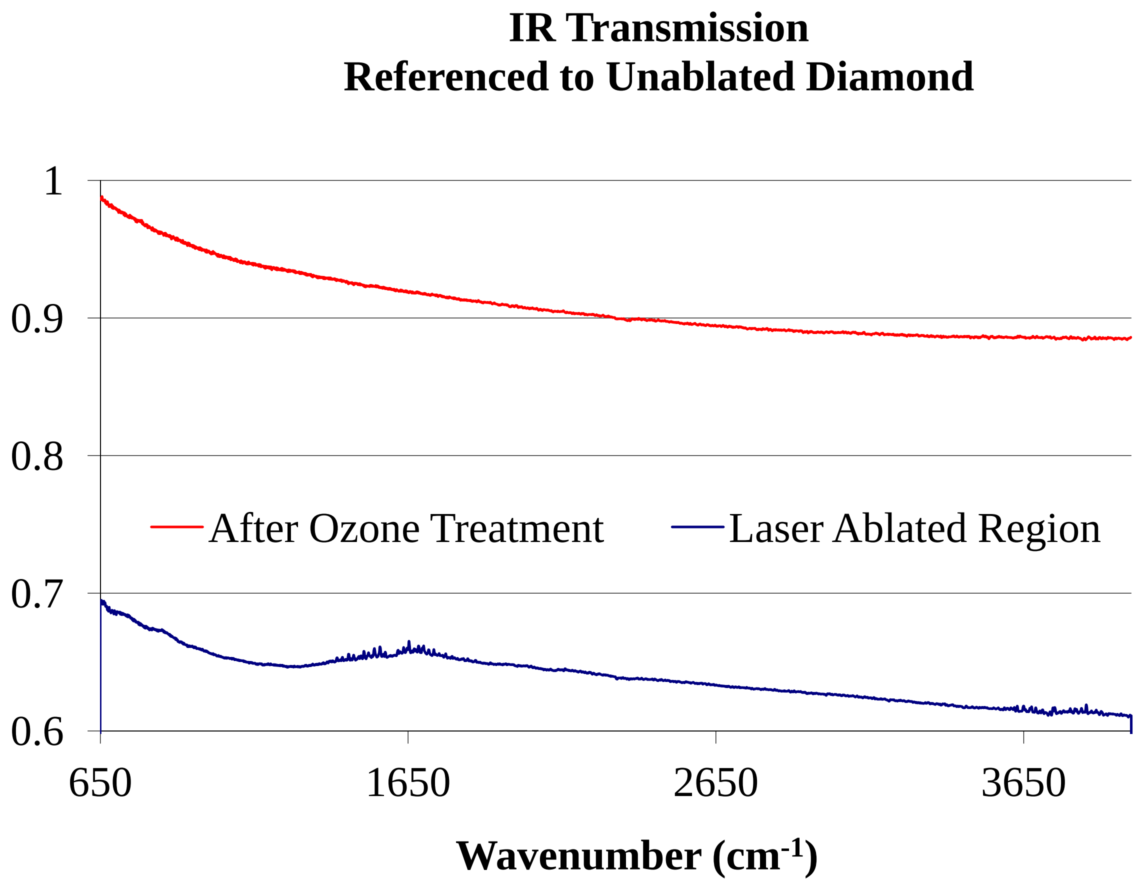
After laser ablation, the surface is entirely amorphous carbon

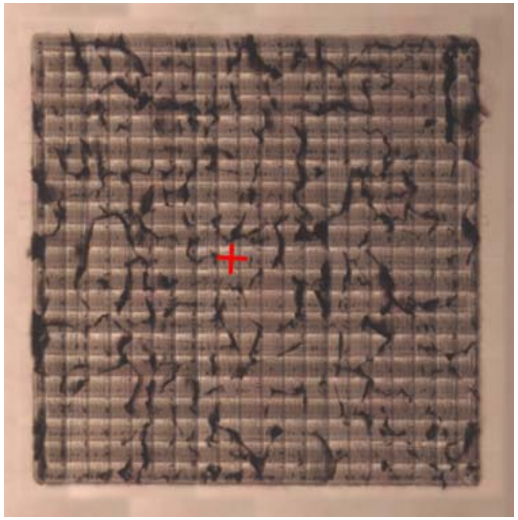


U7A

Ozone Cleaning

6 hrs of exposure to UV lamp in air reduced non-diamond carbon thickness by at least x4





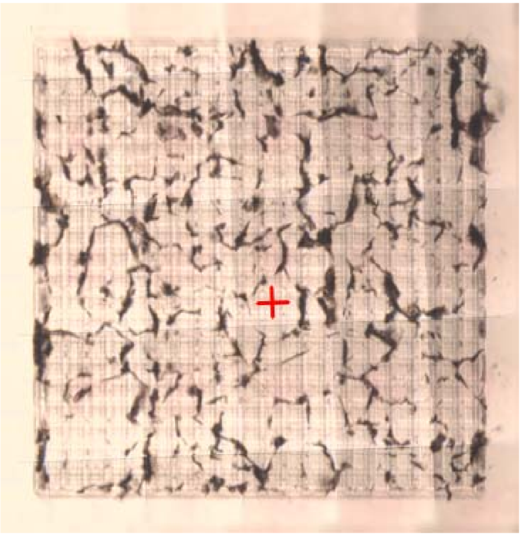
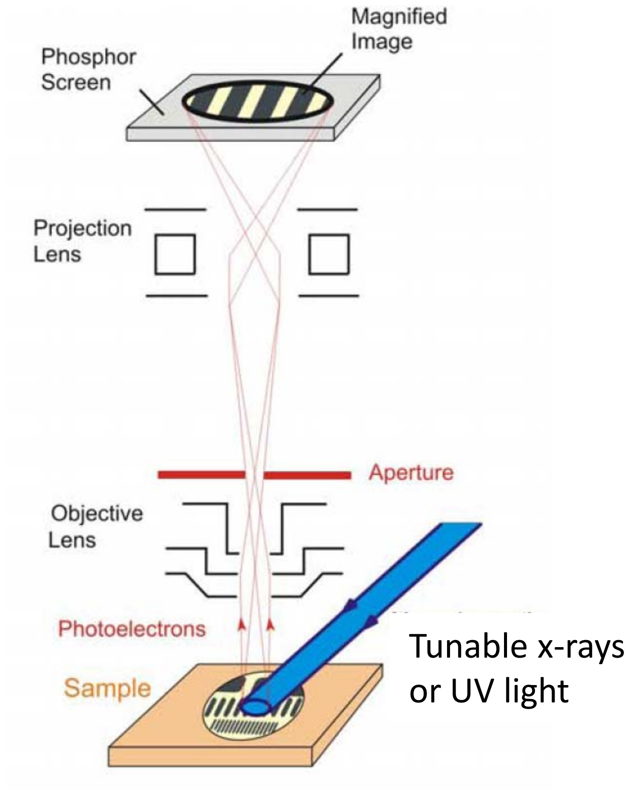
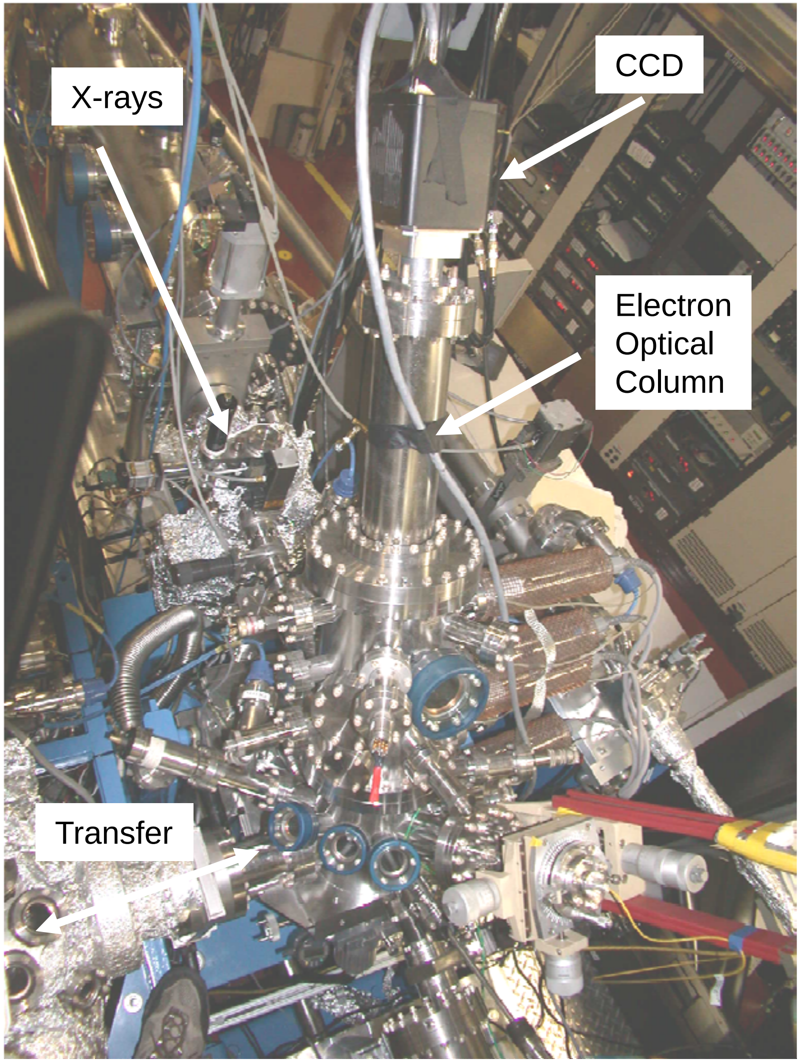


Photo-Emission Electron Microscopy





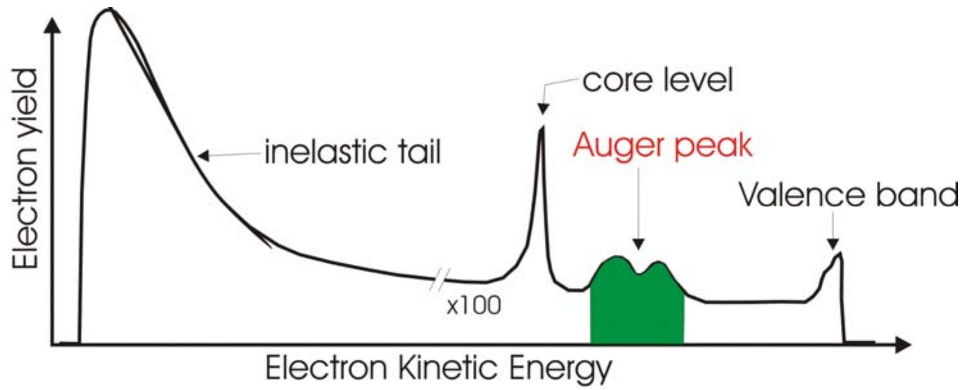
- Full field imaging of electrons (ie. parallel detection)

- Real time

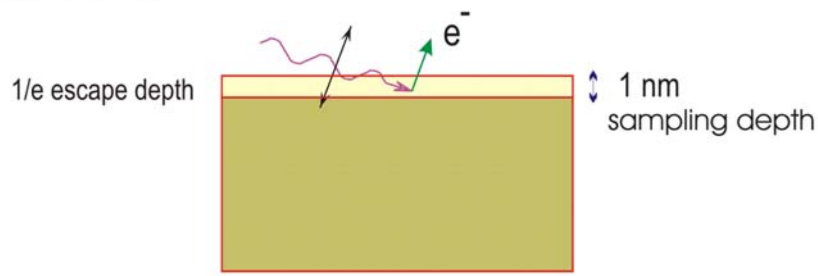
- UV or tunable synchrotron x-rays

- < 5 nm (UV) and 25 nm (x-ray) resolution

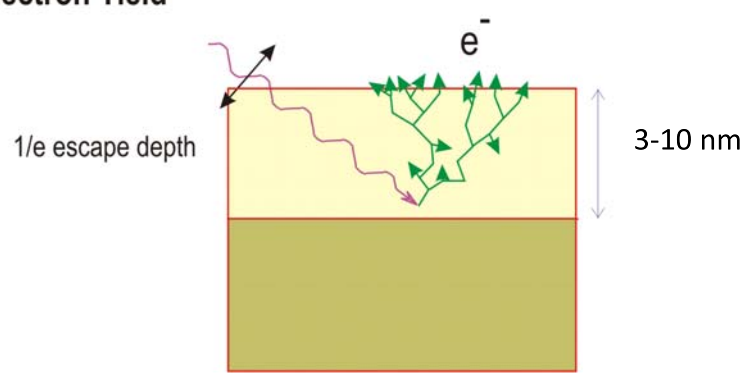
Electron Yield Sampling Depth



Auger Electron Yield



Total Electron Yield



UV Photo-Emission Electron Microscopy

266 nm image of LCLS copper cathode, 30 x 30 microns

-UV imaging

- work function contrast
- < 10 nm resolution

- variable energy

- measure of yield (energy)
- extract local work function

- User facilities make things much easier!
  - Synchrotrons for x-ray science
  - Nanocenters for surface science
- Using them is easy, and generally free
- Best of all, you get access to materials experts to help you with your experiments