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$_2$Te, Cs$_3$Sb, CsK$_2$Sb)
  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
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**
- **LEED**
  - Low Energy Electron Diffraction
  - Diamond crystal quality, localization and identification of defects

## 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

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

 photon source

energy analyser

hv

e-

sample

UHV - Ultra High Vacuum (p < 10^{-7} mbar)
Laser ARPES
Boron Doped Diamond, H Terminated, [001]

Used 6 eV photons – below direct transition band gap
(synchrotron ARPES gives direct PE behavior- no thermoilization)
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

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

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
Temporal response, Soft X-rays

![Graph showing temporal response, Soft X-rays with voltage (V) on the y-axis and time (ns) on the x-axis. Three curves represent different field strengths: 0.8 MV/m (black), 0.4 MV/m (green), and 0.3 MV/m (blue).]
IR Spectroscopy (FTIR)

- CVD electronic polycrystalline after use
- CVD detector single crystal
- CVD electronic polycrystalline
- CVD optical polycrystalline
- Natural Diamond

Absorption Coefficient (cm⁻¹)

Wavenumber (cm⁻¹)

3800 3300 2800 2300 1800 1300 800
Photoluminescence

- Apollo
- E6 optical grade
- E6 optical grade
- E6 electronic grade
- Natural IIA, ~10 ppm Nitrogen

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
ICP RIE
50 sccm O₂/ 8 sccm Ar
850W P_{ICP}, 15W of P_{RF}
65–80 nm/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.
Ozone Cleaning

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

IR Transmission
Referenced to Unablated Diamond

![Graph showing IR Transmission](image)

- Red line: After Ozone Treatment
- Blue line: Laser Ablated Region
Photo-Emission Electron Microscopy

- Full field imaging of electrons (i.e., 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

3-10 nm
UV Photo-Emission Electron Microscopy

- UV imaging
  - work function contrast
  - < 10 nm resolution
- variable energy
  - measure of yield (energy)
  - extract local work function

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