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Putting Synchrotron Radiation to Work for Technology: Analytic Methods

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Putting Synchrotron Radiation to Work for Technology: Analytic Methods

Report of the Workshop
at
Lawrence Berkeley Laboratory
January 17, 1992

Organized by:

A.S. Schlachter, Lawrence Berkeley Laboratory
and
J. Stöhr, IBM Almaden Research Center

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

February 1992

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PUTTING SYNCHROTRON RADIATION TO WORK FOR TECHNOLOGY: ANALYTIC METHODS

Friday, January 17, 1992, Bldg. 2 – Room 100B
Lawrence Berkeley Laboratory

8:00 – 8:30 A.M.	Registration: Bldg. 2, lobby	

Session Chair: Jo Stöhr

8:30 – 8:35	Welcome	Jay Marx Director, ALS
8:35 – 9:00	Introduction to the ALS	Fred Schlachter Scientific Program Coordinator, ALS
9:00 – 9:50	Ultra-ESCA: Advanced Capabilities of XPS with High-Brightness Synchrotron Radiation	Brian Tonner University of Wisconsin
9:50 – 10:40	High-Resolution (20 nm) XPS and XANES with the ALS	Harald Ade SUNY/Stony Brook
10:40 – 11:00	BREAK	
11:00 – 11:50	Photoelectron Spectroscopy in Industry: Current Capabilities, Needs, and Possible Roles for the ALS	Mike Kelly Stanford University
11:50 – 12:30 P.M.	TOUR of the ALS	Alan Jackson Deputy Project Director, ALS
12:30 - 1:40	LUNCH: Bldg. 6, lobby	

Session Chair: Fred Schlachter

1:40 – 2:30	Materials Analysis by Photoemission: Is This Practical at ALS?	Richard Brundle IBM/Alamaden
2:30 - 3:20	Applications of Long-Wavelength X-Ray Fluorescence Spectrometry and X-Ray Powder Diffractometry	Ron Jenkins International Center for Diffraction Data, Swathmore, PA
3:20 - 3:40	BREAK	
3:40 - 4:00	Industry and Industrial Participation at LBL	Mark Alper Associate Division Director–Material Science Division, LBL Rick Inada Acting Director–Sponsored Projects, LBL
4:00 - 5:00	Round-Table Discussion	
5:00 - 6:00	RECEPTION: Bldg. 2, lobby	

PUTTING SYNCHROTRON RADIATION TO WORK FOR TECHNOLOGY: ANALYTIC METHODS
January 17, 1992

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January 17, 1992

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Preface

An Advanced Light Source (ALS) workshop titled "Putting Synchrotron Radiation to Work for Technology: Analytic Methods" was held at the Lawrence Berkeley Laboratory on January 17, 1992. The ALS will be the world's brightest synchrotron-radiation source of soft x-ray and ultraviolet (XUV) radiation when it begins serving the industrial, academic, and government research and development communities in the spring of 1993. The purpose of the workshop was to reach out to the industrial research community and to determine the most effective way to make the advanced research capabilities of the ALS available to members of that community who require enhanced materials-analysis capabilities above and beyond those provided by commercially available instrumentation.

Fred Schlachter (Lawrence Berkeley Laboratory) opened the workshop with an overview of the ALS and the research opportunities associated with it. The prime beneficiaries of high-brightness XUV radiation will include those who can make use of, either singly or in combination

- high spectral resolution
- high spatial resolution
- the ability to probe nondestructively with depth below sample surfaces.

X-ray photoelectron spectroscopy (XPS) is the experimental technique most suited to exploit the unique characteristics of the ALS in the context of materials analysis, in part because of its traditional chemical-state specificity, as reflected in the well-known alternate name electron spectroscopy for chemical analysis or ESCA. XPS was, therefore, the focus of attention for most of the workshop. Mike Kelly (Stanford University) provided a solid foundation for subsequent discussion with his summary of the capabilities and limitations of state-of-the-art commercial XPS instrumentation for the laboratory. Kelly also included examples of industrial uses of XPS ranging from urgent troubleshooting (about 50% of applications), to routine monitoring of production processes (about 30% of applications), to long-term R&D (about 20% of applications). He concluded by looking forward to areas of opportunity for the ALS and by pointing out the importance of economics. The information gained by materials analysis must be worth the cost of obtaining it. For example, it may be less expensive to throw out a plating bath than to determine what is contaminating the bath and understand how the contaminants got there. The ability to sample small areas 1 micron or less in diameter represents an opportunity for the ALS. The minimum spot size for commercial "small spot" XPS instrumentation is now about 20 microns.

Deciding when to use synchrotron radiation is not always easy. The effort of traveling to a synchrotron radiation source must be balanced against the benefits of continuous photon-energy tunability, high brightness, high spectral resolution, and small spot size. Brian Tonner (University of Wisconsin) guided those attending the workshop through some of these features and provided some quantitative comparisons of count rates from laboratory instruments and synchrotron sources. Major benefits of photon-energy tunability include increasing elemental sensitivity and enhancing or reducing surface sensitivity, as appropriate. Specific elements or even chemical states can be selected by tuning the photon energy to the appropriate spectral features. In general, sensitivity is also improved by operating at low photon energies where photoionization cross sections are the highest. On the quantitative side, with the ALS, it is possible to achieve megahertz count rates from illuminated spots only 50 microns in diameter while maintaining a spectral resolution of 10,000 (10 meV at 100 eV).

One of the frontiers of XPS is achieving spatial resolution far beyond that suggested by a spot 50 microns in diameter. Spatially resolved XPS is sometime called spectromicroscopy or spectroscopic imaging. Maps of chemically specific spectral features of inhomogeneous surfaces can be made with a spatial resolution eventually approaching 200 Å. Spectroscopic imaging techniques fall into two broad categories: direct imaging and scanning. Harald Ade (SUNY-Stony Brook) provided an overview of spectroscopic imaging techniques. In direct imaging, electron optics or a strong solenoidal magnetic field are used to collect photoelectrons and to preserve their spatial relationship on the way to an area detector. For scanning, it is necessary to focus the x-rays to a small spot, which is rastered across the sample (in practice, the sample is moved through the spot) to generate the image. There are several methods of focusing the x-rays with somewhat complementary strengths and weaknesses. An electron-energy analyzer gives chemical-state specificity because the image contains only electrons with kinetic energies corresponding to a specific spectral feature, such as a chemically-shifted peak. Omitting the energy analyzer and collecting all the photoelectrons while scanning the photon energy yields spatially resolved x-ray absorption spectroscopy. The ALS will be equipped with instruments of both types.

Ron Jenkins (International Center for Diffraction Data) departed from the XPS theme of the workshop in his presentation on long-wavelength x-ray fluorescence analysis by means of wavelength-dispersive and energy-dispersive spectrometers. In fluorescence analysis, as the atomic number of the element to be analyzed decreases, the energy of the fluorescence photons also drops. At low photon energies, however, decreasing fluorescent yield, increasing absorption by window materials, and increasing absorption by the specimen work together to reduce the detection sensitivity. The high flux of a synchrotron source counteracts this discouraging trend by dramatically raising the signal and hence the sensitivity. Jenkins also described the considerable interest in long-wavelength powder diffraction of materials with large d-spacings, such as organic materials with characteristic spacings of about 10 Å. At high photon-energies, the peaks in a powder pattern for such a material are compressed into a narrow range at a low angle, making them difficult to resolve. At low photon energies, readily available at high intensities with a synchrotron source, the same peaks occur over a wider angular range at a higher angle.

Given the limitations of commercial laboratory instrumentation for XPS and the advantages of synchrotron radiation, it remained for Richard Brundle (IBM Almaden Research Center) to examine the question: "Materials Analysis by Photoemission: Is it Practical at the ALS?" The focus was on "real world" problems presented to the materials analyst on a daily basis, as opposed to R&D projects. What is present, how much is present, and how is it distributed are questions to be answered for a wide range of materials in a variety of physical forms. To justify the use of synchrotron radiation, it is necessary to demonstrate that the information required is not obtainable with laboratory instrumentation or else is not obtainable in a practical way by XPS or some other analytical technique.

After identifying types of problems for which laboratory instrumentation is inadequate, Brundle opened the question of what a dedicated beamline at the ALS for materials analysis would include and how it would be administered. The roundtable discussion at the close of the day elicited considerable interest in an "ultra-ESCA" facility with a spot size of about 1-micron that would be accessible to industrial users on short notice and would be adequately staffed to provide support services. The means of financing and running an ultra-ESCA facility at the ALS are under consideration.

INTRODUCTION TO THE ADVANCED LIGHT SOURCE

The ALS will be the world's brightest synchrotron-radiation source in the extreme ultraviolet and soft x-ray regions of the spectrum when operation begins in fifteen months.

How can this facility serve as an analytic tool for industry?

Fred Schlachter
Scientific Program Coordinator
Advanced Light Source

THE ALS: OUTLINE OF TALK

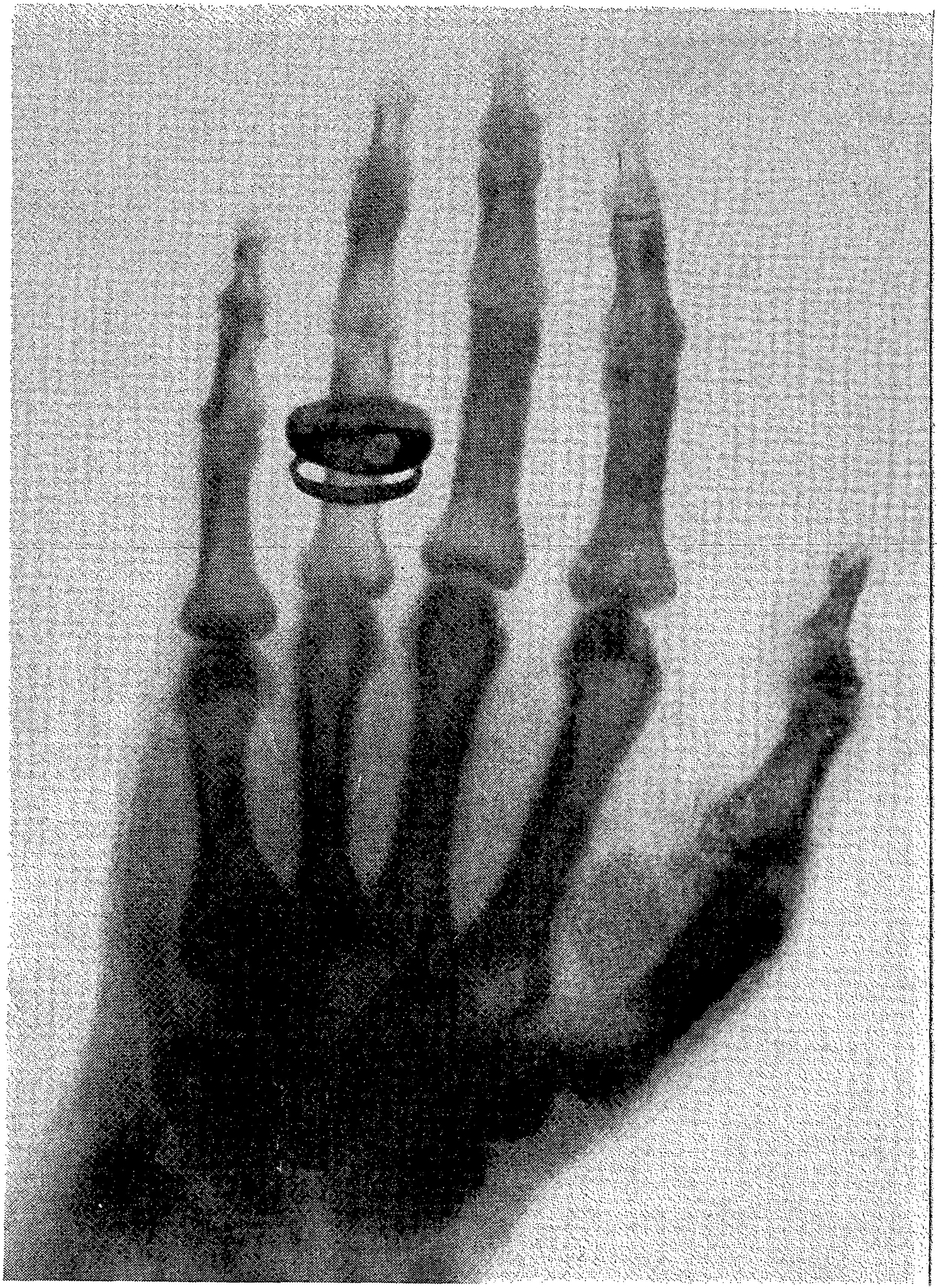
- X rays are a useful probe of matter
- The ALS is the first of a new generation of synchrotron radiation sources
- High brightness is the main feature of the ALS
- The ALS provides exciting new opportunities for research
- The ALS is progressing on schedule
- A diverse scientific program is in place
- The ALS will be user friendly

WORKSHOP ON ANALYTIC METHODS FOR TECHNOLOGY: PURPOSE

• Tell about:	opportunities and capabilities at the ALS
• Learn about:	current commercial capabilities
• Listen to:	needs of potential users in industry
• Discuss:	potential developments to meet these needs

X-RAYS ARE AN IMPORTANT PROBE OF MATTER

- Interact with electrons in atoms ⇒ element selectivity (e.g., K, L edges)
- Energy appropriate for inner shells of atoms
- Short wavelength ⇒ image small objects
- Absorption coefficient appropriate ⇒ penetrate matter
- Relatively easy to produce and detect
- Can be polarized (linear, circular)
- Variable (tunable) energy
- Short-pulse time structure



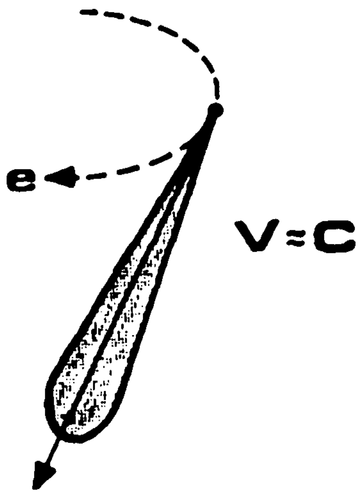
THE ADVANCED LIGHT SOURCE: OVERVIEW

ALS

- National user facility
- Provides UV and soft x-ray beams of unprecedented brightness: (<10eV to ~10 keV)
  - Broadly tunable with narrow spectral features (resolution 10,000)
  - Partially coherent (optics, interference)
  - 35 psec time structure (life times, time of flight)
  - Polarized (linear, circular)
- Utilized by researchers from industry, academic, and national laboratory communities:
  - Materials and surface science
  - Atomic and molecular physics
  - Chemistry
  - Life sciences
  - Technology

  overlap with spectral range of lasers
- Construction project began in late 1986
- Begin operations in spring 1993
- Construction cost – $99.5 million

RELATIVISTIC ELECTRON IN CIRCULAR ORBIT RADIATES SYNCHROTRON RADIATION (CONT.)



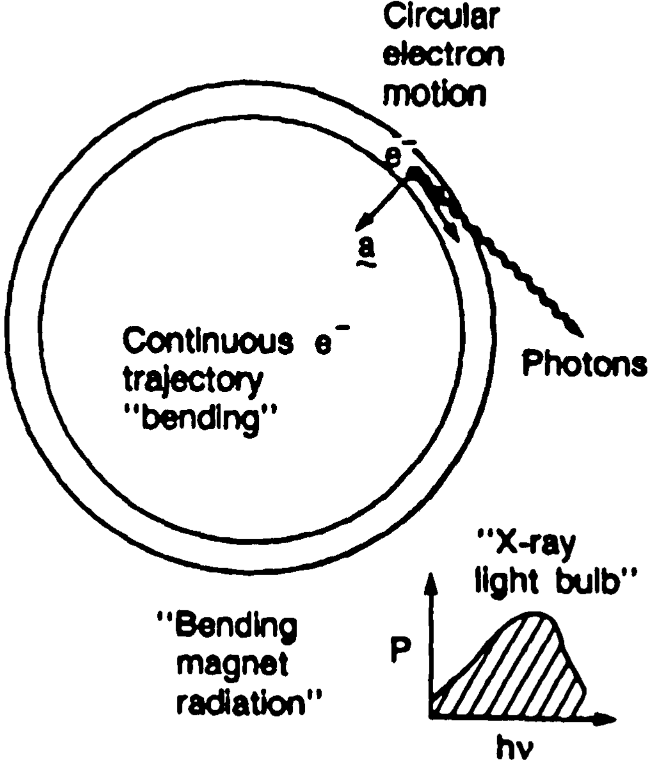
Relativistic angular distribution of the radiation emitted by an electron circulating at a speed close to the speed of light. Notice the concentration to a narrow angular range.

- For E = 1.5 GeV, $\gamma \sim 3000$

$$\frac{1}{\gamma} \sim \frac{1}{3000} \sim \frac{1}{3} \text{ mrad}$$

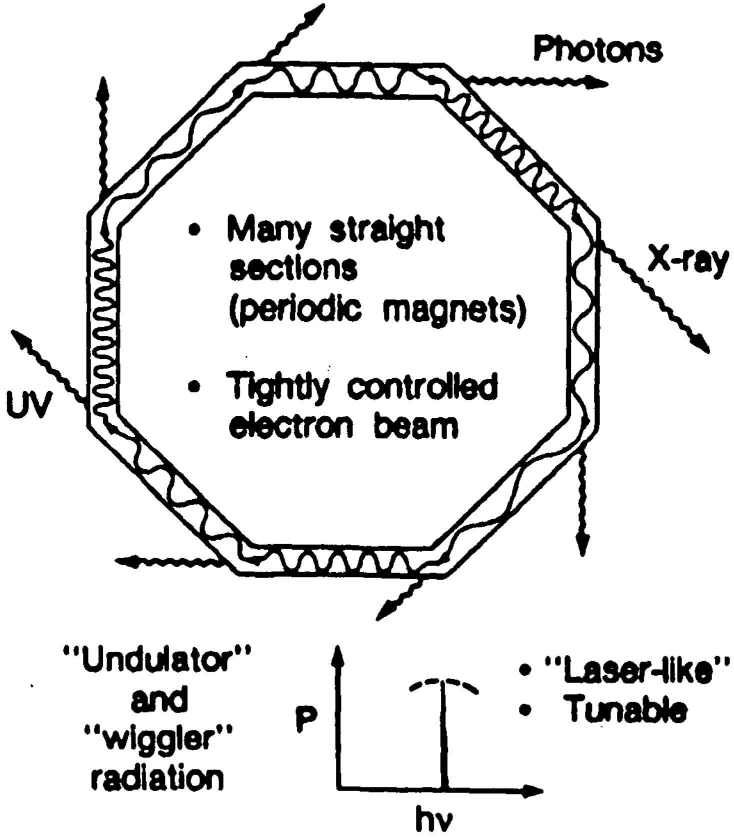
EVOLUTION OF SYNCHROTRON RADIATION

Today's Synchrotrons:



"Bending magnet radiation"

Tomorrow's Synchrotrons:



- Many straight sections (periodic magnets)
- Tightly controlled electron beam

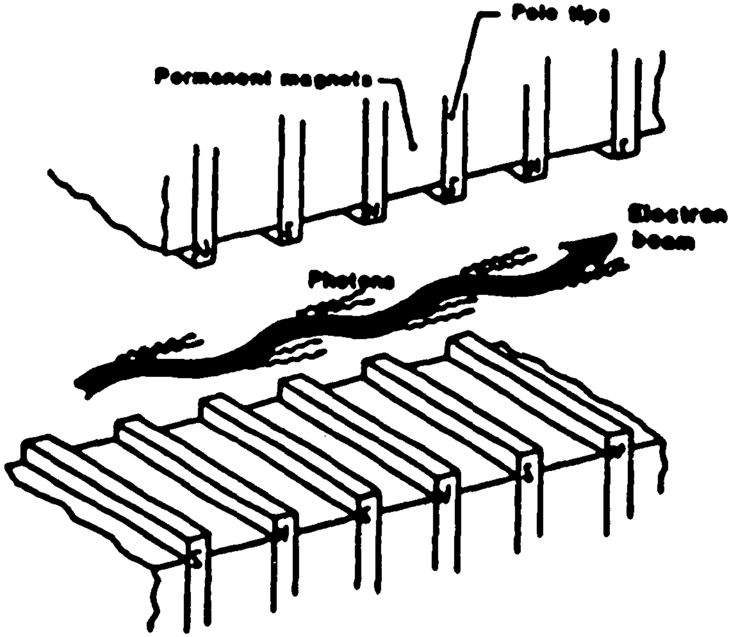
"Undulator" and "wiggler" radiation

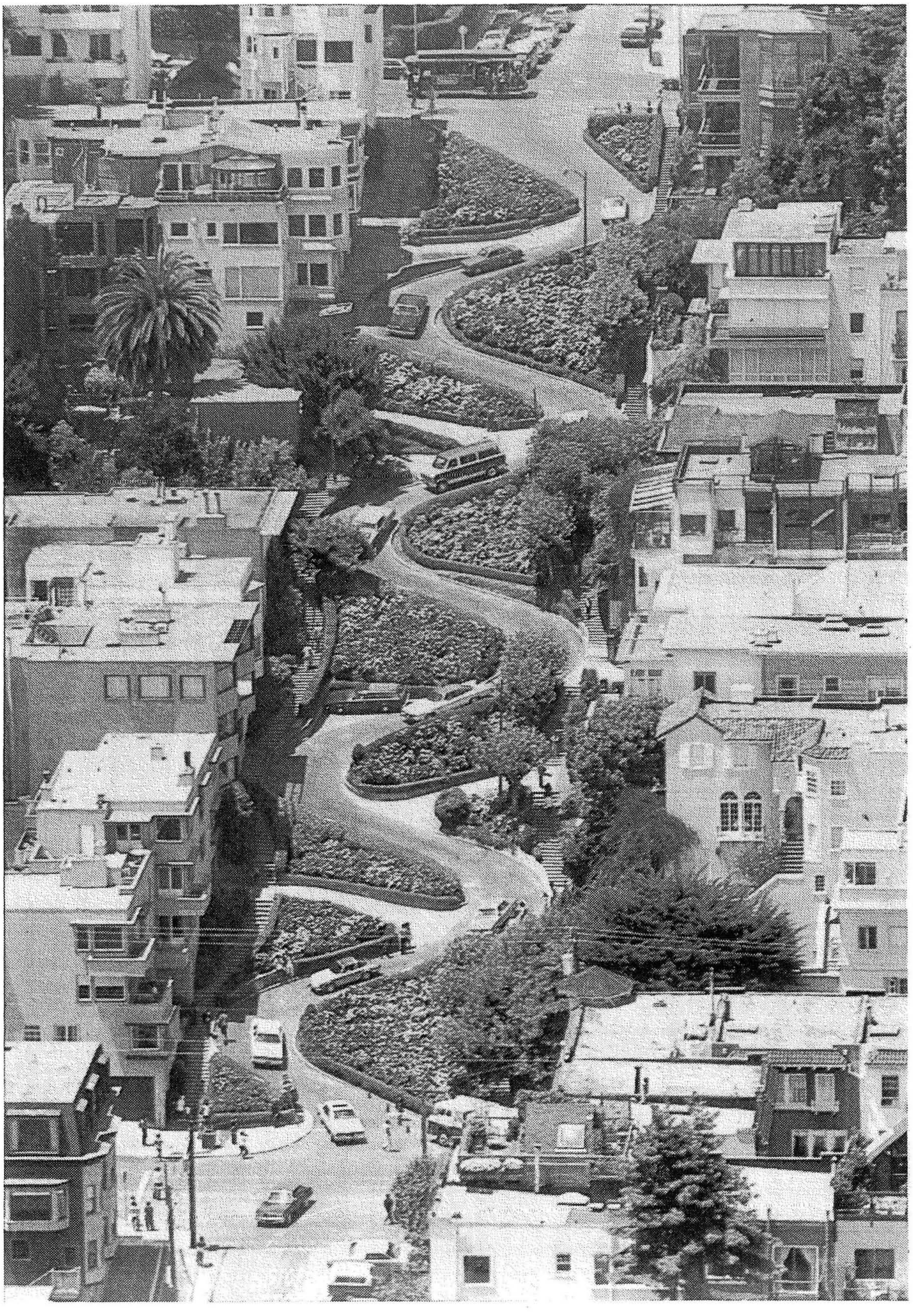
- "Laser-like"
- Tunable

XBL 888-8937

INSERTION DEVICES (UNDULATORS AND WIGGLERS) DRAMATICALLY IMPROVE X-RAY PRODUCTION

- **Periodic magnetic structure**
- **Usually array of alternating permanent magnets**





UNDULATORS AND WIGGLERS ENHANCE X-RAY PRODUCTION

- Both are periodic magnetic structure
- Radiation is emitted at each bend into angle $1/\gamma$

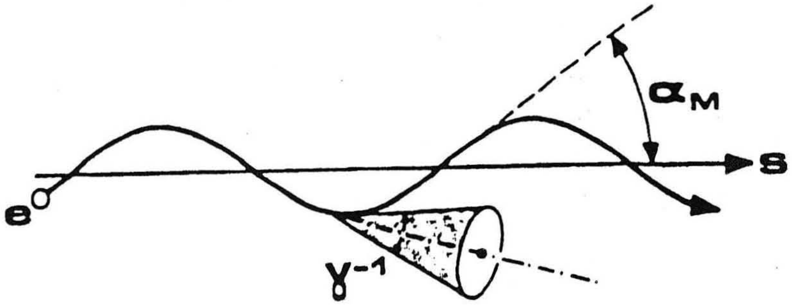
(1/γ ~ 1/3 milliradian for 1.5 GeV electrons)

- Wiggler produces high flux:

— Electrons deflected through large angles ($\alpha > 1/\gamma$, or $K > 1$)
— Incoherent superposition of radiation
— Like a collection of bend magnets

- Undulator produces high brightness:

— Electrons deflected through small angles ($\alpha < 1/\gamma$, or $K < 1$)
— Coherent superposition of radiation leads to interference
— Produces small spot of nearly monochromatic radiation



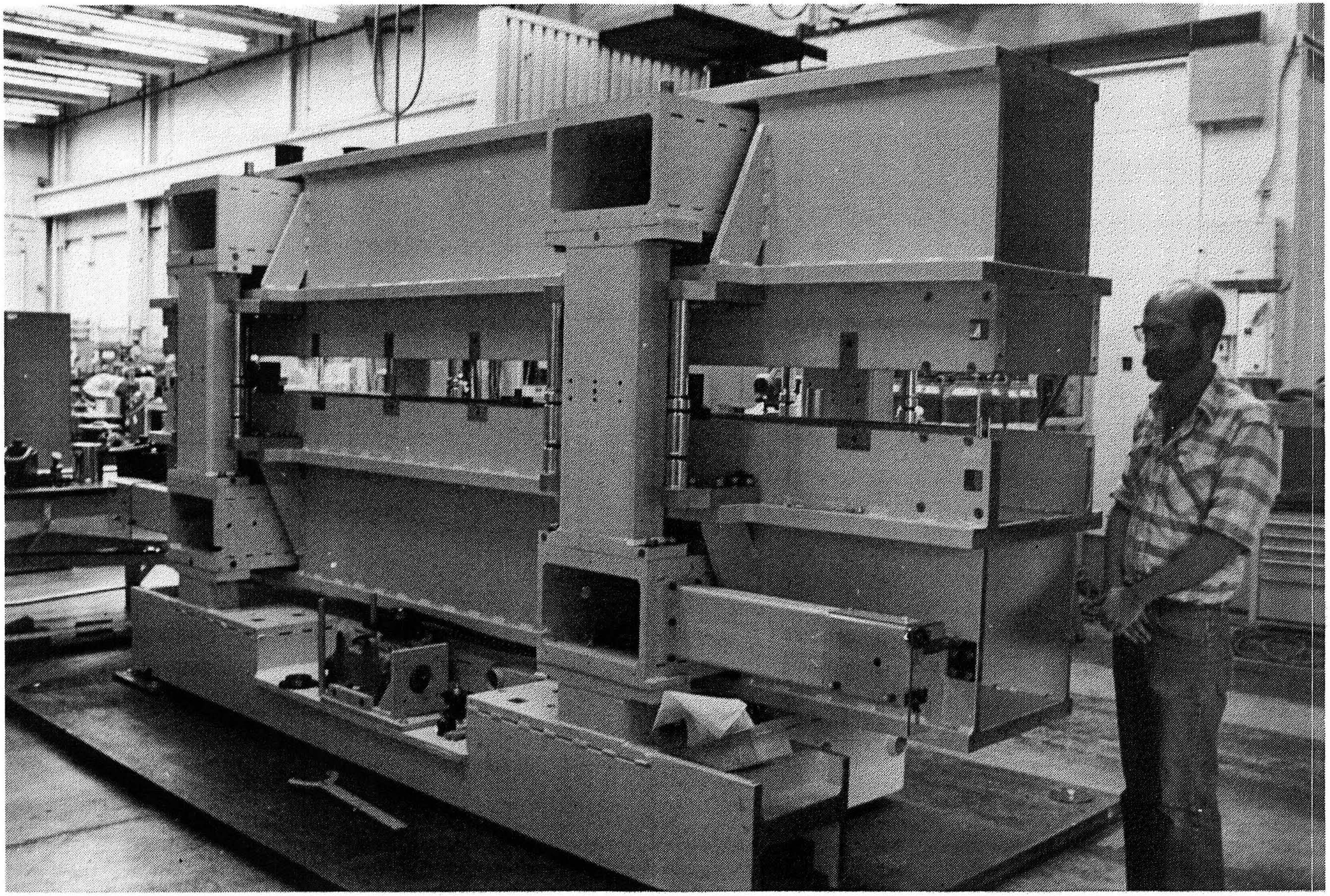
AN UNDULATOR PRODUCES A VERY BRIGHT BEAM OF VUV OR X RAYS

- Coherent superposition of radiation from electrons bent many times in periodic permanent-magnet structure

- Properties of undulator radiation:

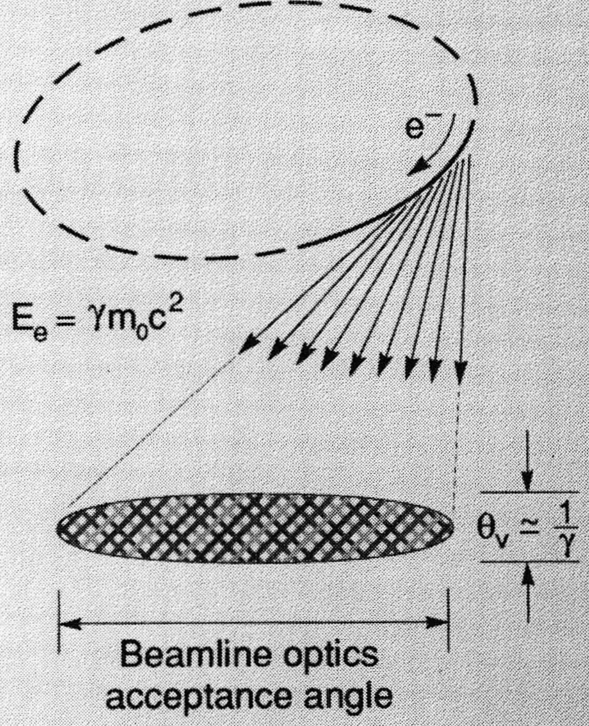
  — High brightness
  — Tunable photon energy
  — Partial coherence
  — High linear polarization
  — Picosecond time structure

An undulator is a tunable soft-x-ray picosecond strobe light with laser-like properties

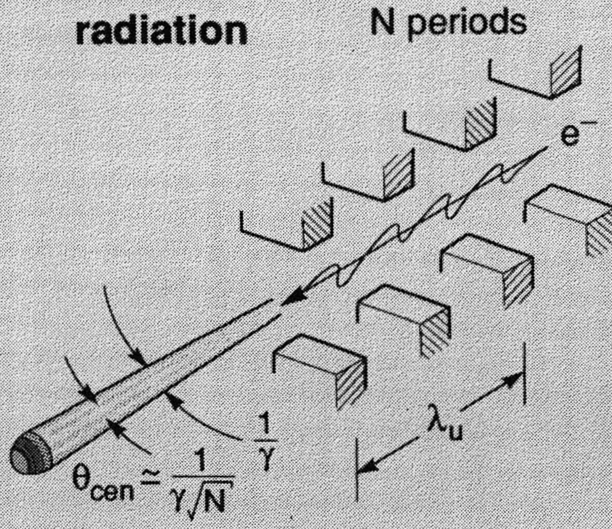


The ALS Has Both Undulators and Bending Magnets

Bending magnet radiation (sweeping searchlight)



Undulator radiation



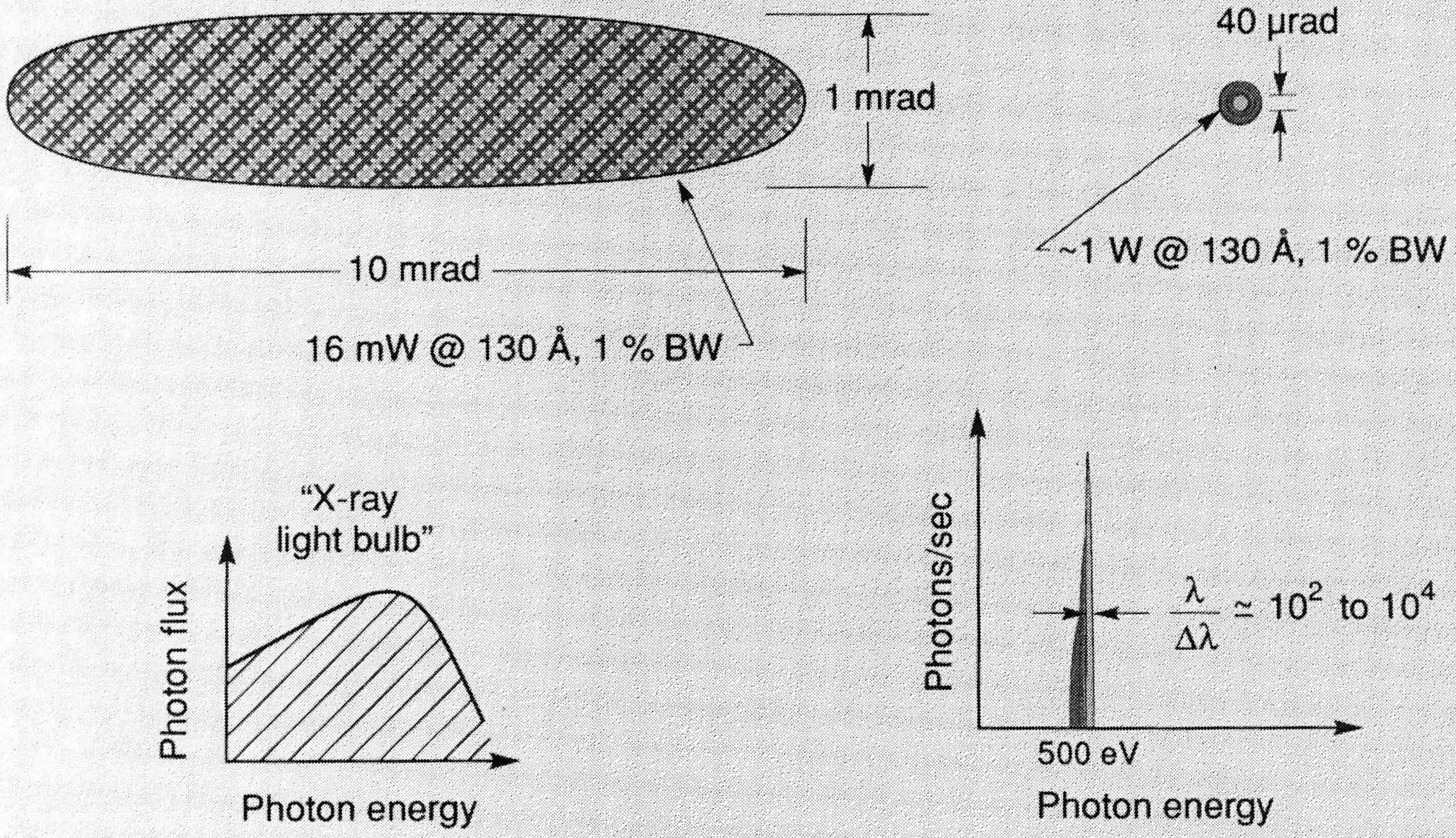
$$\lambda_x = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right)$$

in the central radiation cone:

$$\frac{\Delta\omega}{\omega} \simeq \frac{1}{N}$$

$$\theta_{cen} \simeq \frac{1}{\gamma\sqrt{N}}$$

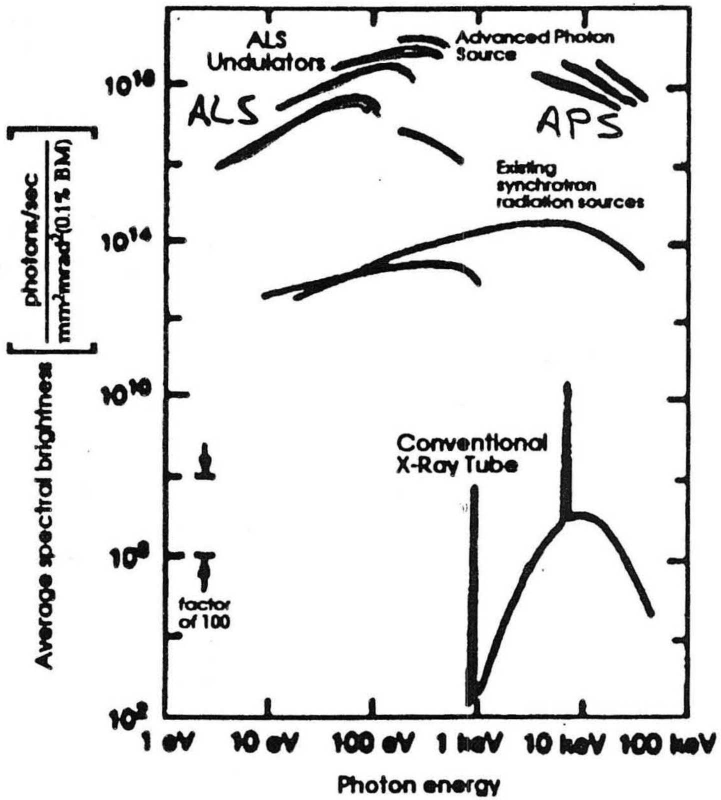
Angular Divergence of Bending Magnet and Undulator Radiation



HIGH BRIGHTNESS IS THE MAIN FEATURE OF THE ALS

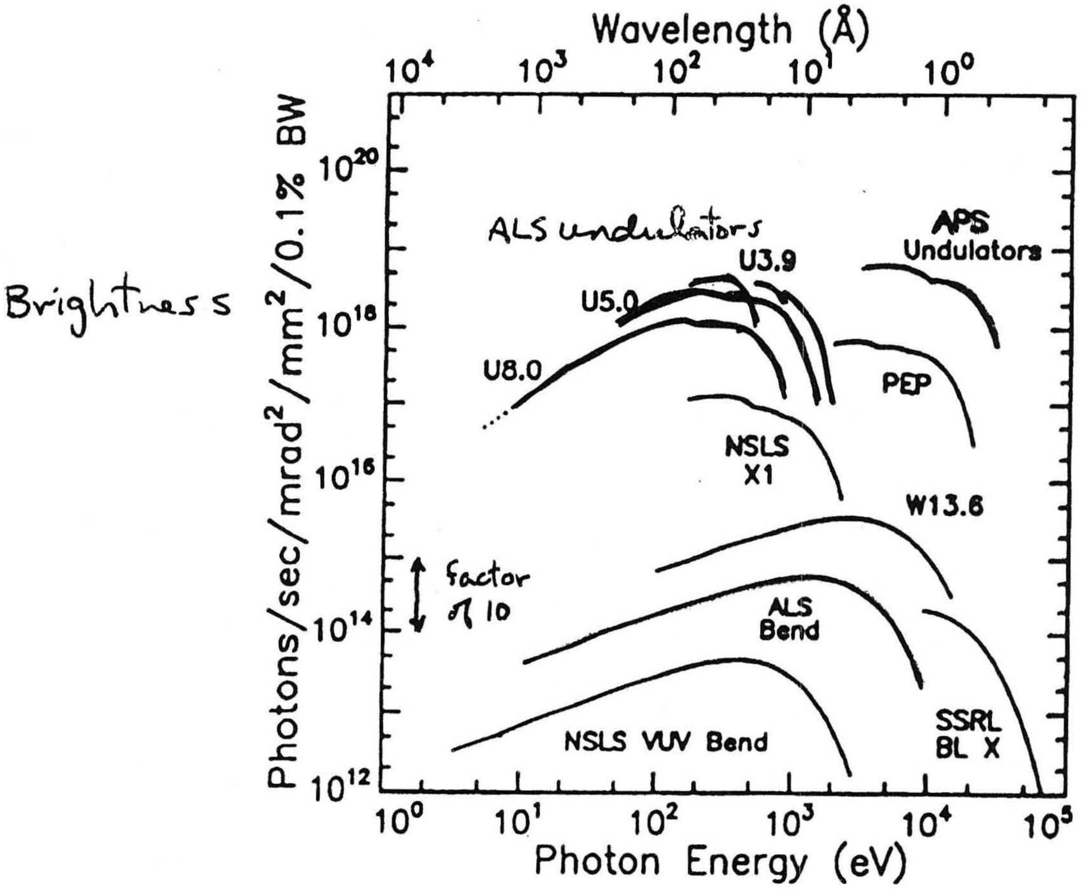
- High flux onto a small spot
- High resolution
- Ease of focussing ⇒ microscopy
- Element-specific sensitivity
- Partial coherence
- Broad tuning range (< 10 eV to > 1 keV)
- Short pulses

Brightness: an important measure of quality

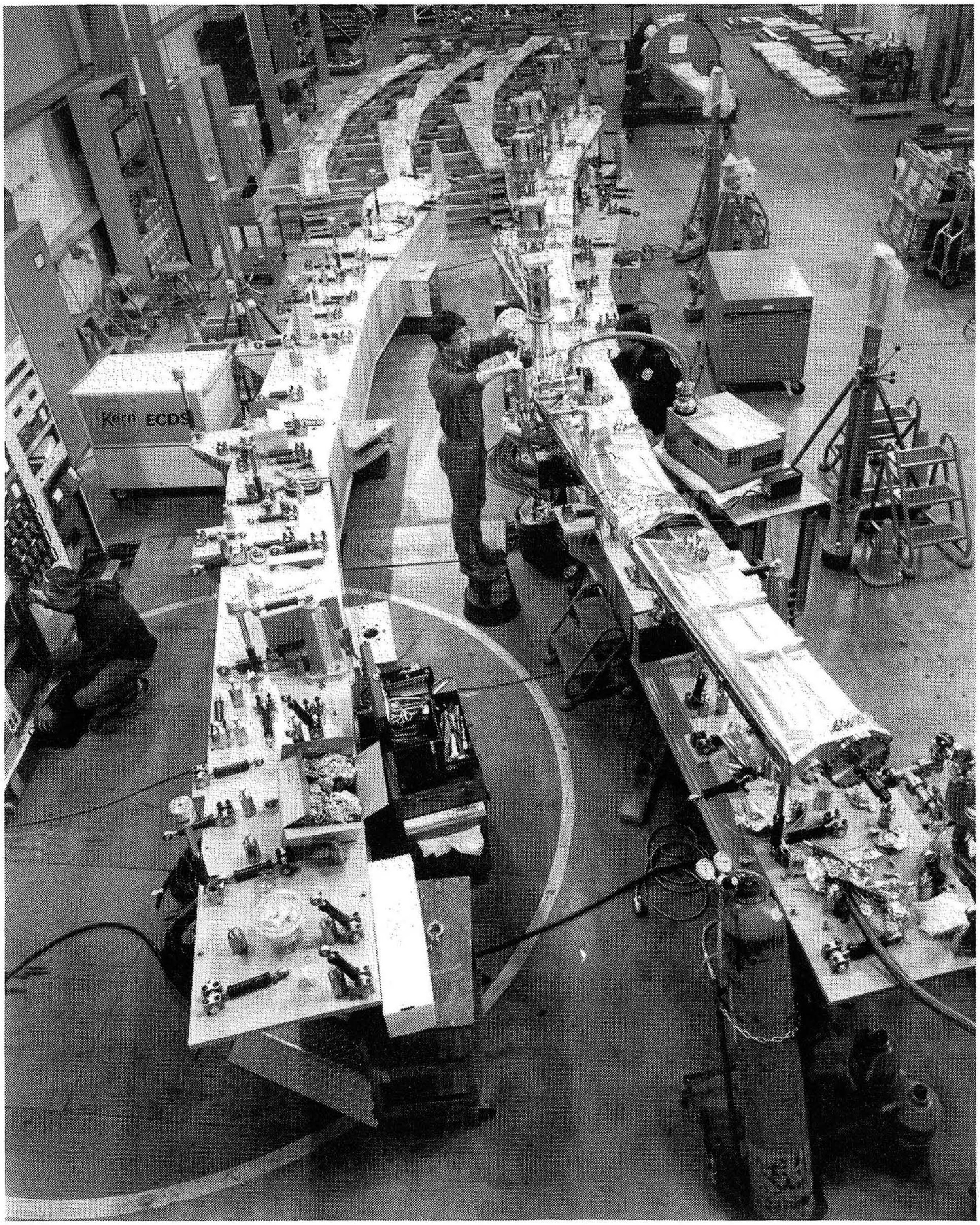


THIRD-GENERATION SYNCHROTRON-RADIATION SOURCES HAVE HIGH BRIGHTNESS

ALS



- **ALS undulators produce a beam which is a factor of 10,000 brighter than that from bend magnets**


Kern ECDS

NEW CAPABILITIES, NEW RESEARCH

A L S

Next-Generation VUV Synchrotron-Radiation Facility Optimized for Insertion Devices

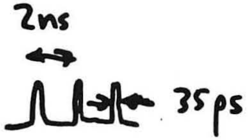
- **INTENSITY, BRIGHTNESS**
- **COHERENCE**
- Polarization
- **SHORT PULSES: 35 ps** ***(35 trillionths of a second)***
- **TUNABILITY**

⇒

- **Biological imaging**
- **Measurements on small or dilute samples**
- **Studies of ultrafast processes**
- **Studies of dynamic processes in biological systems**
- **Bond-selective chemistry**
- **High-spatial-resolution studies**
- **Lithography for chip fabrication**

TIME STRUCTURE IS USEFUL FOR SOME EXPERIMENTS

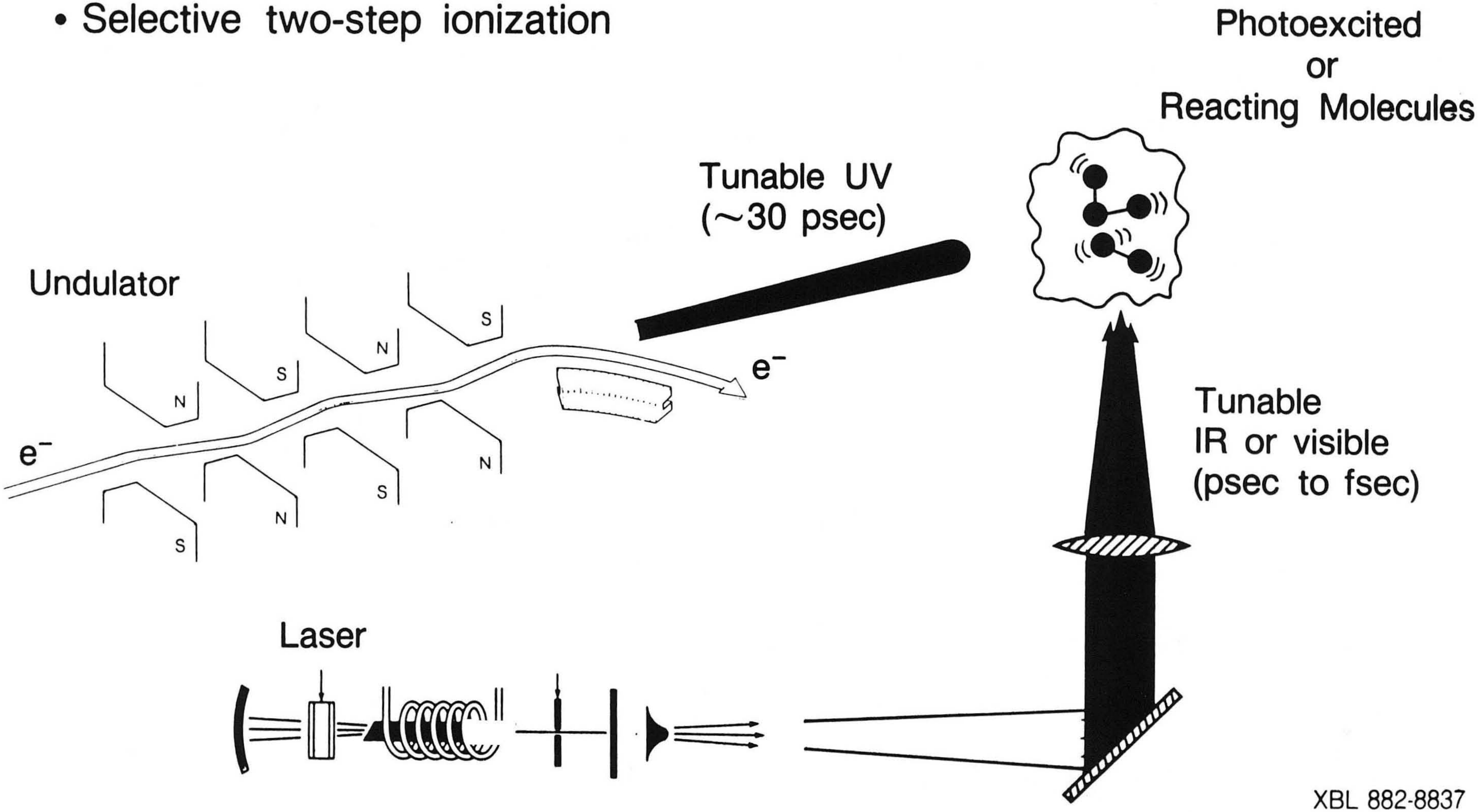
- Time structure of storage ring is different from that of laser
  - CW laser
  - Pulsed laser
    - Low repetition rate
    - Pulsed length depends on laser (μs to fs)
  - Storage ring (ALS)



    - High repetition rate (500 MHz)
    - 35-ps pulse at 2-ns intervals standard
    - Variable filling pattern changes pulse spacing (e.g., single bunch with 650 ns between pulses; pseudo-random filling pattern)
- Select physical problems on ps, or longer, time scale
- Can use multiple photons with time delay (pump-probe)
  - Laser synchronized with storage ring
  - Photons from undulator and bend magnet
- Energy per pulse is lower with SR than with laser
  - Laser: high-pulse energy for harmonic generation
  - SR: low-pulse energy; undulator output includes harmonics

Time Resolved Two-Color Photochemistry and Chemical Kinetics

- High resolution intermediate state spectroscopy
- Bond selective photodissociation
- Selective two-step ionization



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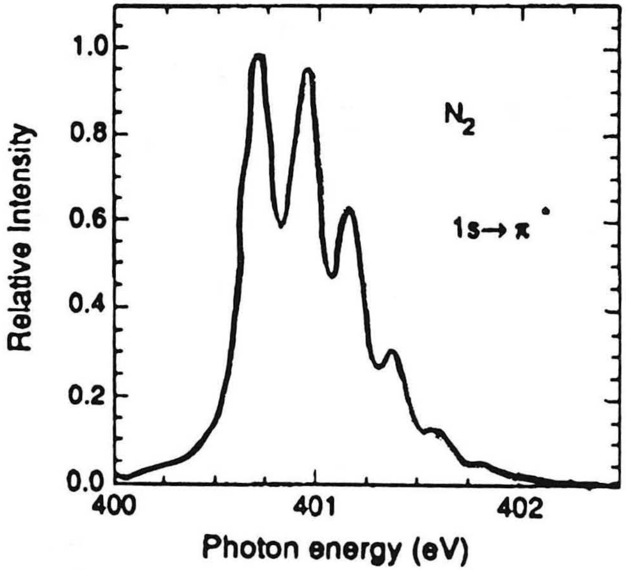
HIGH-RESOLUTION MEASUREMENTS PROVIDE DETAILED LOOK AT MOLECULES

ALS

- Vibrational structure in N_2 observed with high resolution (BL-VI at SSRL)

- Resolution of 60 meV at 400 eV ($E/\Delta E$ = 7,000)

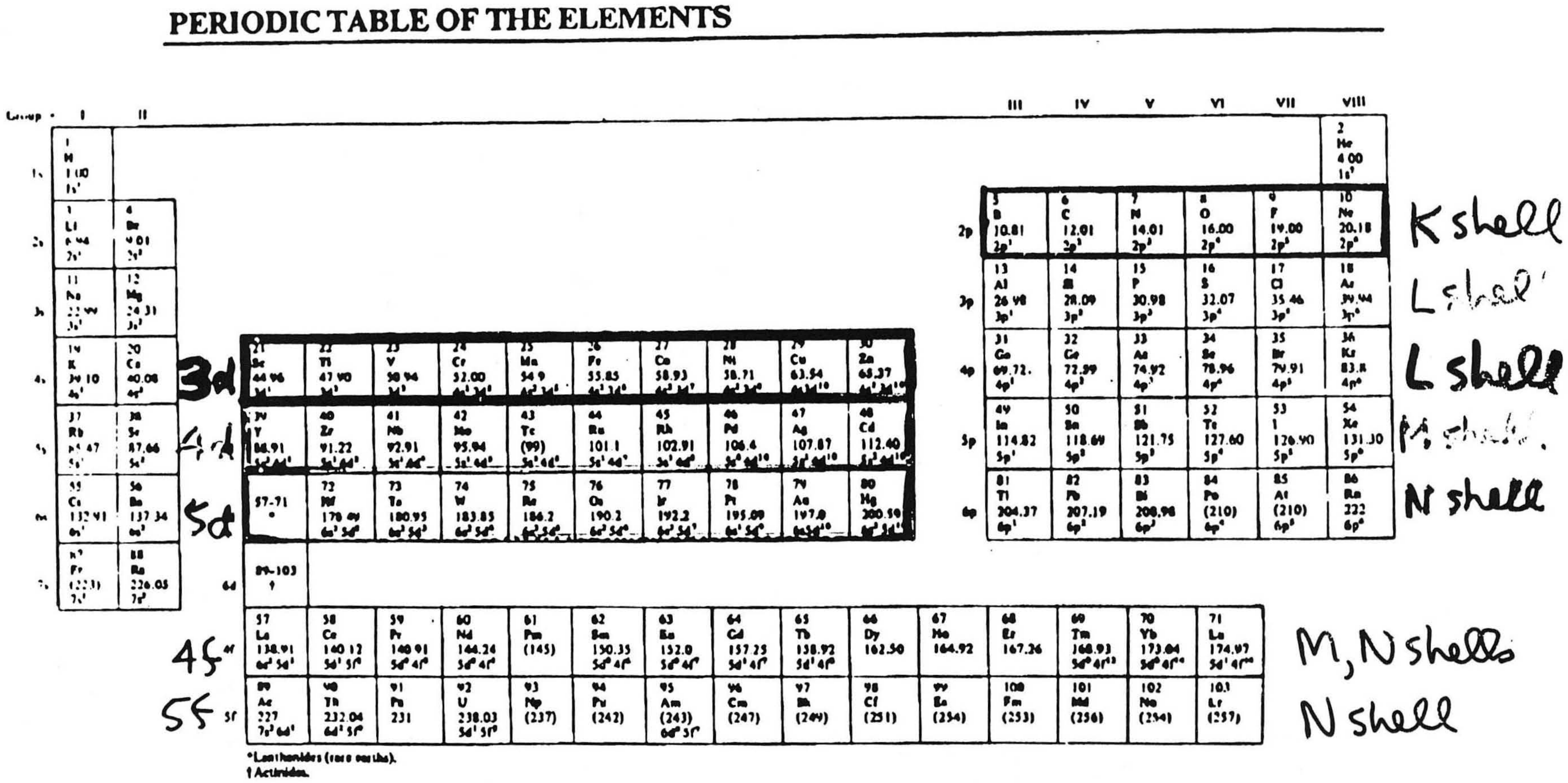


X-ray absorption spectrum of gaseous molecular nitrogen, showing vibrational structure of $1s \rightarrow \pi^*$ electronic transition

Ref: Heimann et al., VUV Conference (1989)

SSRL

ALS CAN ACCESS CORE LEVELS OF ESSENTIALLY ALL ELEMENTS: (200 - 1200 eV)



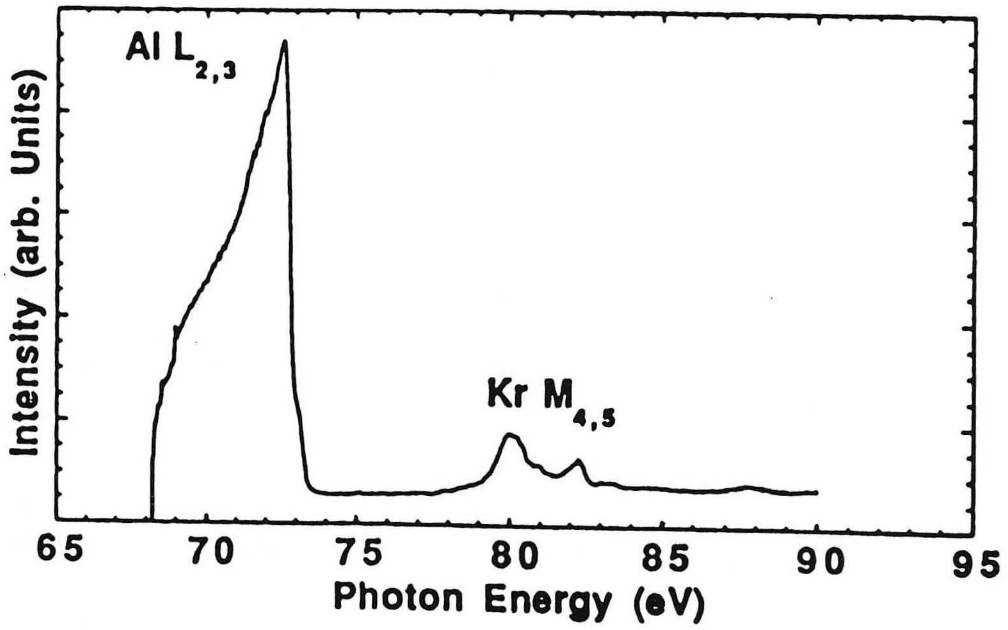
"PHOTONS—MOTHER NATURE'S FINEST TEST PROBES"

Dave Ederer

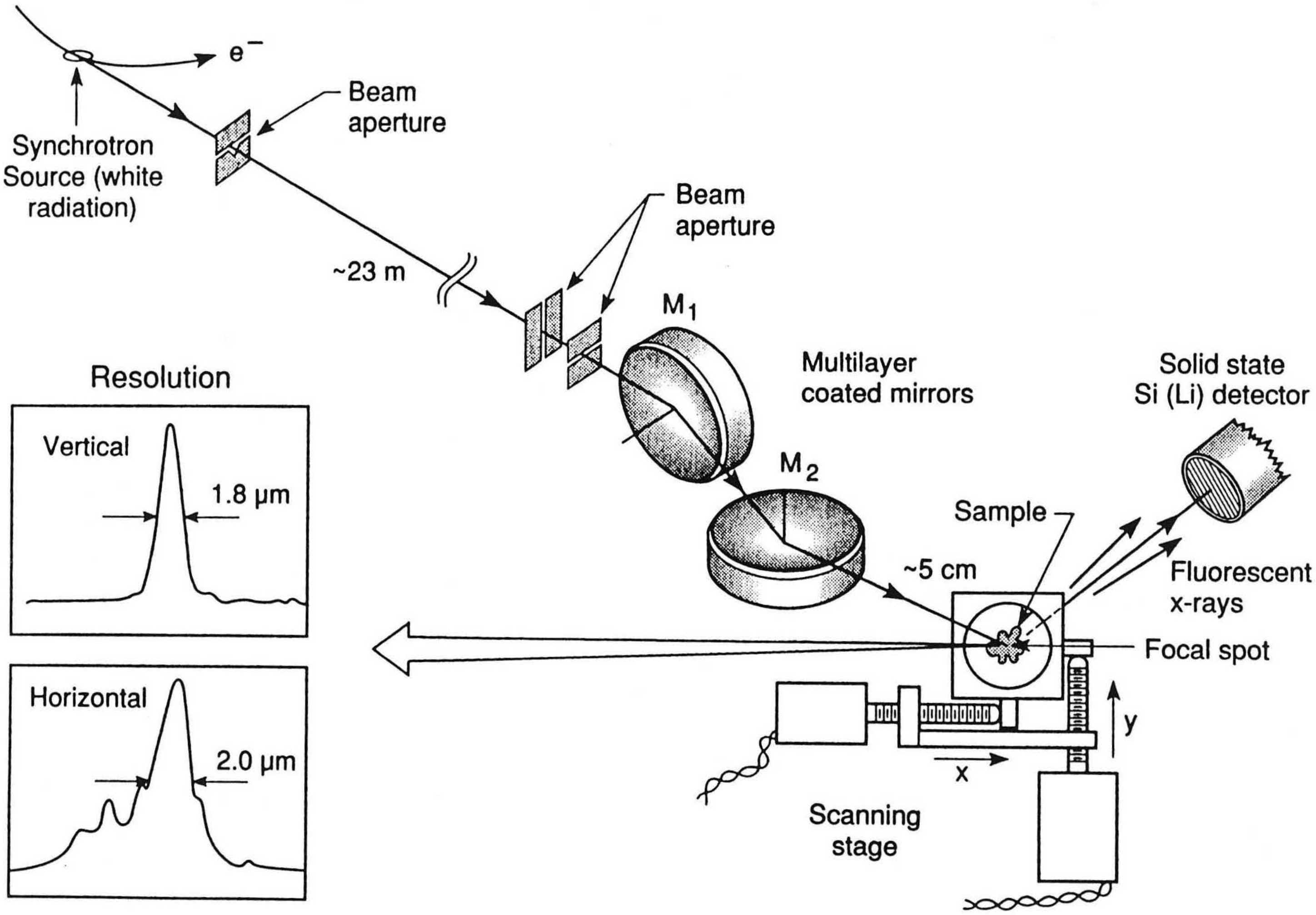
- **X-ray fluorescence excited by x rays has several beneficial features**

  — High spectral resolution
  — Low background
  — Easy to polarize photons
  — Low damage to samples by photons
  — Ultrahigh vacuum not required
  — Can be bulk or surface sensitive

e.g., photons are a perfect nondestructive probe for atoms buried in a substrate as illustrated by 10% krypton implanted in aluminum, where the krypton forms little balls about 1000 Å below the surface (Ref: D. Ederer, NIST, 1991)



X-Ray Microprobe Using Synchrotron Radiation



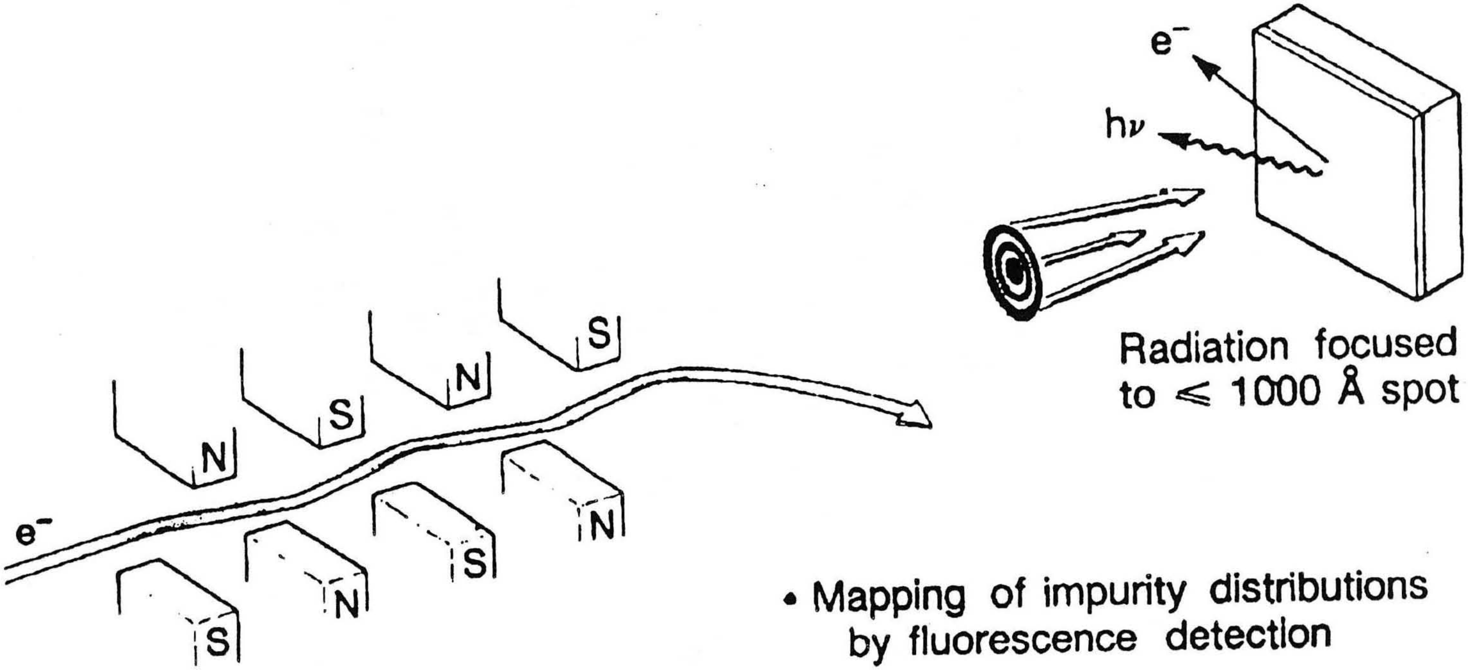
XBL 903-5796

X-ray Microscopy:

A new tool for the life sciences

SPATIALLY RESOLVED SPECTROSCOPIES FOR DILUTE IMPURITY AND DEFECT SYSTEMS

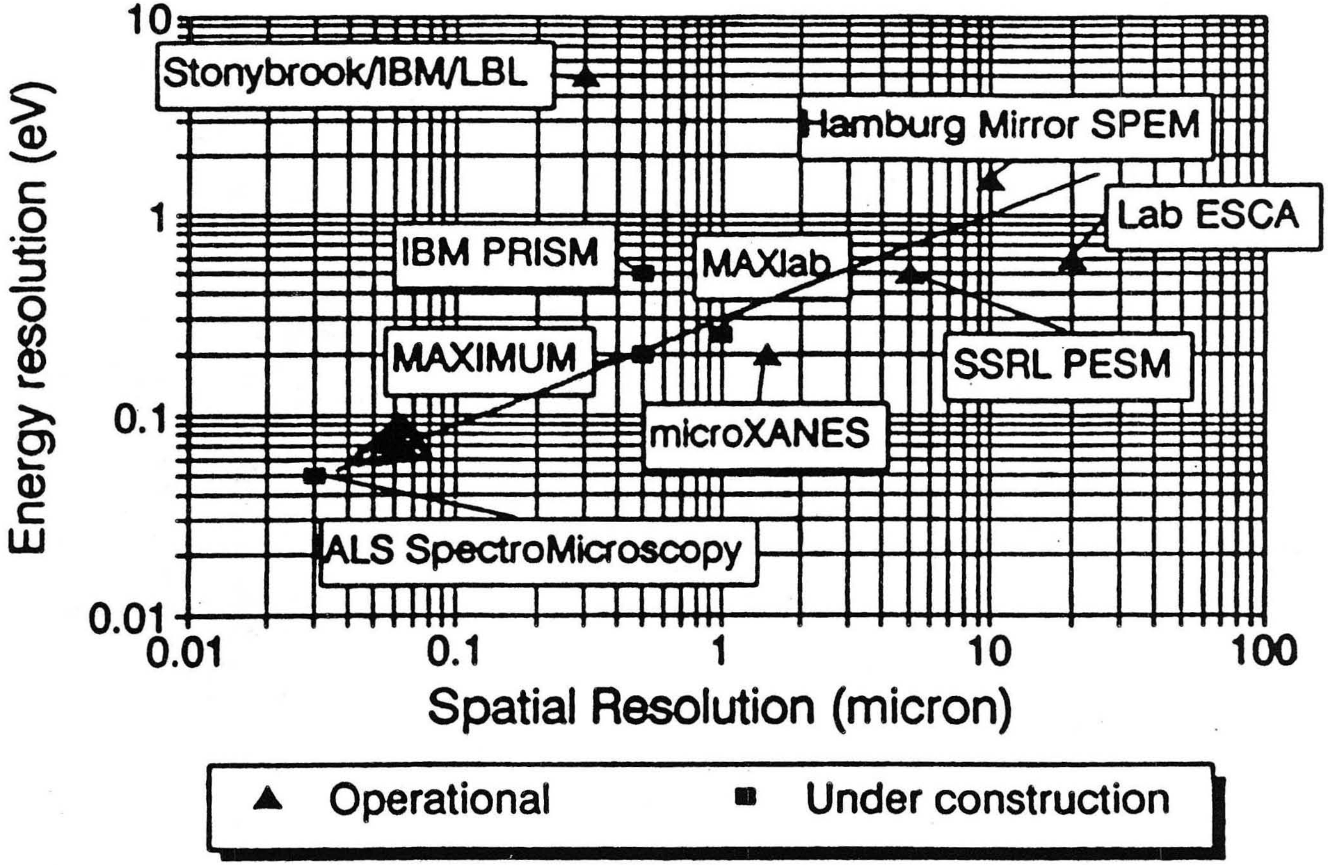
Spectromicroscopy



Radiation focused to ≤ 1000 Å spot

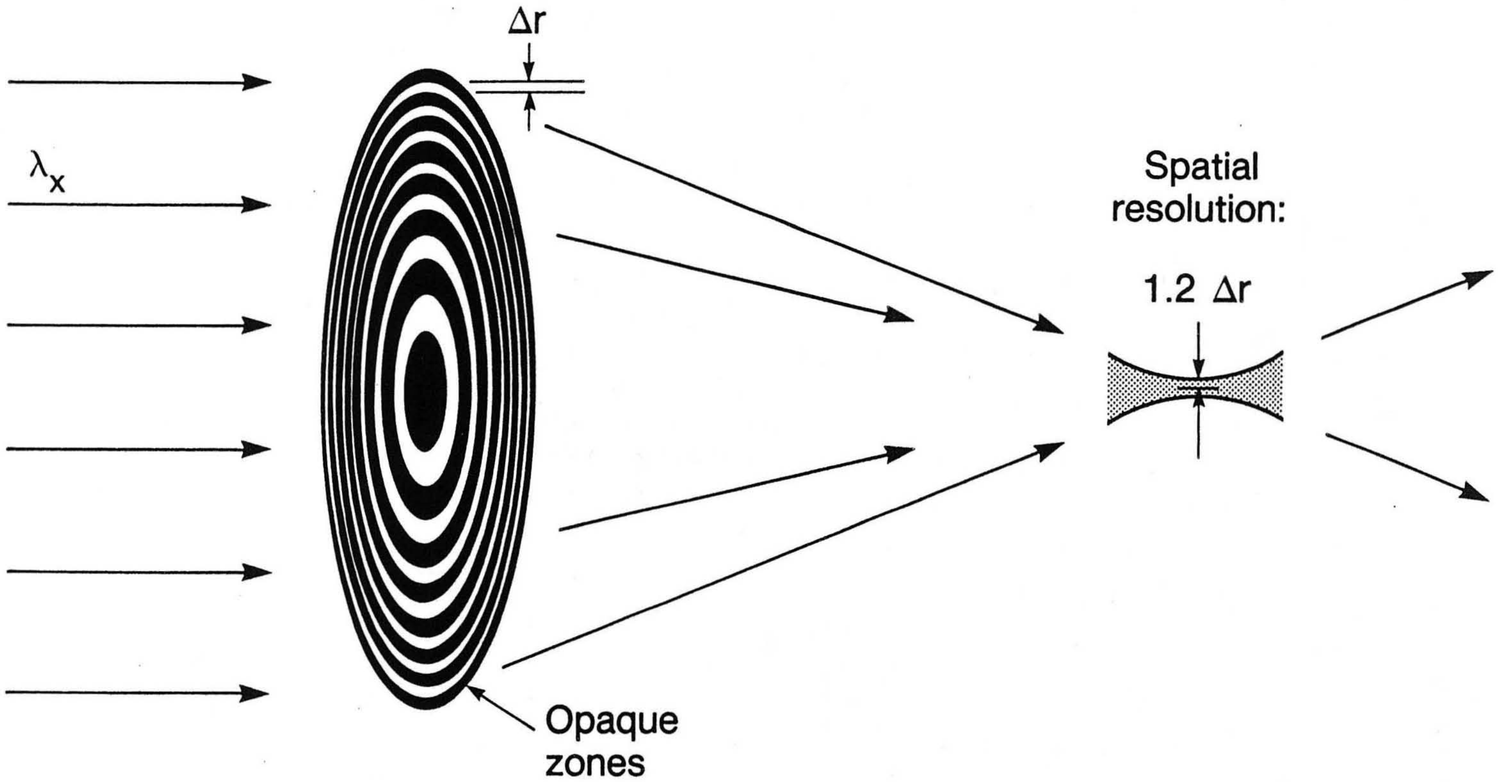
- Mapping of impurity distributions by fluorescence detection
- Mapping of bonding defects by photoemission

SpectroMicroscopy Phase Space



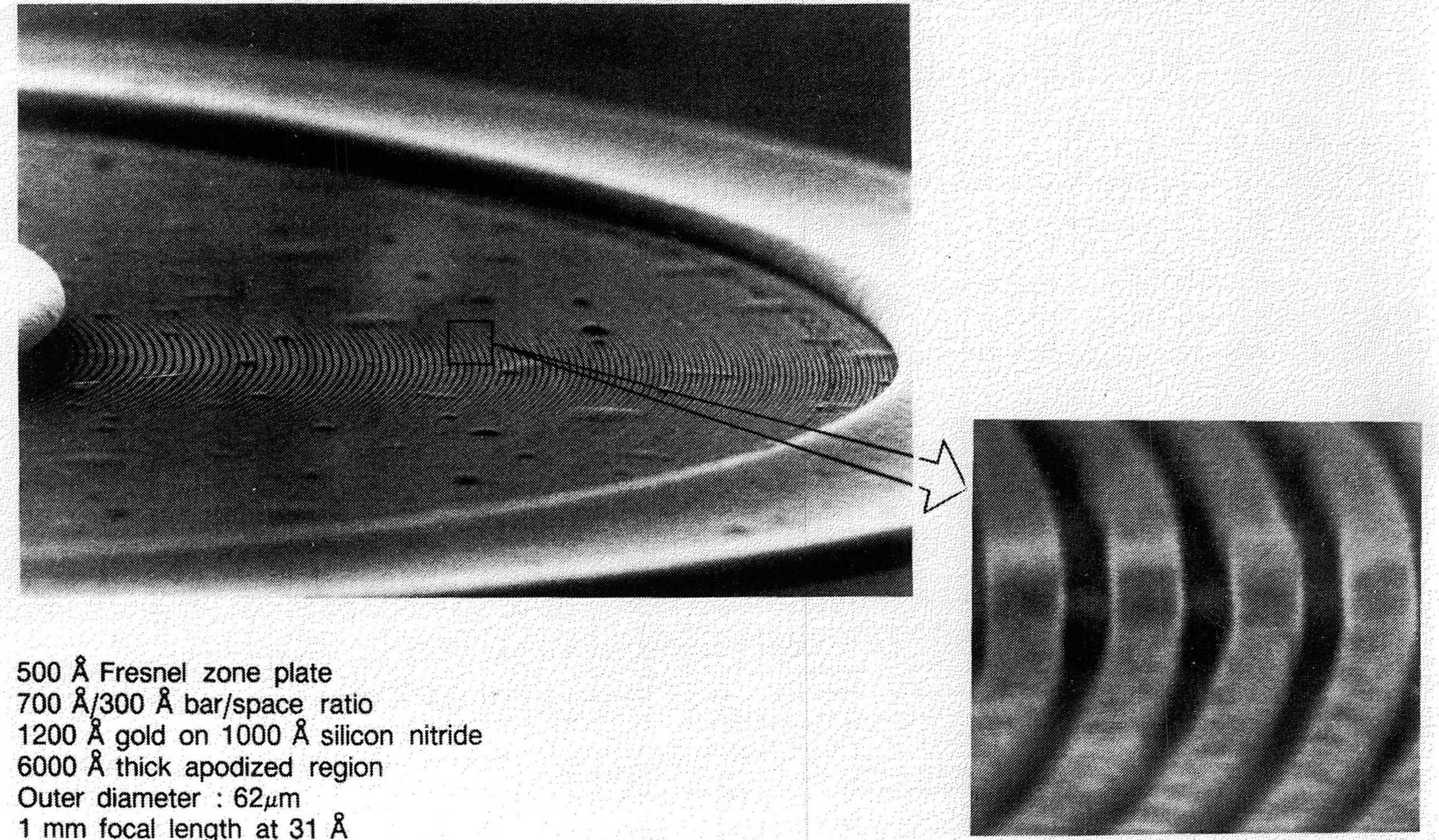
Spectromicroscopy at ALS:
- high energy resolution
- high spatial resolution.

Fresnel Zone Plate Lens for Diffractive Focusing of X-Rays:



XBL 842-9405

500 Å Zone Plate for High Resolution X-ray Microscopy



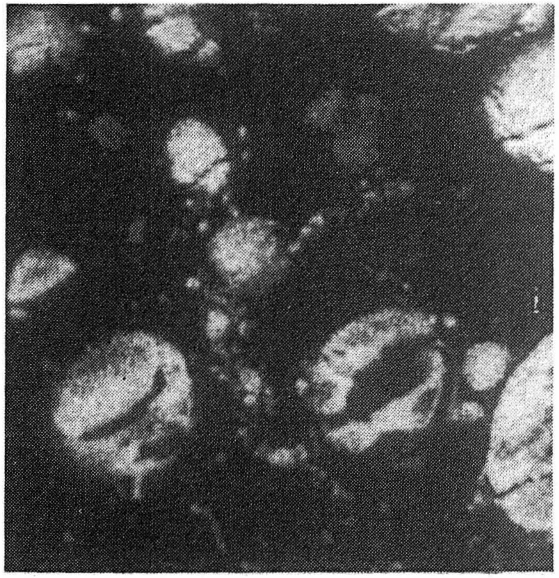
500 Å Fresnel zone plate
700 Å/300 Å bar/space ratio
1200 Å gold on 1000 Å silicon nitride
6000 Å thick apodized region
Outer diameter : 62μm
1 mm focal length at 31 Å

ELEMENT-SENSITIVE DETECTION WITH SCANNING

- **Object: diseased human tendon**

E < 350 eV

E > 350 eV



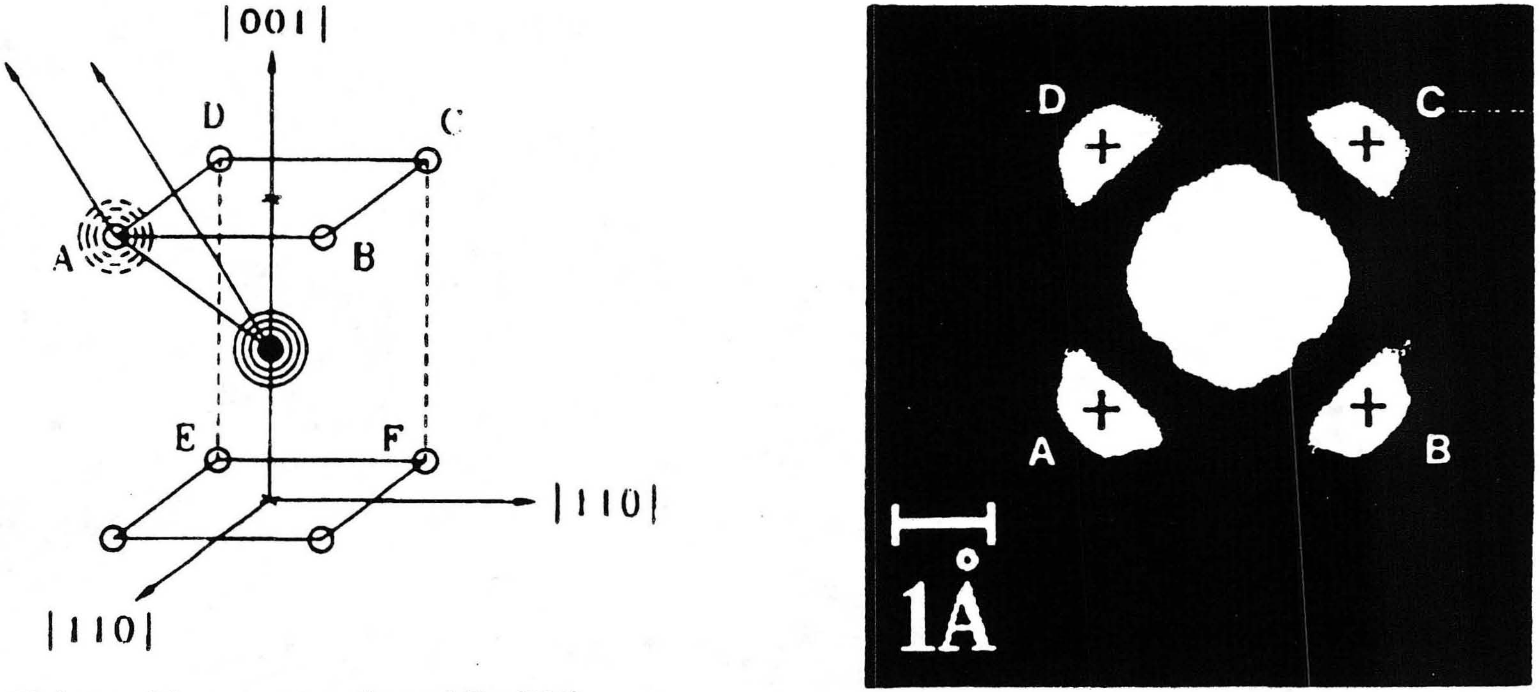
Subtractive image
shows calcium

Ca L ~ 347 eV

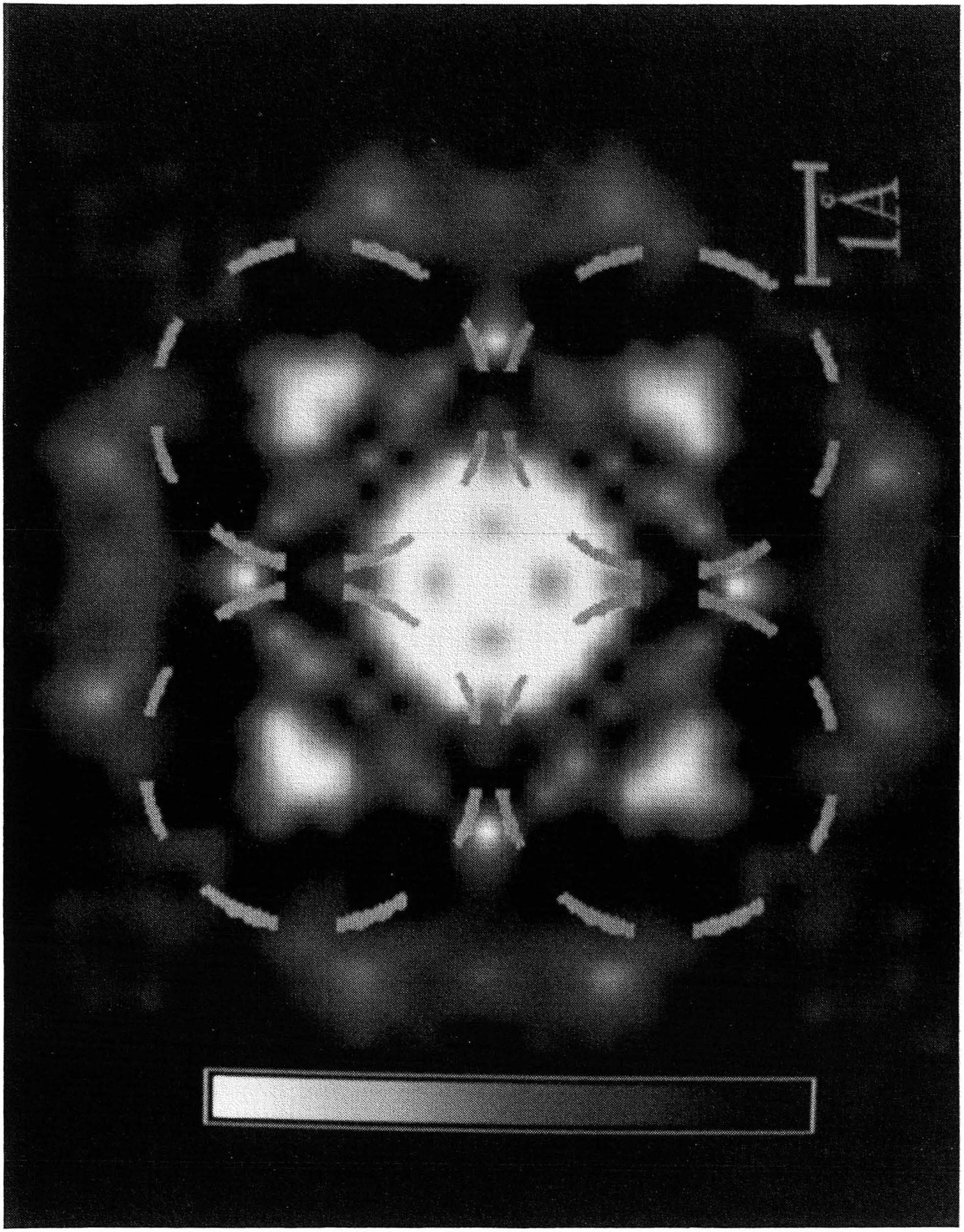
ATOMIC-RESOLUTION ELECTRON HOLOGRAPHY

ALS

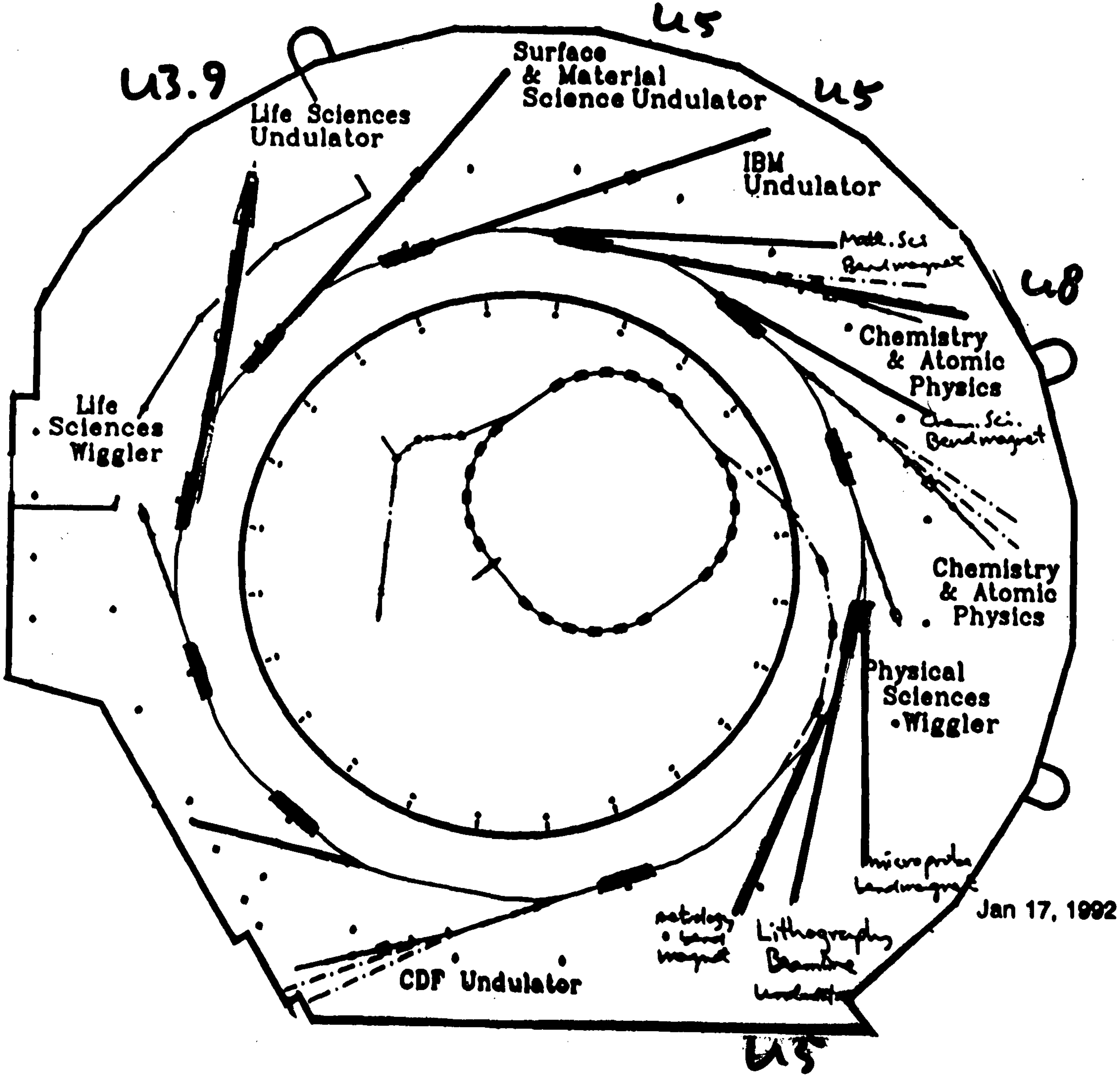
- Image near-neighbor environment of specific chemical species in three dimensions
- Measure photoelectron diffraction pattern produced by x ray to select chemical species
- High resolution needed to resolve chemical shifts



Holographic reconstruction of Cu (001)
Ref: Harp et al., *Phys. Rev. Lett.* 65, 1012 (1990); *Phys. Rev. B* 42, 9199 (1990)


1Å

The ALS will have ten beamlines in 1994



Jan 17, 1992

PARTICIPATING RESEARCH TEAMS (PRTs)

ALS

Insertion Device Teams

Insertion Device	Scientific Focus	Spokesperson	Date Ready
U10	Chemical dynamics	Tomas Baer, U. of North Carolina Yuan Lee,LBL	Future
U8.0	Atoms, molecules, ions	Denise Caldwell, U. of Central Florida	1993
U8.0	Pump-probe, timing, dynamics experiments	R. Stanley Williams, UCLA	Future
U5.0	Surfaces and interfaces	B. Tonner, U. of Wisconsin	1993
U5.0	Surfaces and interfaces	Joachim Stöhr, IBM Almaden Research Center	1993
U5.0	Optics characterization	Nate Ceglio, LLNL	1994
U3.9	X-ray imaging and optics for the life and physical sciences	Dave Attwood, LBL Steve Rothman, UCSF	1994
W16	Atomic, molecular, optical physics, materials science	Bernd Crasemann, U. of Oregon Phil Ross, LBL	Future
W16	Life sciences	Stephen Cramer, UCD Sung Hou Kim, LBL	Future

PARTICIPATING RESEARCH TEAM (PRTs) [CON'T]

ALS

Bend Magnet Teams

Scientific Focus	Spokesperson	Date Ready
EUV and soft x-ray spectroscopy; x-ray optics	James H. Underwood, LBL	1994
Infrared spectroscopy; fast IR detectors	Gwyn P. Williams, Brookhaven National Laboratory	Future
Polarized photon studies; biology	Stephen Cramer, LBL	Future
Materials studies and optical component characterization	Marvin Weber, LLNL	1993?
High-resolution studies in materials and chemical sciences	Charles Fadley, LBL	1993
Microprobe	Al Thompson, LBL	1993
Atomic and materials sciences	Dennis Lindle, University of Nevada, Las Vegas	Future

ALS FEATURES

- High brightness
  - Focus to small spot
  - High resolution with high flux
- Fast pulse (35 ps)
- Tunable over wide range (VUX, soft X ray)
- Partial coherence
- Polarization (linear, circular)

THE ALS WILL ONLY BE USEFUL TO INDUSTRY IF:

- easily and quickly accessible
- user friendly
- appropriate support
- runs reliably full time
- facilities meet needs of users
- appropriate management climate
- available for proprietary research

DOING RESEARCH AT THE ALS

- Research opportunities
  - Join a PRT
  - Form a PRT
  - Independent investigator
  - Company/consortium/service bureau
- Additional information

Fred Schlachter
Scientific Program Coordinator
MS 46-161
Advanced Light Source
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Phone: (510) 486-4892
Fax: (510 486-4873
E-mail: fred@lbl.gov

Ultra-ESCA: Advanced Capabilities of XPS with High-Brightness Synchrotron Radiation

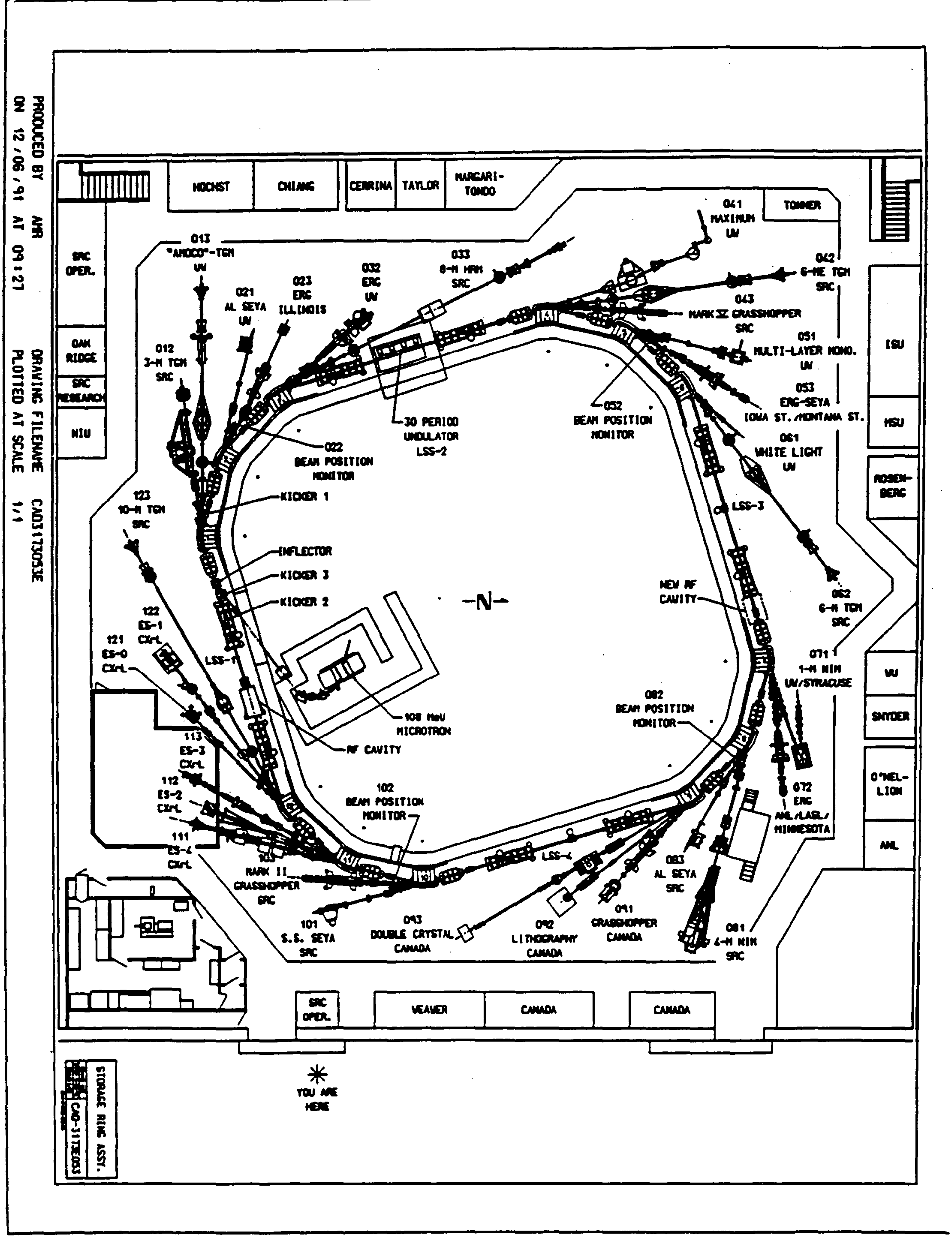
B. Tonner

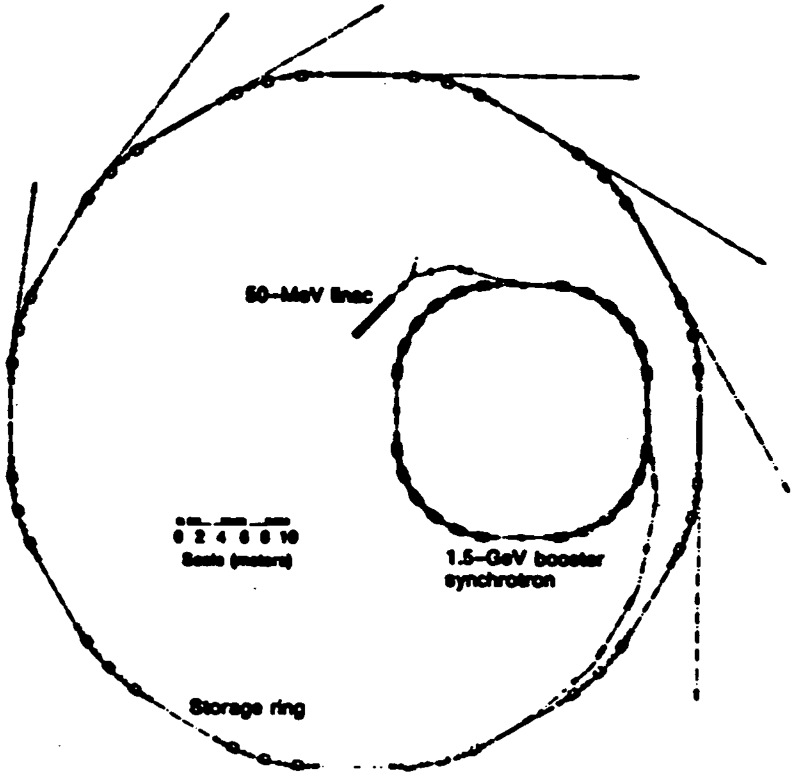
University of Wisconsin

Materials Science and Technology at the Aladdin 1 GeV Synchrotron Radiation Center

Brian Tonner
Associate Director, Research
UW Synchrotron Radiation Center
Stoughton, WI 53589

SRC


PRODUCED BY AMR
ON 12/06/91 AT 09:27
DRAWING FILENAME CAD3173053E
PLOTTED AT SCALE 1/1
HOCHST
CHIANG
CERRINA
TAYLOR
MARGARI-TONDO
TONNER
SRC OPER.
OAK RIDGE
SRC RESEARCH
NIU
013 "AMOCO"-TGM UV
021 AL SEYA UV
023 ERG ILLINOIS
032 ERG UV
033 8-M HRM SRC
041 MAXIMUM UV
042 6-ME TGM SRC
043 MARK XI GRASSHOPPER SRC
051 MULTI-LAYER MONO. UV
053 ERG-SEYA IOWA ST./MONTANA ST.
061 WHITE LIGHT UV
062 6-M TGM SRC
071 1-M NIM UV/SYRACUSE
072 ERG ANL/LASL/MINNESOTA
081 4-M NIM SRC
083 AL SEYA SRC
091 GRASSHOPPER CANADA
092 LITHOGRAPHY CANADA
093 DOUBLE CRYSTAL CANADA
101 S.S. SEYA SRC
103 MARK II GRASSHOPPER SRC
111 ES-4 CXrL
112 ES-2 CXrL
113 ES-3 CXrL
121 ES-0 CXrL
122 ES-1 CXrL
123 10-M TGM SRC
012 3-M TGM SRC
022 BEAM POSITION MONITOR
30 PERIOD UNDULATOR LSS-2
052 BEAM POSITION MONITOR
082 BEAM POSITION MONITOR
102 BEAM POSITION MONITOR
KICKER 1
INFLECTOR
KICKER 3
KICKER 2
LSS-1
LSS-3
LSS-4
NEW RF CAVITY
RF CAVITY
108 MeV MICROTRON
N
ISU
MSU
ROSEN-BERG
WU
SNYDER
O'NEL-LION
ANL
SRC OPER.
WEAVER
CANADA
CANADA
YOU ARE HERE
STORAGE RING ASST.
CAD-3173EC03


50-MeV linac
1.5-GeV booster synchrotron
0 2 4 6 8 10
Scale (meters)
Storage ring

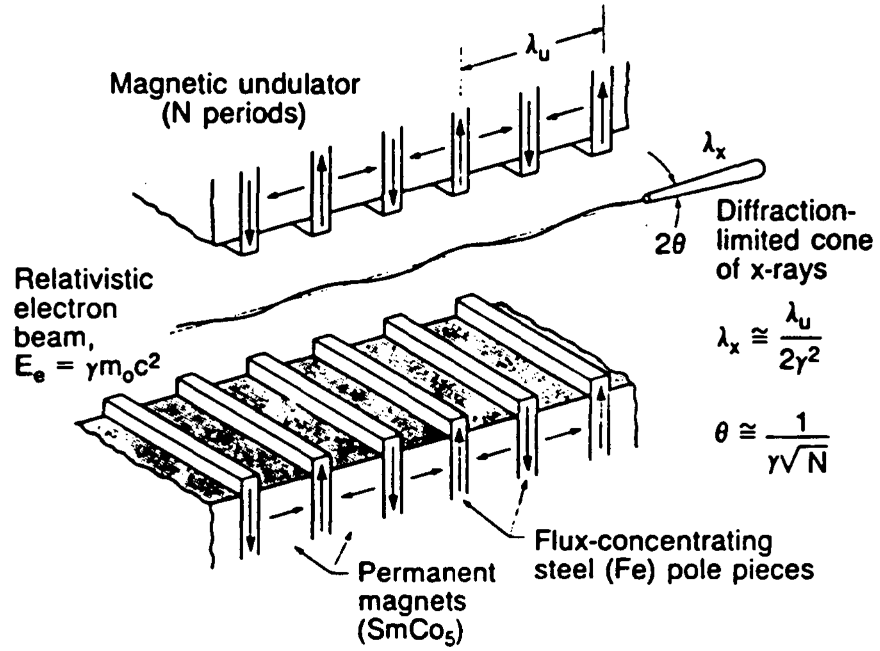
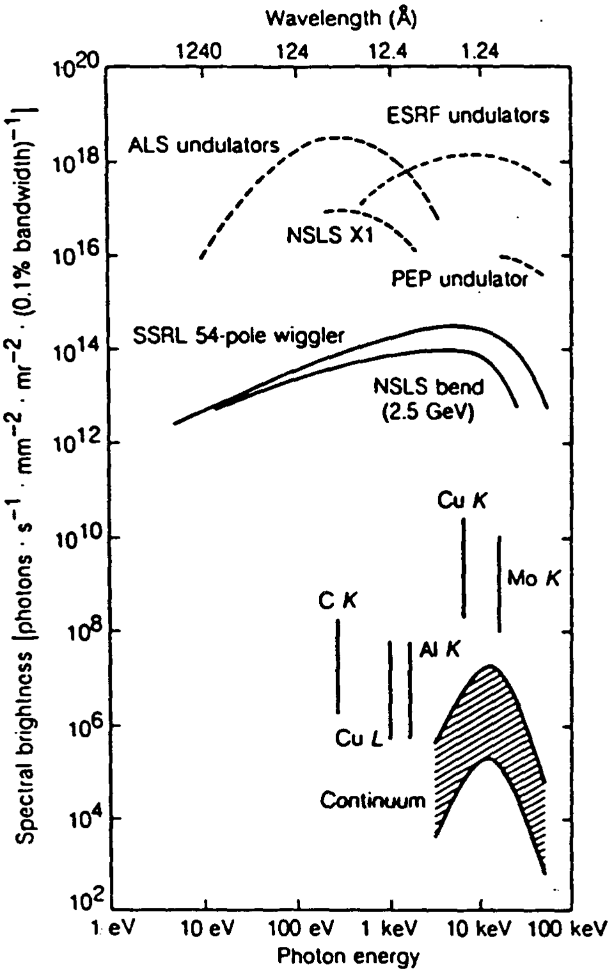


Fig. 2-2. Schematic of a periodic magnet structure (an undulator) of period λ_u and with a number of periods, N. The oscillations of the electron beam (of energy $\gamma m_0 c^2$) passing through the structure produce ultraviolet and soft x-ray radiation (photons) of high spectral brightness and high coherent power. The radiation occurs at a wavelength λ_x in a narrow spectral width $(\lambda_x/\Delta\lambda_x) \simeq N$, and is propagated forward in a narrow cone of half-angle $\theta \simeq (\gamma\sqrt{N})^{-1}$.



Spectral brightness for several synchrotron radiation sources and conventional x-ray sources. The data for conventional x-ray tubes should be taken as rough estimates only, since brightness depends strongly on such parameters as operating voltage and take-off angle. The indicated two-order-of-magnitude ranges show the approximate variation that can be expected among stationary-anode tubes (lower end of range), rotating-anode tubes (middle), and rotating-anode tubes with microfocusing (upper end of range).

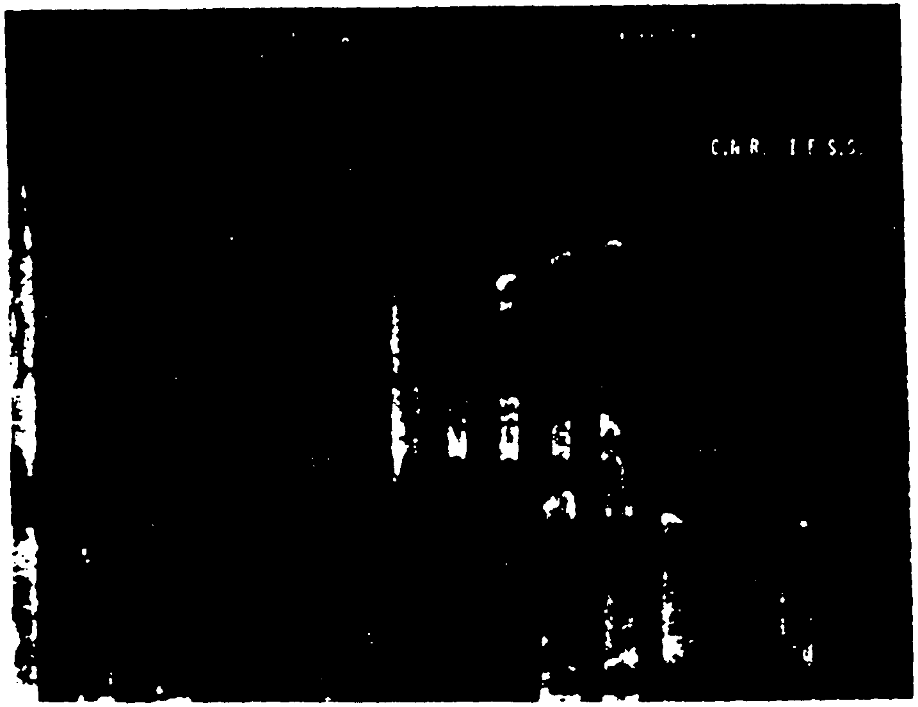
Materials Science and Technology at the Aladdin 1 GeV Synchrotron Radiation Center

- X-ray Lithography
- X-ray Micromachining
- X-ray Assisted Chemical Processing
- X-ray Analysis

CXrL

M. Gentili, L. Luciani,
P. De Gasperis, G. Petrocco,
L. Mastrogiacomo (IESS)

D. Plumb, Q. Leonard,
M. Sisco, F. Cerrina (CXrL)

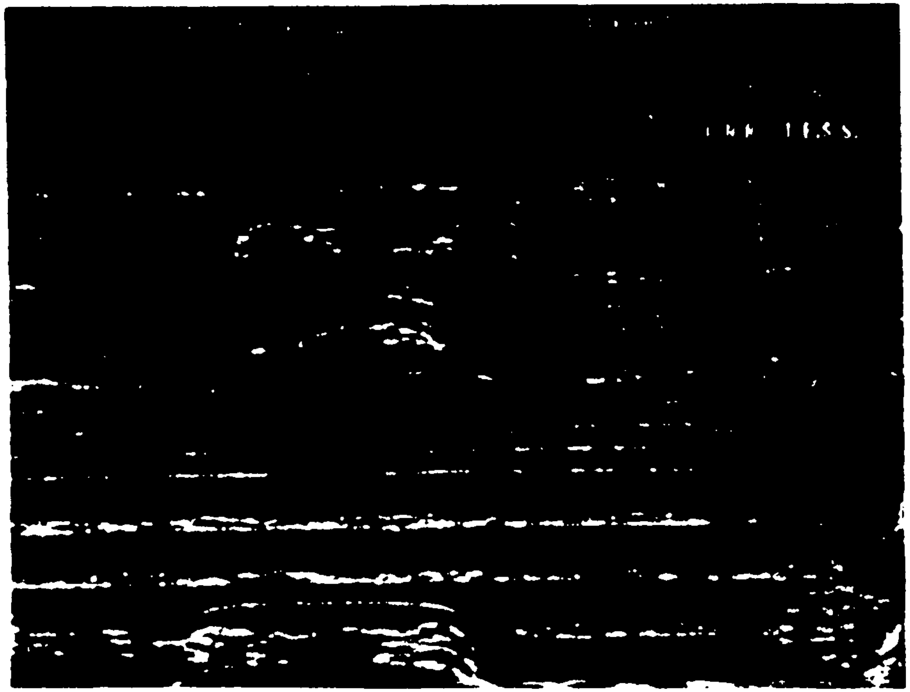


PMMA over Topography

Exposures on ES-I
August 1990

M. Gentili, L. Luciani,
P. De Gasperis, G. Petrocco,
L. Mastrogiacomo (IESS)

D. Plumb, Q. Leonard,
M. Sisco, F. Cerrina (CXrL)



wafers supplied by
SGS - Agrate ([illegible])

PMMA over Topography

Exposures on ES-I
August 1990

MICROMECHANICS & MICROMAGNETICS

SOURCE:

Henry Guckel, Todd Christenson, Ken Skrobis, Johnathon Klein

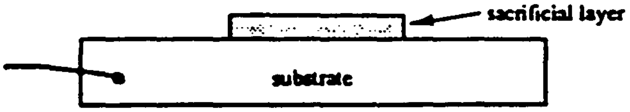
Wisconsin Center for Applied Microelectronics

Department of Electrical and Computer Engineering

University of Wisconsin

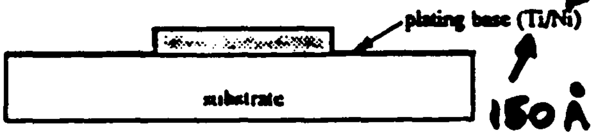
NICKEL (DURABLE, MAGNETIC) BETTER THAN SILICON
(BRITTLE, NON-MAGNETIC)
MAGNETIC DRIVE BETTER THAN ELECTROSTATIC

1) Pattern sacrificial (removable) layer

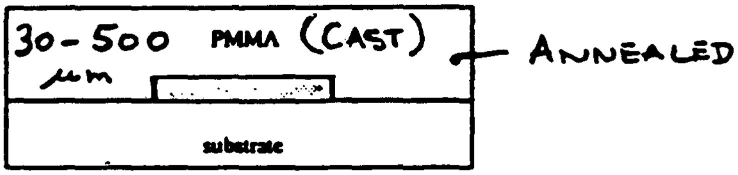


SOFT POLYMIDE POLYMER

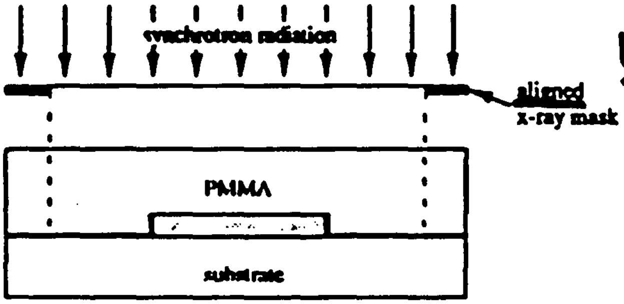
2) Sputter plating base



3) Cast and anneal PMMA

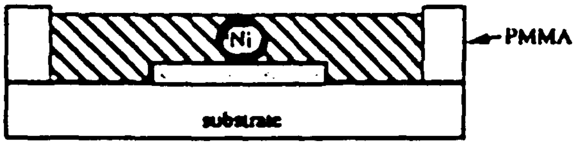


4) Align X-ray mask and expose PMMA



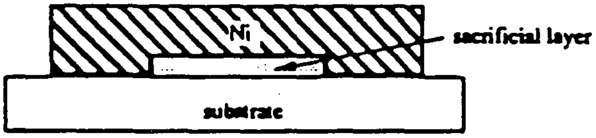
1µm SiN
5µm Au

5) Develop PMMA and electroplate Ni

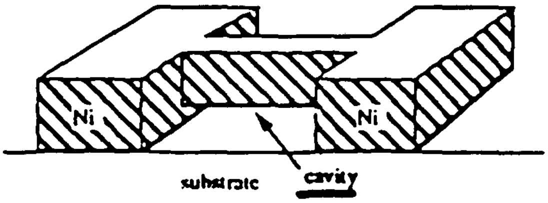


Ni DURABLE, MAGNETIC

6) Remove PMMA and plating base to clear access to the sacrificial layer



7) Etch sacrificial layer thereby undercutting and freeing Ni structure



Frame #012103 This is an electrostatic stepping linear actuator and was fabricated using a patterned sacrificial layer. That is, a layer of material (polyimide in this case) was patterned in the areas where it was desired to have a free structure. This layer is then removed after forming the nickel structure. This requires alignment of an x-ray mask to a previously patterned substrate. The same actuator was fabricated from Si at NEC but required 5 masks and was limited to $\approx$ 10 μm height (compared to 2 masks (1 x-ray) and > 100 μm).

Frame #211000 An example of assembly. Assembly of completely freed components can be used to make more complicated structures.

Frame #611011 A nickel hose clamp. This particular clamp is used to hold a gear captive on its shaft by clamping it on the shaft above the gear.

Frame #035006 A magnetic micromotor coupled to a 3-gear gear train. The operation of this micromotor was demonstrated in May 1991. The shape of the rotor allows operation of the motor as a reluctance motor (that is, it has a preferable magnetic axis which aligns to the stator pole pair carrying the magnetic flux. Operation was achieved by external excitation with mating electromagnets and also rotating permanent magnets. Such external excitation limits the performance of the motor, and, as a result, current effort is aimed at integrating windings on the stator.

This was the first magnetic planar micromotor demonstrated, as well as the first planar micromotor to demonstrate the ability to couple motion out of the rotor. Previous planar micromotors turned only themselves.

Frame #411003 Band and pulleys. Two pulleys were assembled on the the shafts shown, which are permanently attached to the substrate. A nickel band, which was initially circular, was stretched over the pulleys, and thus coupling them. Turning one pulley does indeed turn the other pulley. The purpose of the structure was to show that large displacements may be obtained with micro-components.

BAND HEIGHT = 4 μm

X-ray Analysis
by
Soft X-ray Spectroscopy

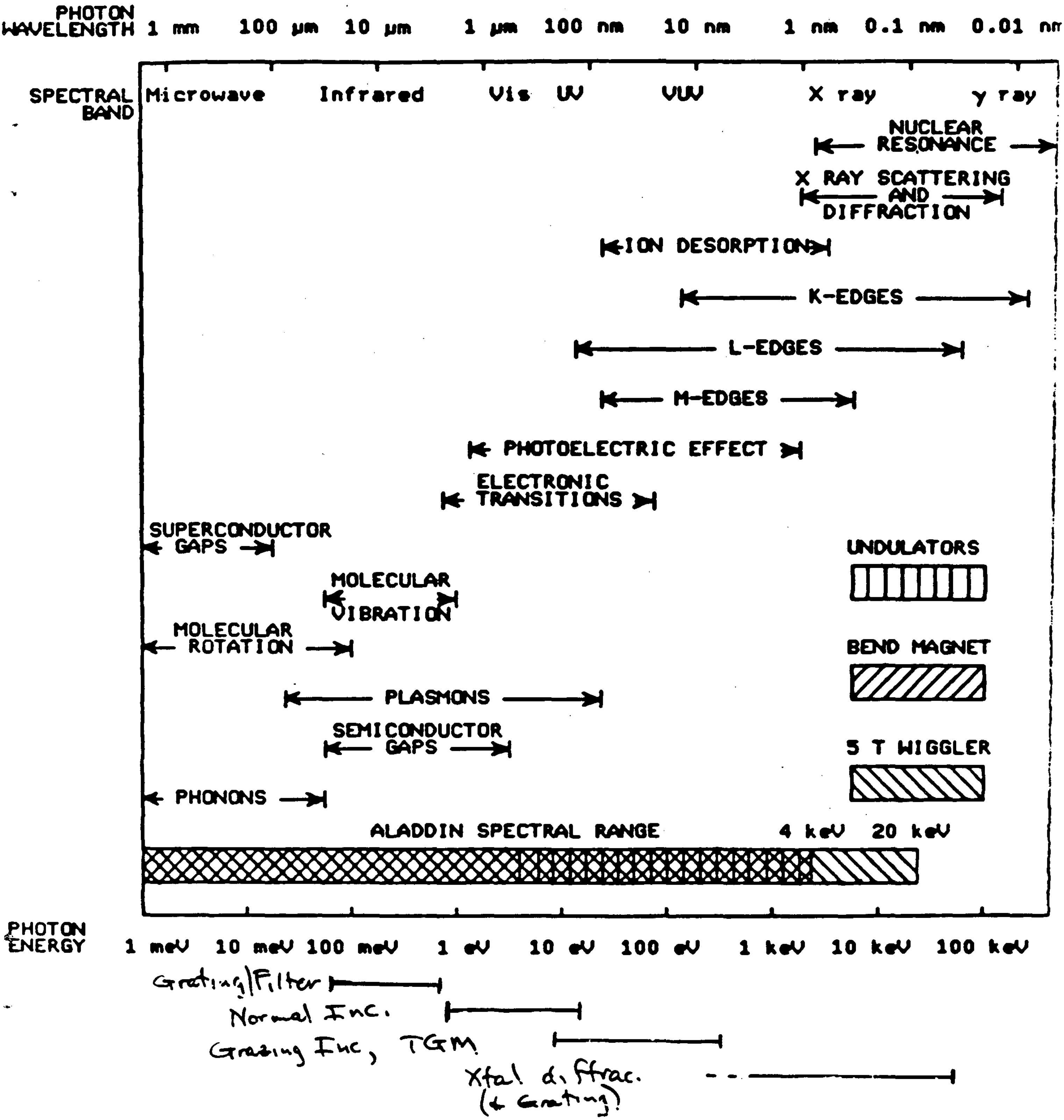
- X-ray Photoemission Spectroscopy (SXPS, ultraESCA) Photon in, electron out. Binding energies of occupied orbitals.
- X-ray Absorption Spectroscopy (XAS, XANES, NEXAFS)

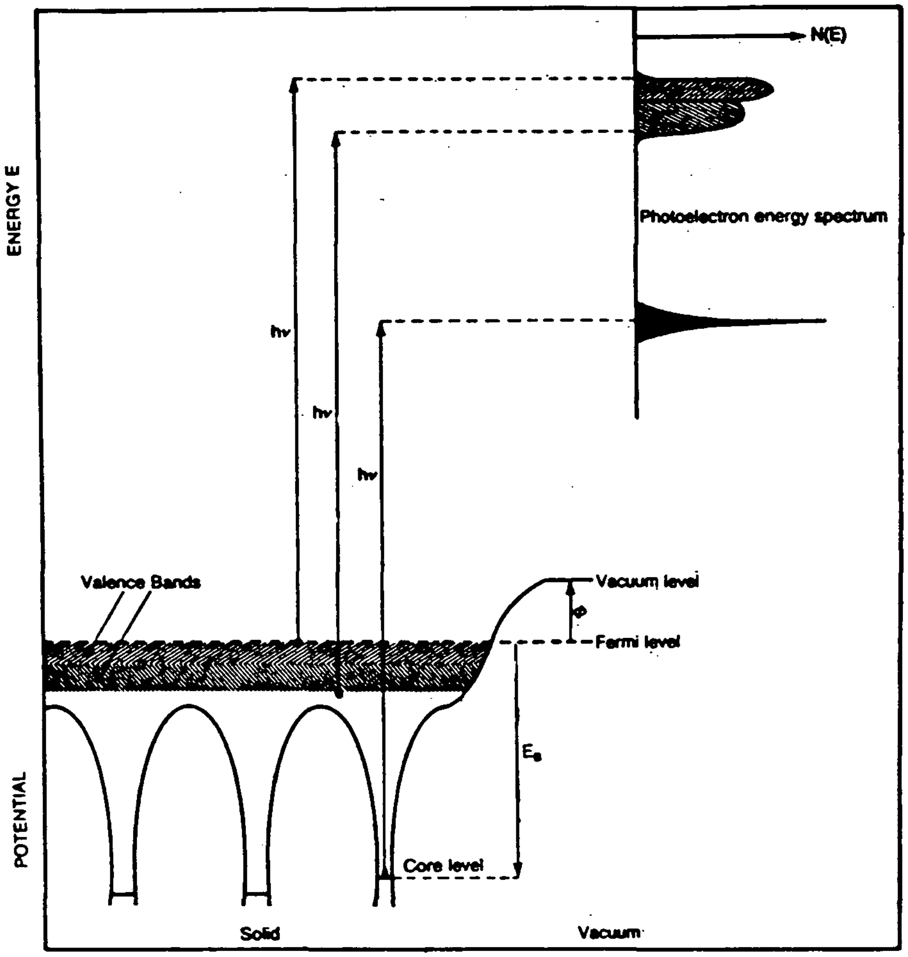
  Photon in, electron or photon out. Energies of unoccupied orbitals.

XPS
with
Synchrotron Radiation

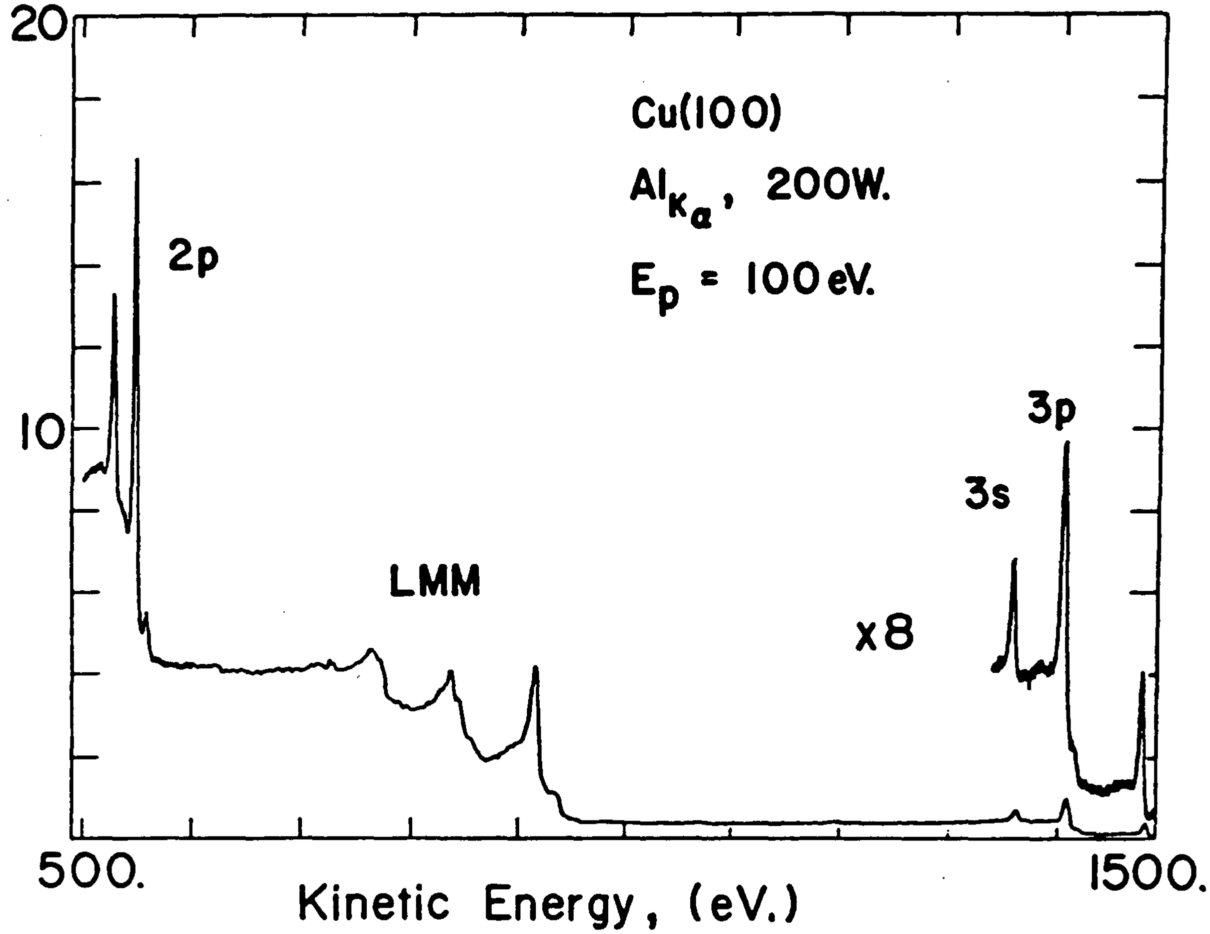
- Tunable energy:
  Enhance elemental sensitivity by orders of magnitude.
  Enhance surface sensitivity.
- Highly collimated:
  Extremely high resolution (10's of millivolts).
- Small spot size:
  Less than 1 mm.
- Polarized:
  Selection rules.
- High intensity:
  Time resolution, spin detection, microscopy.

SPECTRAL RANGES OF PHYSICAL PROCESS





Photoelectron spectroscopy. Schematic energy level diagram for a solid showing photoemission from valence bands and from a core level.


20
10
500.
1500.
Kinetic Energy, (eV.)
Cu(100)
Al_{K_α}, 200W.
E_p = 100 eV.
2p
LMM
x8
3s
3p

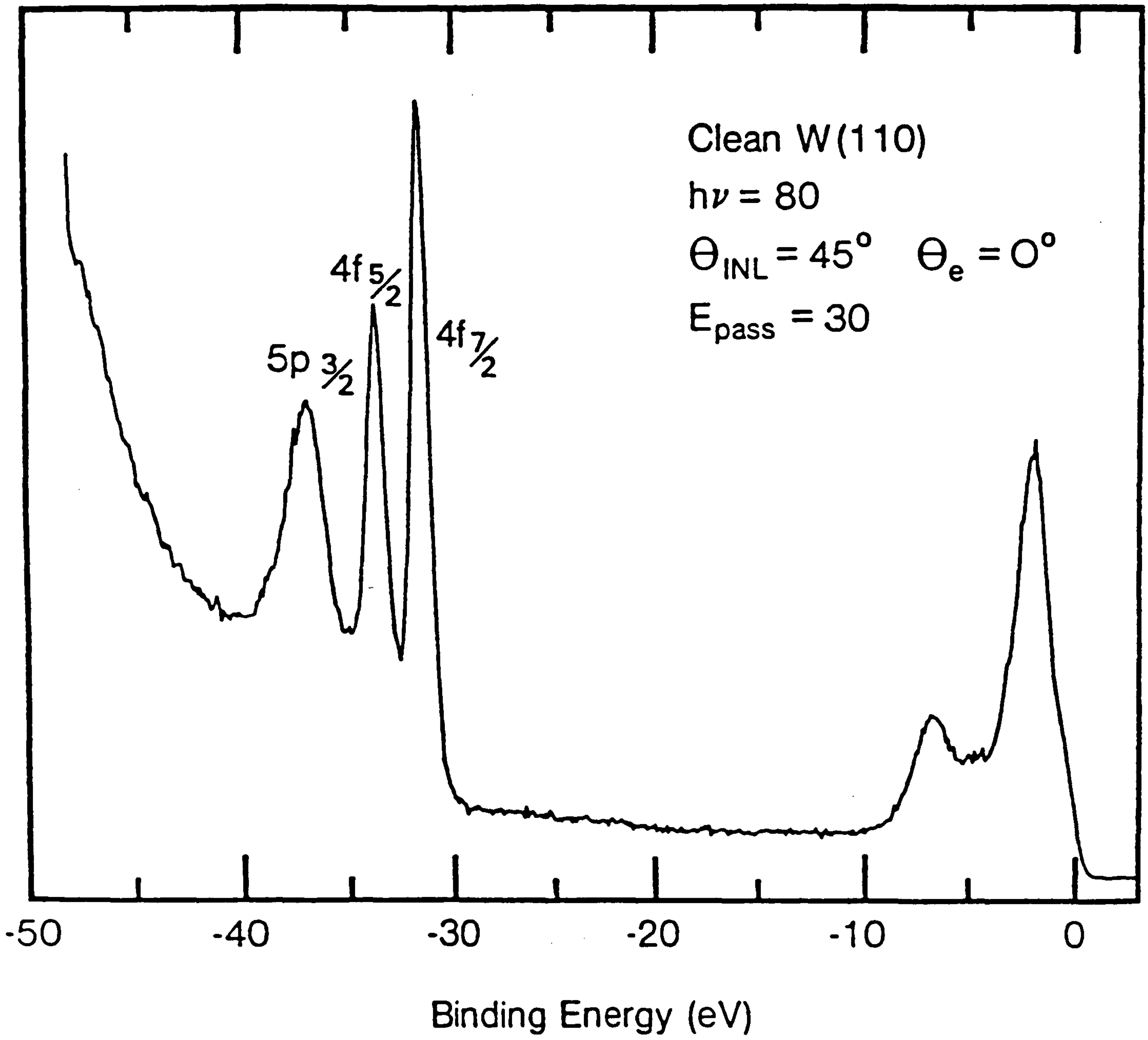
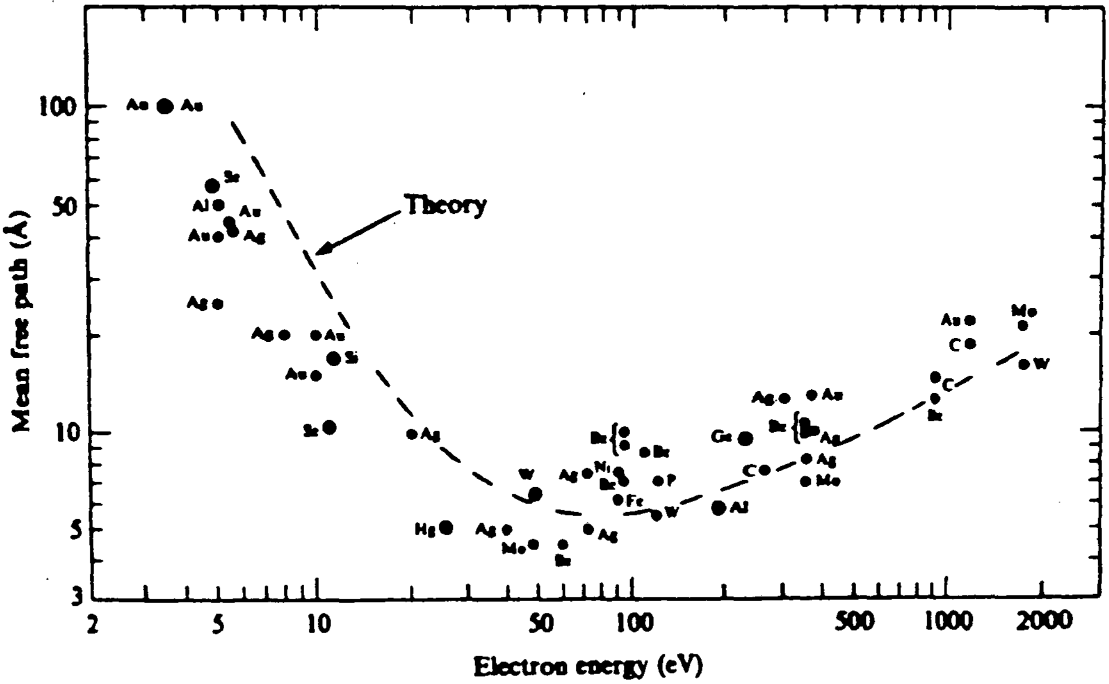

Clean W(110)
hν = 80
ΘINL = 45° Θe = 0°
Epass = 30
4f 5/2
4f 7/2
5p 3/2
-50
-40
-30
-20
-10
0
Binding Energy (eV)

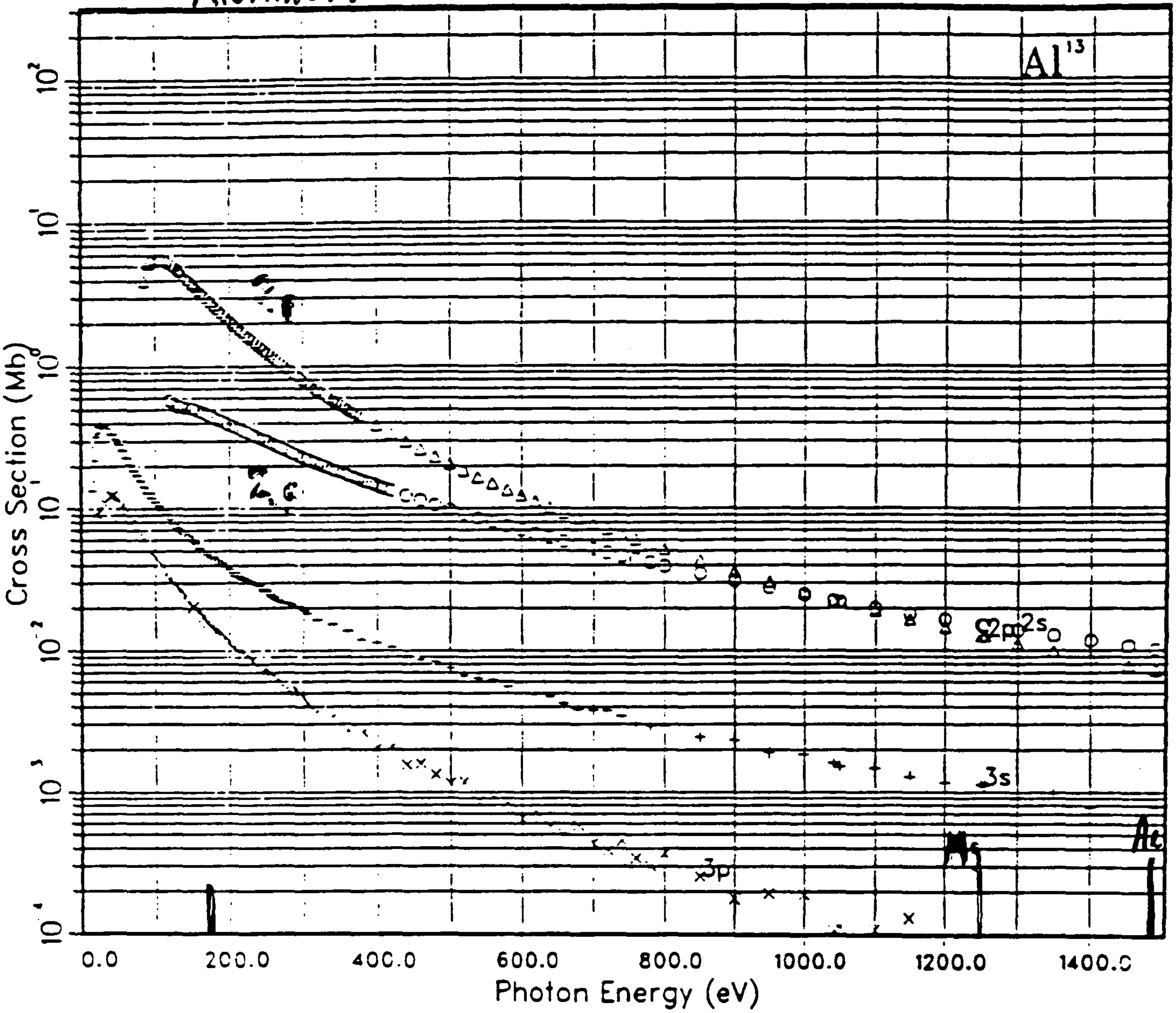
Fig. 2.1. Universal curve of electron mean free path: experiment (Rhodin & Gadzuk, 1979; Somorjai, 1981); theory (Penn, 1976).



$$\underline{\underline{KE}} = \underline{\underline{\hbar\omega}} - |E_B| - e\Phi$$

GRAPH I. Atomic Subshell Photoionization Cross Sections for 0–1500 eV, $1 \leq Z \leq 103$
See page 6 for Explanation of Graphs

Aluminum

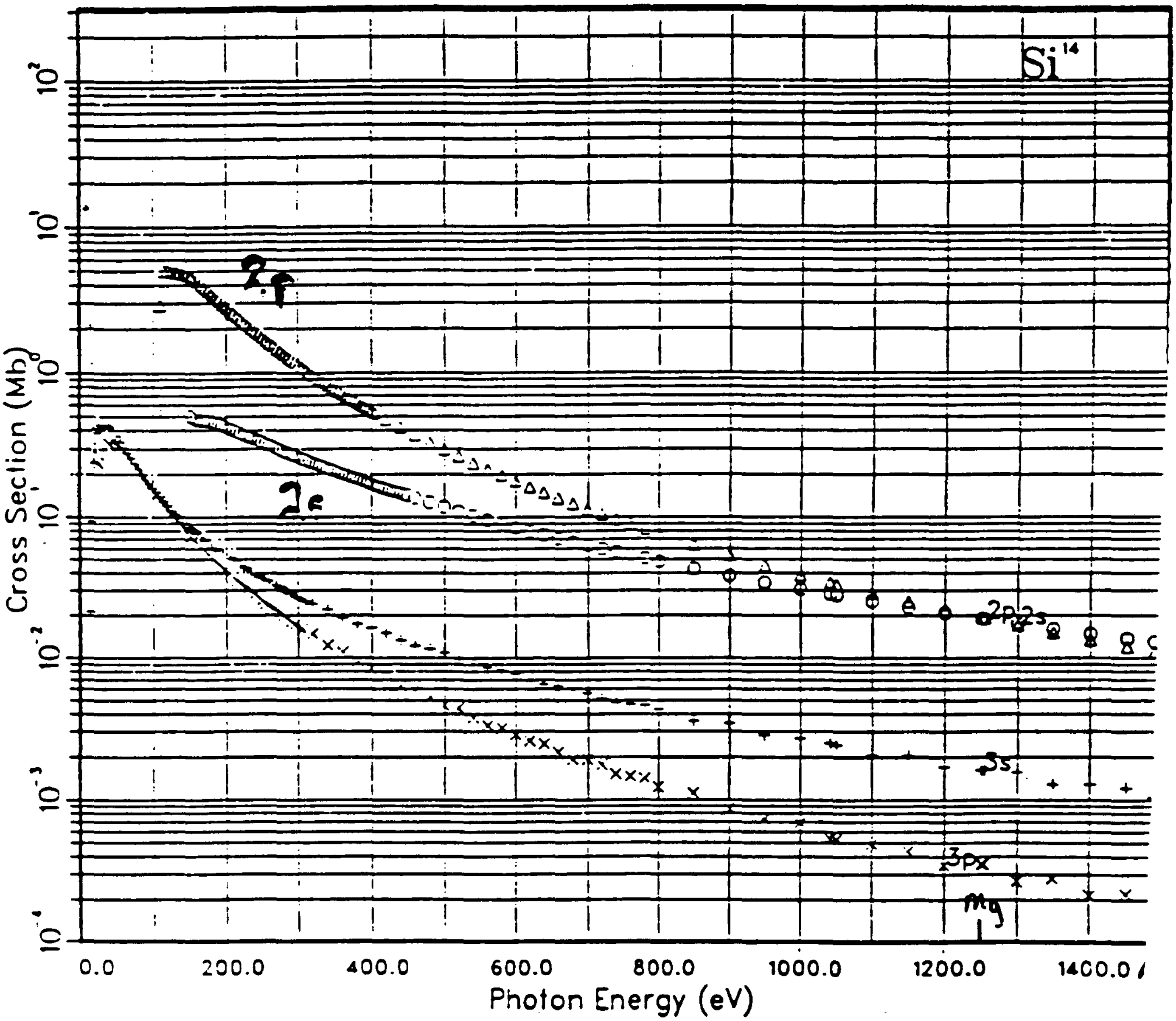


Al binding energies(eV) are:

1s(2) 1546.36
2s(2) 118.563
2p(6) 80.9076
3s(2) 10.1289
3p(1) 4.87331

GRAPH I. Atomic Subshell Photoionization Cross Sections for 0–1500 eV, 1 ≤ Z ≤ 103
See page 6 for Explanation of Graphs

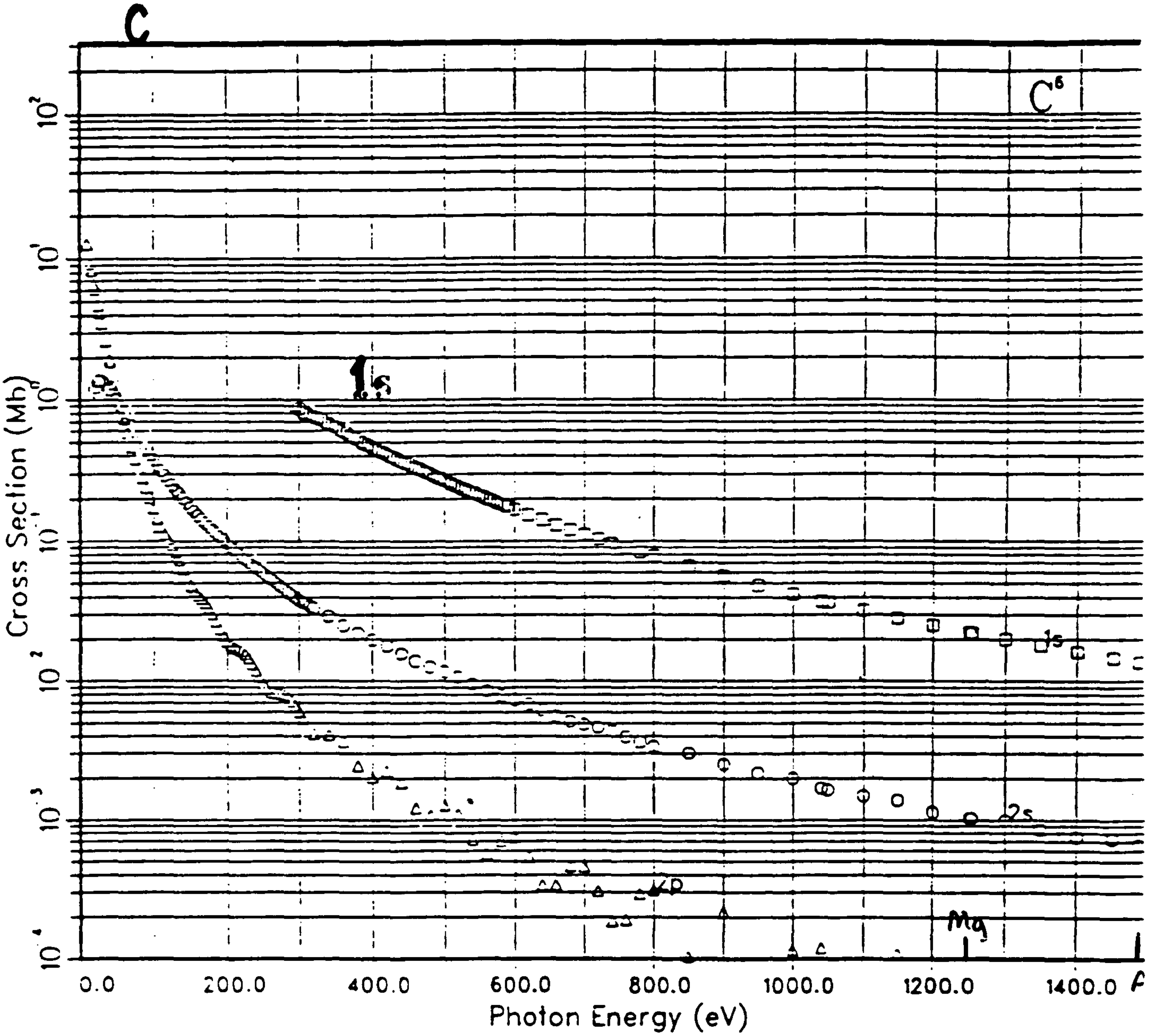
Si



Si binding energies(eV) are:

1s(2) 1823.55	2s(2) 150.847	2p(6) 108.221
3s(2) 13.5696	3p(2) 6.53176	

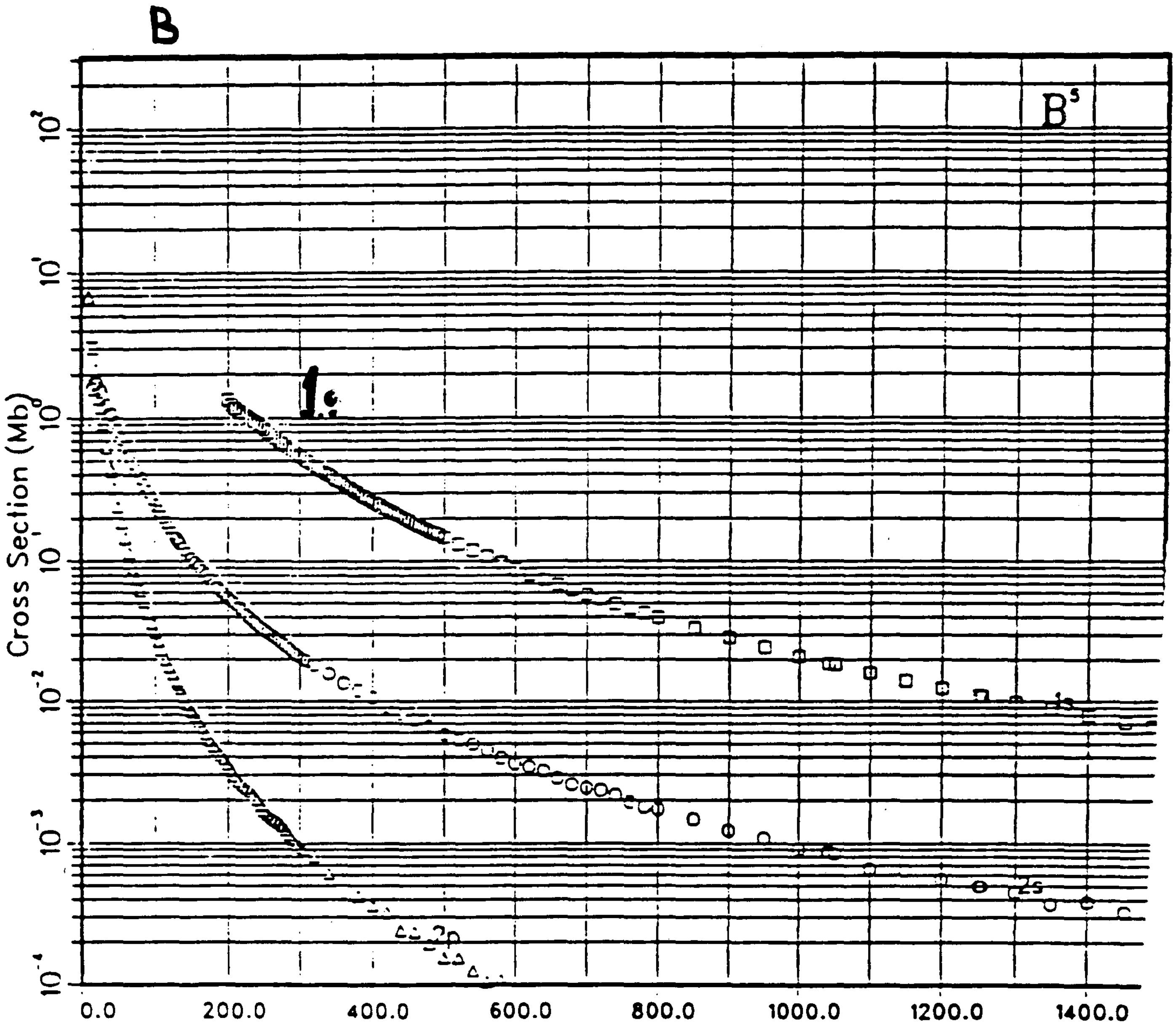
GRAPH I. Atomic Subshell Photoionization Cross Sections for 0–1500 eV, 1 ≤ Z ≤ 103
See page 6 for Explanation of Graphs



C binding energies(eV) are:

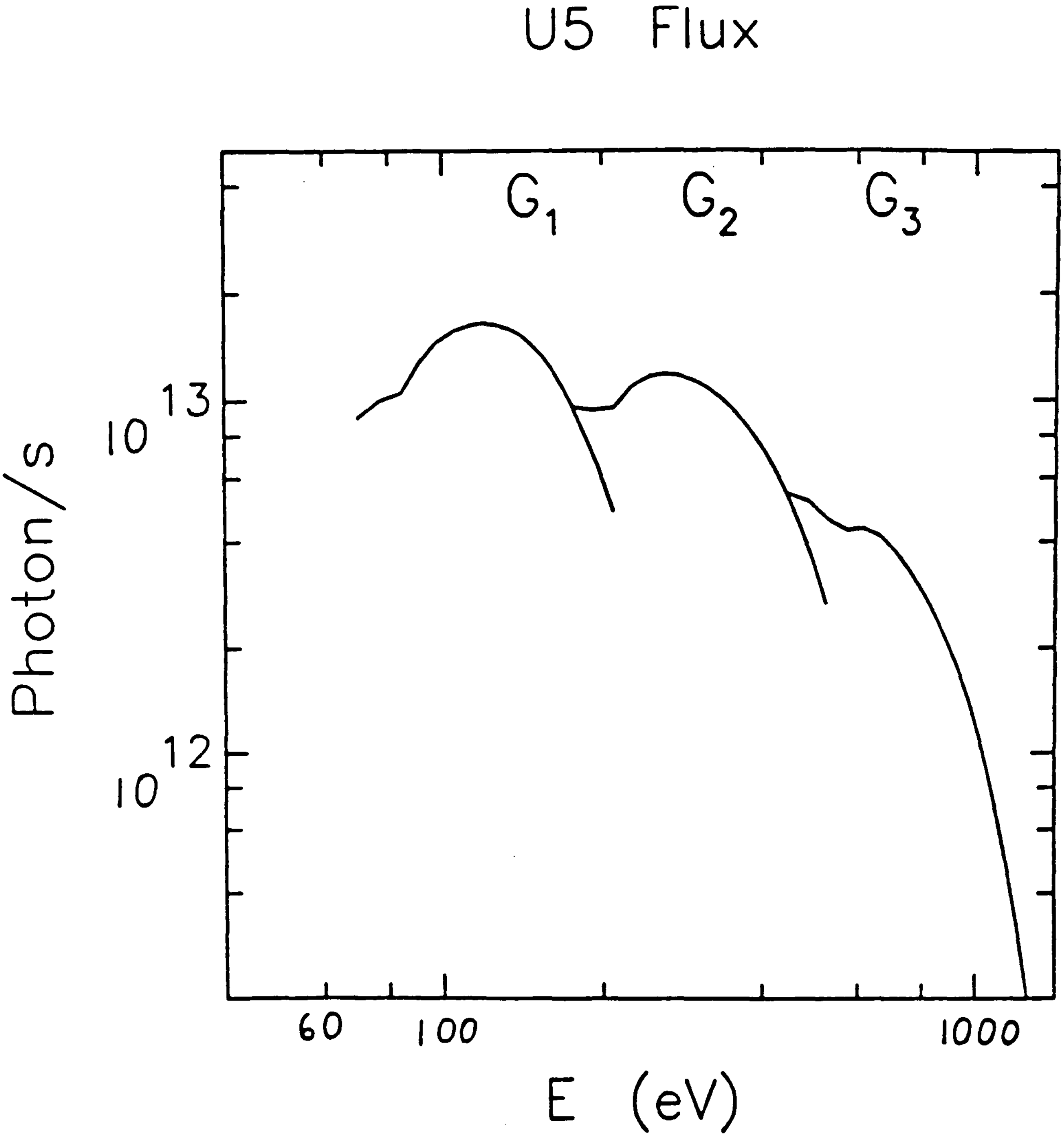
1s(2) 290.860 2s(2) 17.5409 2p(2) 8.98202

GRAPH I. Atomic Subshell Photoionization Cross Sections for 0–1500 eV, 1 ≤ Z ≤ 103
See page 6 for Explanation of Graphs



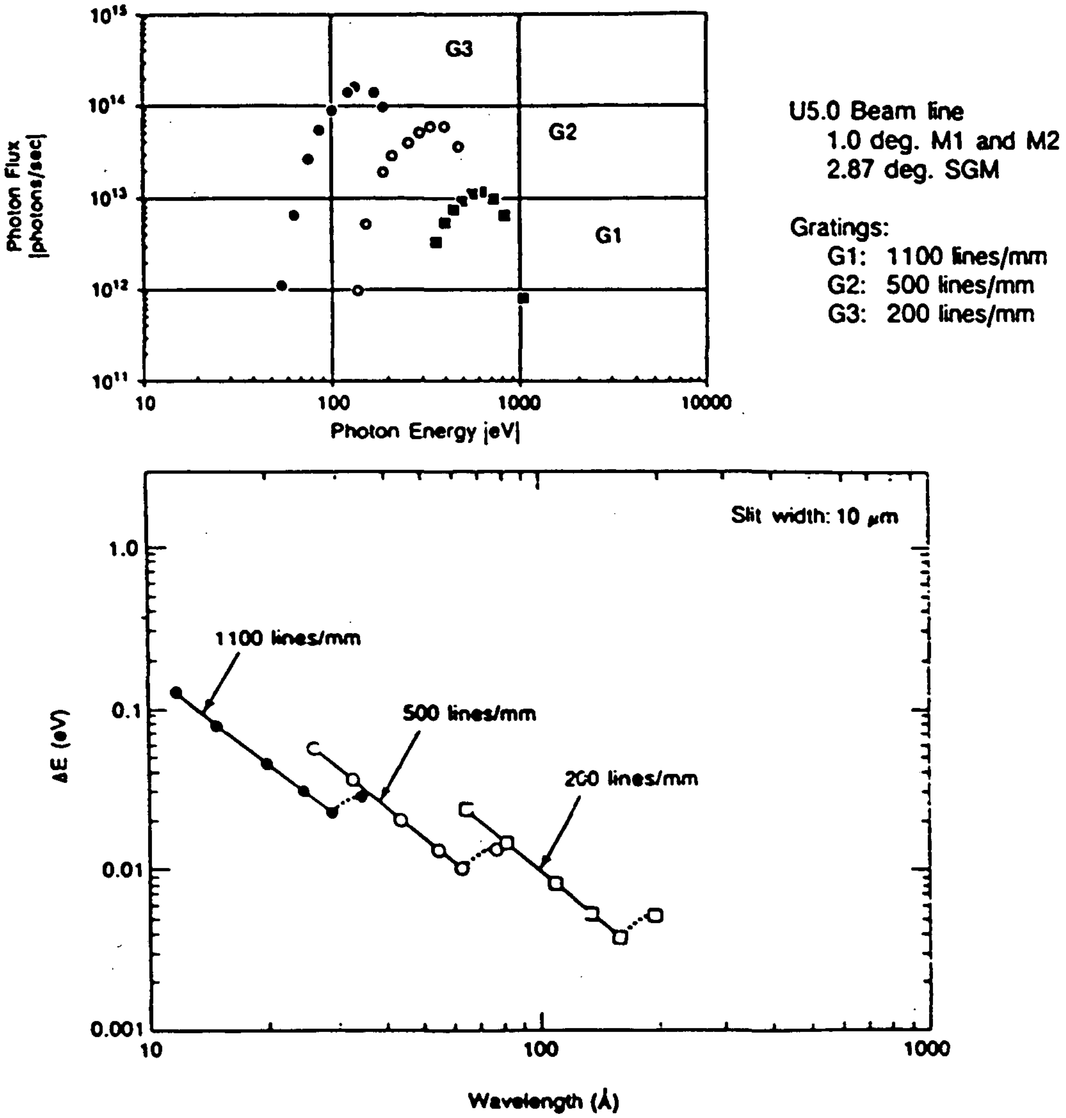
B binding energies(eV) are:

1s(2) 195.538 2s(2) 12.5683 2p(1) 6.66101



Resolved Flux

$\frac{\Delta E}{E} = 10{,}000$

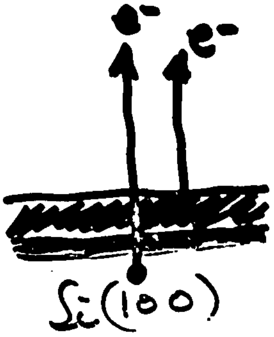


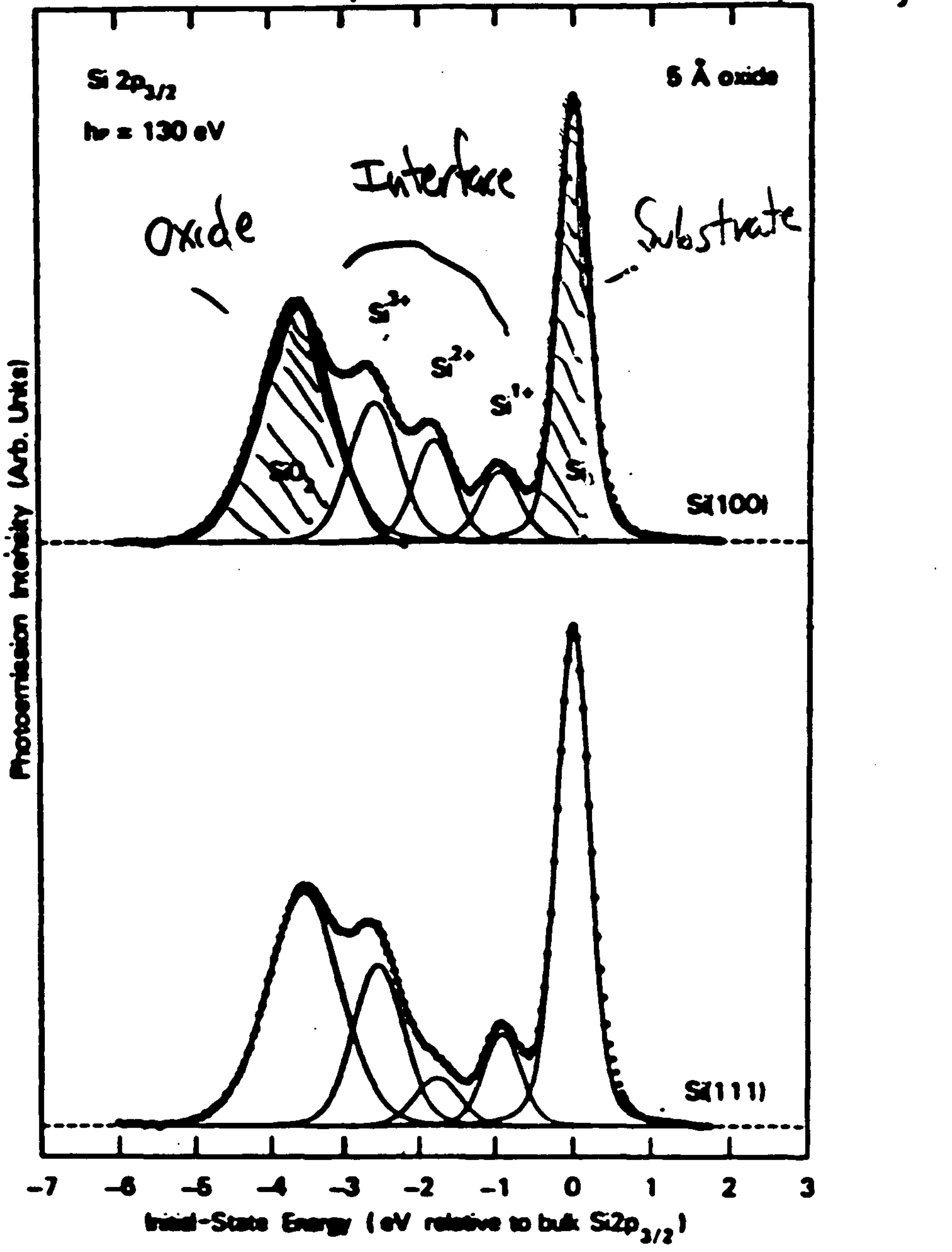
Calculated photon flux and resolution at the sample at station MicroFOCUS-I for the U5 SpectroMicroscopy Beamline. The resolved flux is for 10 μm slits, or slits matched to the diffraction limit. Dotted lines show the aberration-limited region.

ultraESCA

- Tunable energy to maximize elemental sensitivity.
- Tunable energy to vary surface sensitivity.
- Spot size below 100 micron.
- Valence band and core level spectroscopy.
- High intensity/ high resolution (below 0.1 eV throughout range).
- Polarization to identify valence orbital symmetries.
- All of this at the same time in the same place.

Himpsel, McFeeley, Taleb-Ibrahim, Yarmoff, Hollinger*





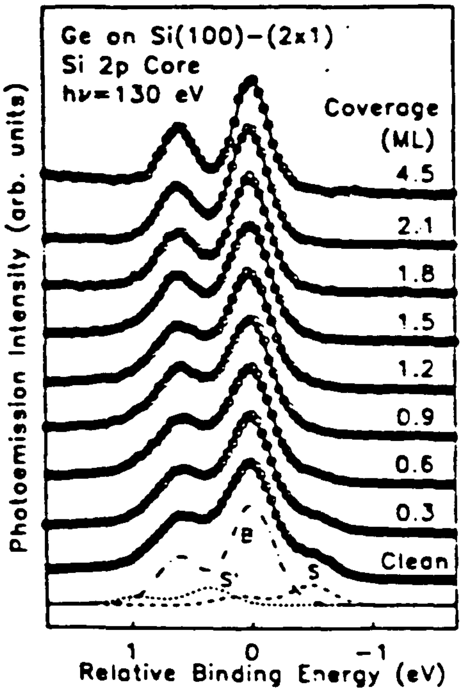
*PRB <u>38</u> 6084 (88)

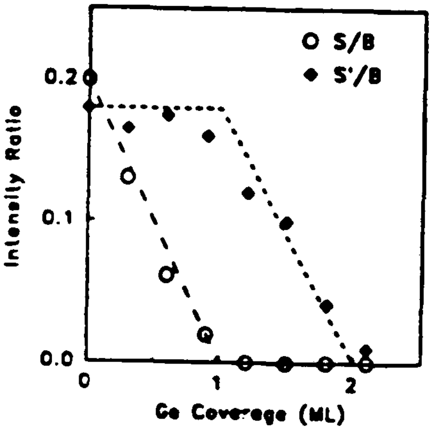
Dimer Charge Asymmetry Determined by Photoemission from Epitaxial Ge on Si(100)-(2 × 1)

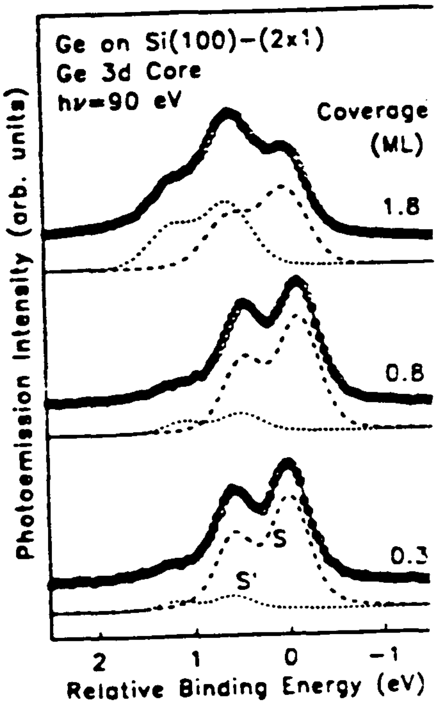
D.-S. Lin, T. Miller, and T.-C. Chiang

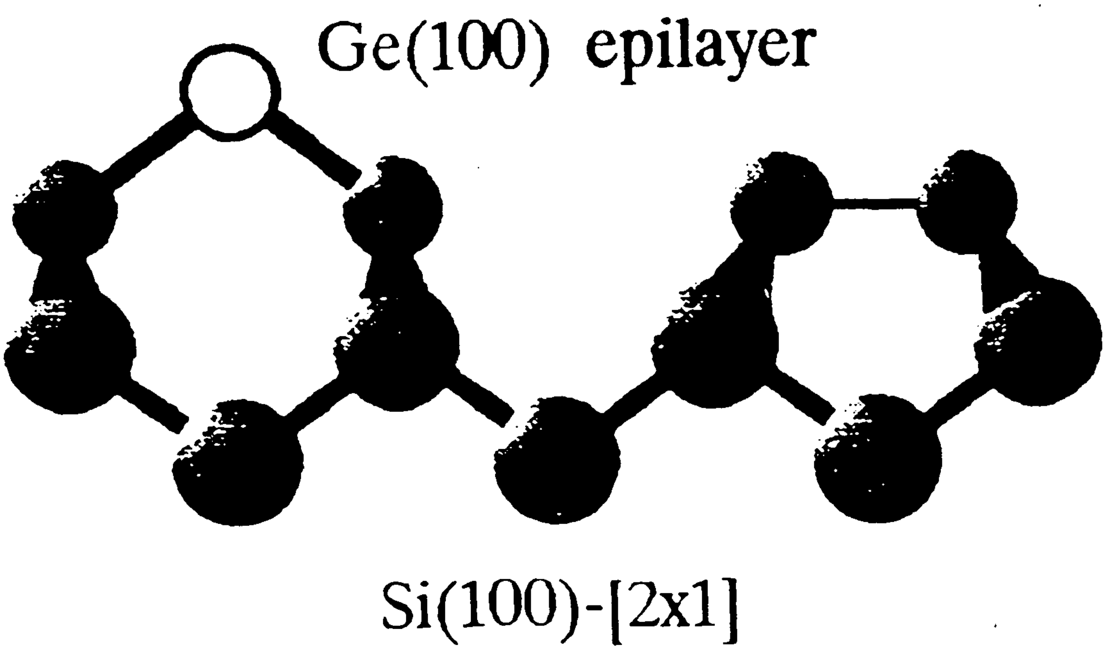
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801
and Materials Research Laboratory, University of Illinois at Urbana-Champaign,
104 South Goodwin Avenue, Urbana, Illinois 61801

(Received 21 June 1991)









ultraESCA vs. Laboratory ESCA

I. Lab Source

- Al K_α source into $\approx 4 \times 10$ mm area.
- Flux of 2×10^{13} photons/sec into 0.8 eV bandwidth.

II. ALS U5 beamline

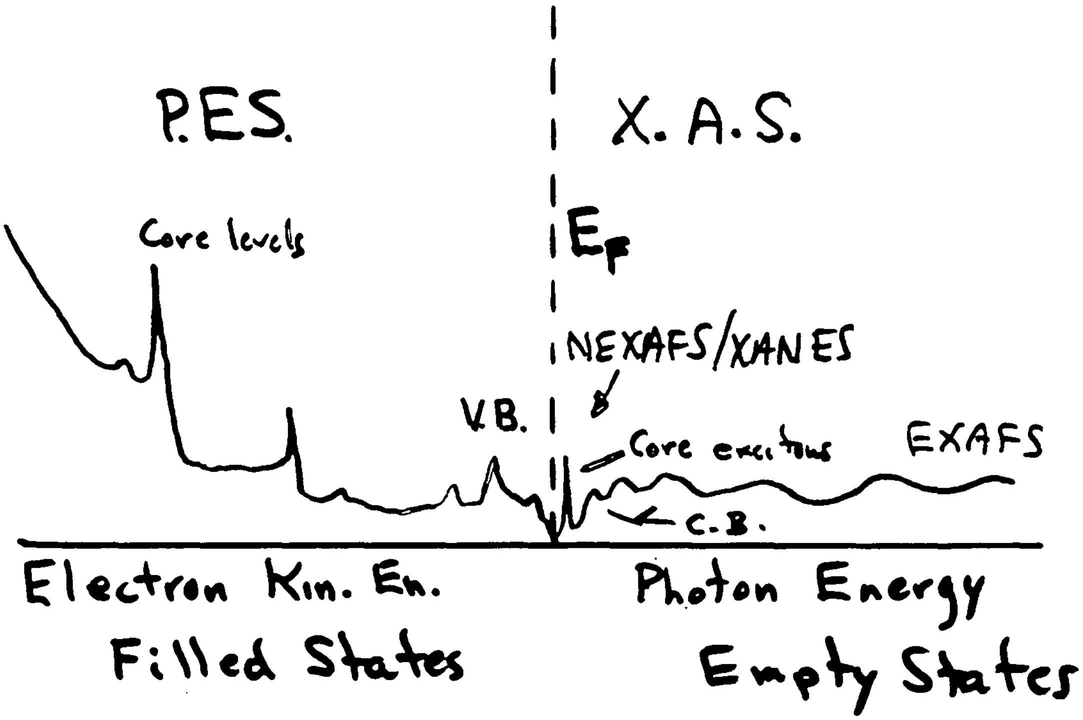
- At 100 eV, have 1.5×10^{13} photons/sec into 0.01 eV, and a 50 μm spot.
- Assuming of orde 10^{-7} yield, will have MegaHertz count rates from 50 micron areas with 10 milli-eV resolution.
- Comparable fluxes and resolutions at 1200 eV (10^{13}), but possibility for better resolution (100 meV) at this energy, and better resolution at lower energies.

III. High intensity-time resolution experiment

- Use 15 channel ESCA analyzer for parallel spectrum acquisition.
- Get 1.5×10^{14} photons/sec into 0.1 eV at 100 eV.
- Assume 10^{-7} quantum yield, 1000 counts/channel.
- Assume 10 bands of 15 channels are accumulated.
- Get 150 points with 1000 counts in **1 milli-second**.

IV. Small-area experiment

- Get 6×10^{11} photons/second at 1000 eV into 0.1 eV BW and 100 micron area.
- Gives 60 kilo-hertz count rates from this area. Implies analysis times of 10's of minutes for high statistics spectra.

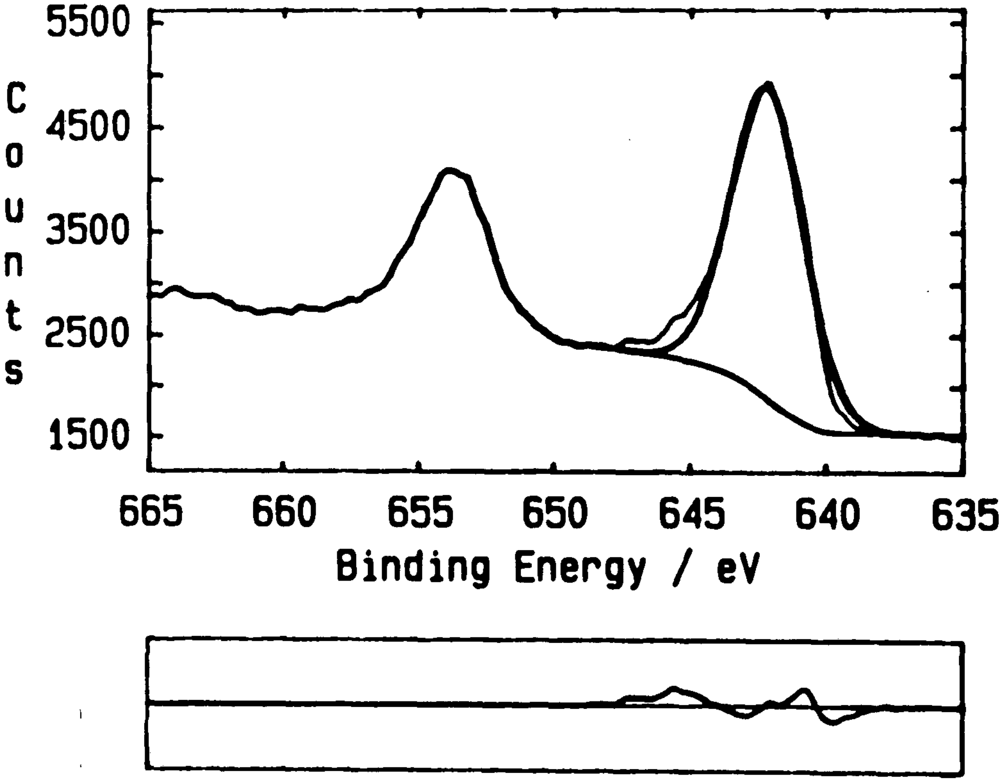


	PES	XAS
Differences:	Fixed $\hbar\omega$, scanned KE	Fixed KE, scanned $\hbar\omega$
	Filled States	Empty states
	Extreme surface sensitivity	Moderate surface sensitivity
	Degraded by insulators	Insensitive to charging problems

Commonalities:

Energy resolution to 0.1 eV
Atomic-species & chemical state specific (core-levels)
Dipole selection rules
Chemical-state structure (XAFS, PEXAFS)

		Peak Synthesis	V.G.Scientific
MA1MONO.DAT	Region 4 / 8	Level 1 / 1	Point 1 / 1



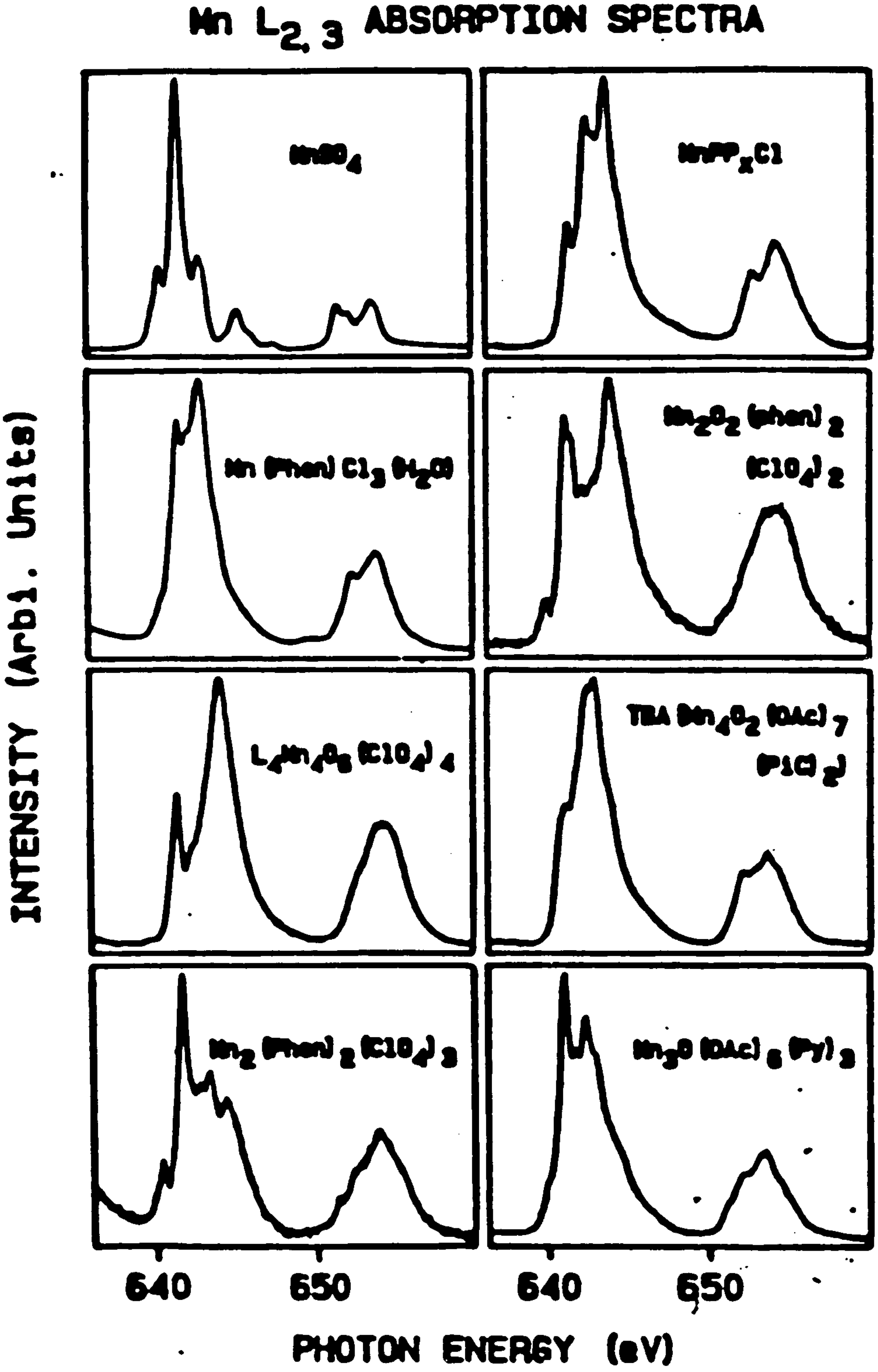
Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
1	642.2	3.23	98	20	100

100% Height (Counts) : 3071
100% Area (kceV/sec) : 1.07
Reduced Chi Squared : 5.78

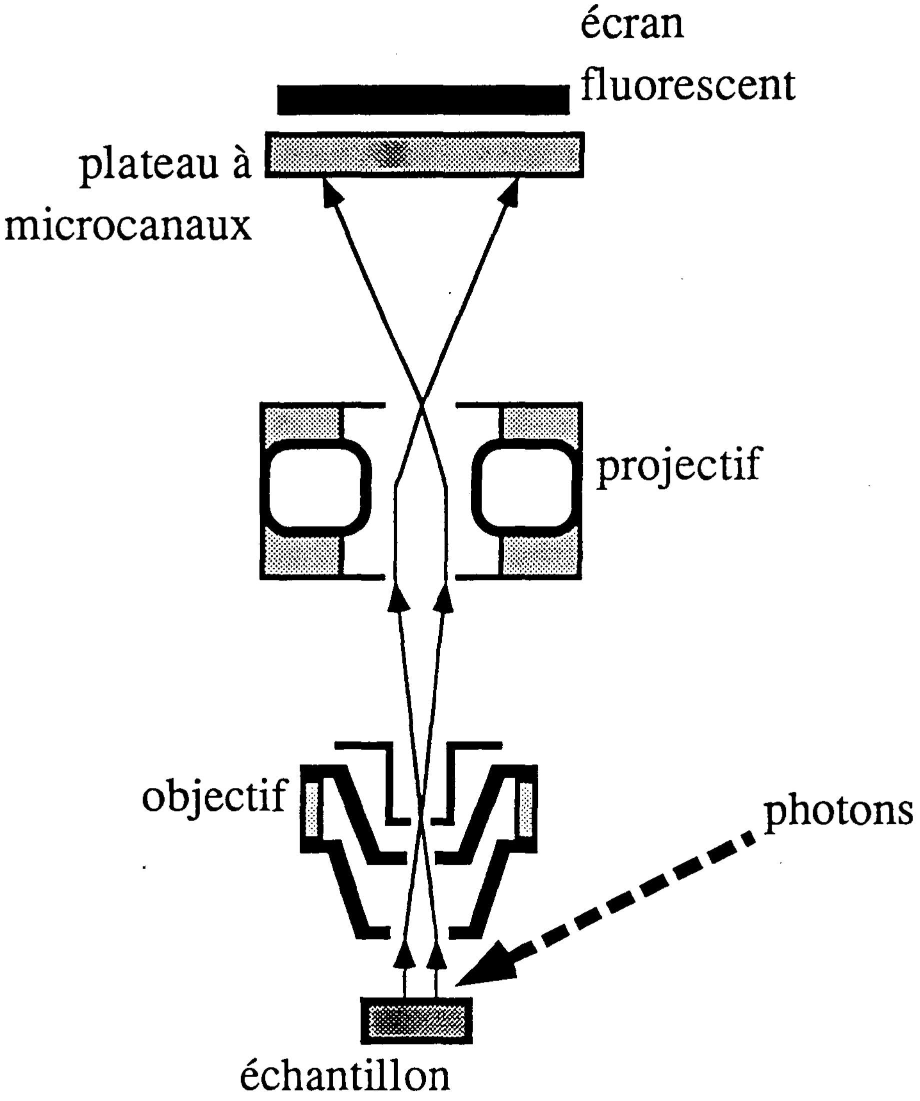
MA1 POWDER SAMPLE AS IS

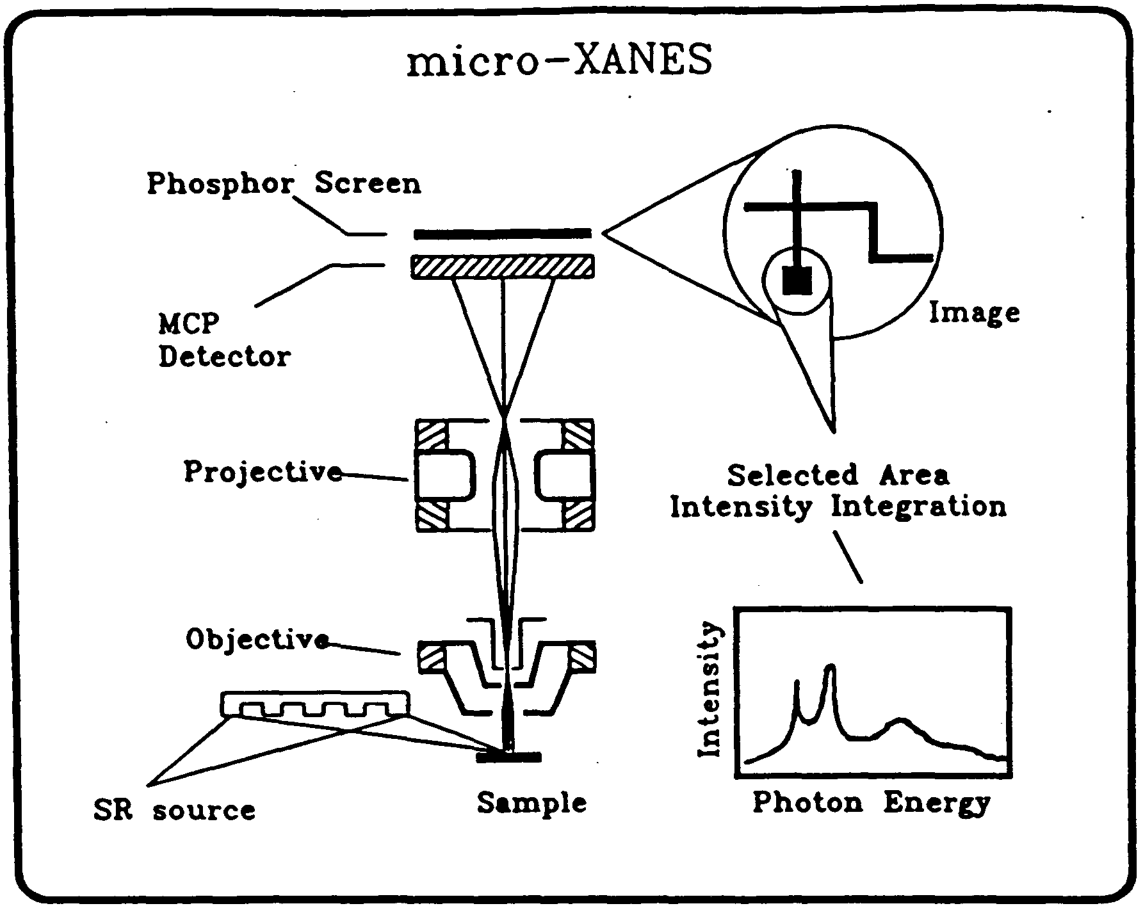
FLOOD GUN OFF

SAMPLE PRESSED INTO A WAFER

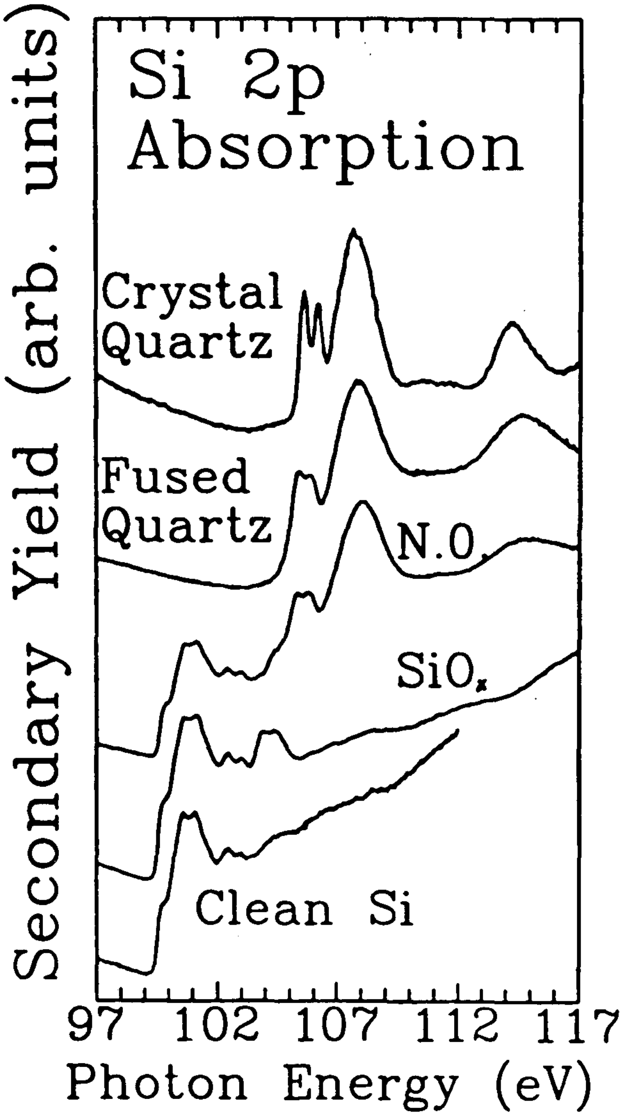

Mn L2,3 ABSORPTION SPECTRA
MnSO4
MnFPxCl
Mn(Phen)Cl3(H2O)
Mn2O2(phen)2(ClO4)2
L4Mn4O6(ClO4)4
TBA Mn4O2(OAc)7(PiC)2
Mn2(Phen)2(ClO4)3
Mn3O(OAc)6(Py)3
INTENSITY (Arbi. Units)
640
650
640
650
PHOTON ENERGY (eV)

Microspectroscope Tonner



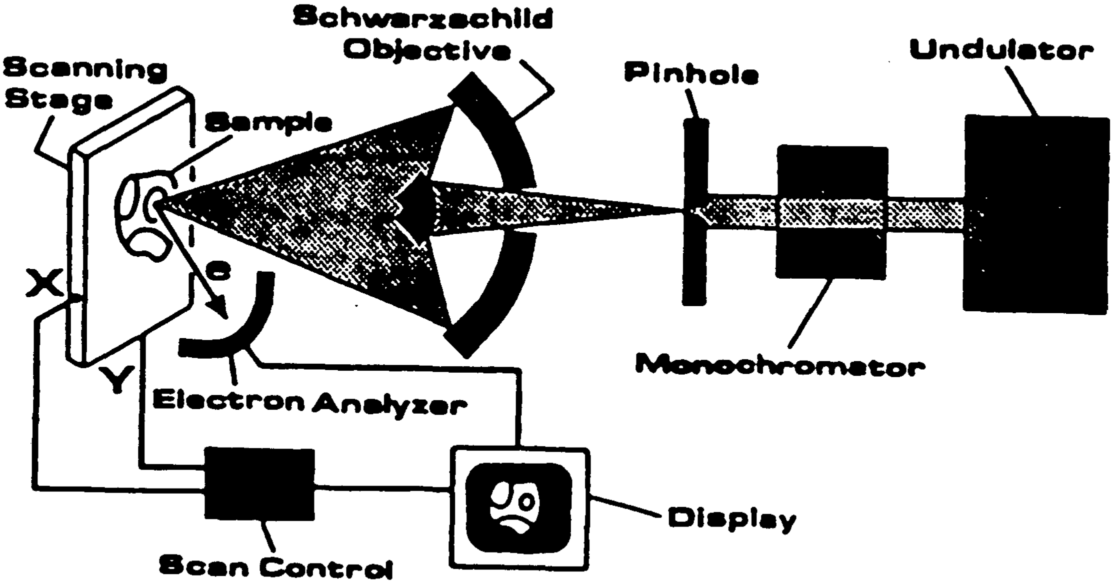

micro-XANES
Phosphor Screen
MCP
Detector
Image
Projective
Selected Area
Intensity Integration
Objective
Intensity
SR source
Sample
Photon Energy

μXANES
G.R. Harp & B.P. Tonner

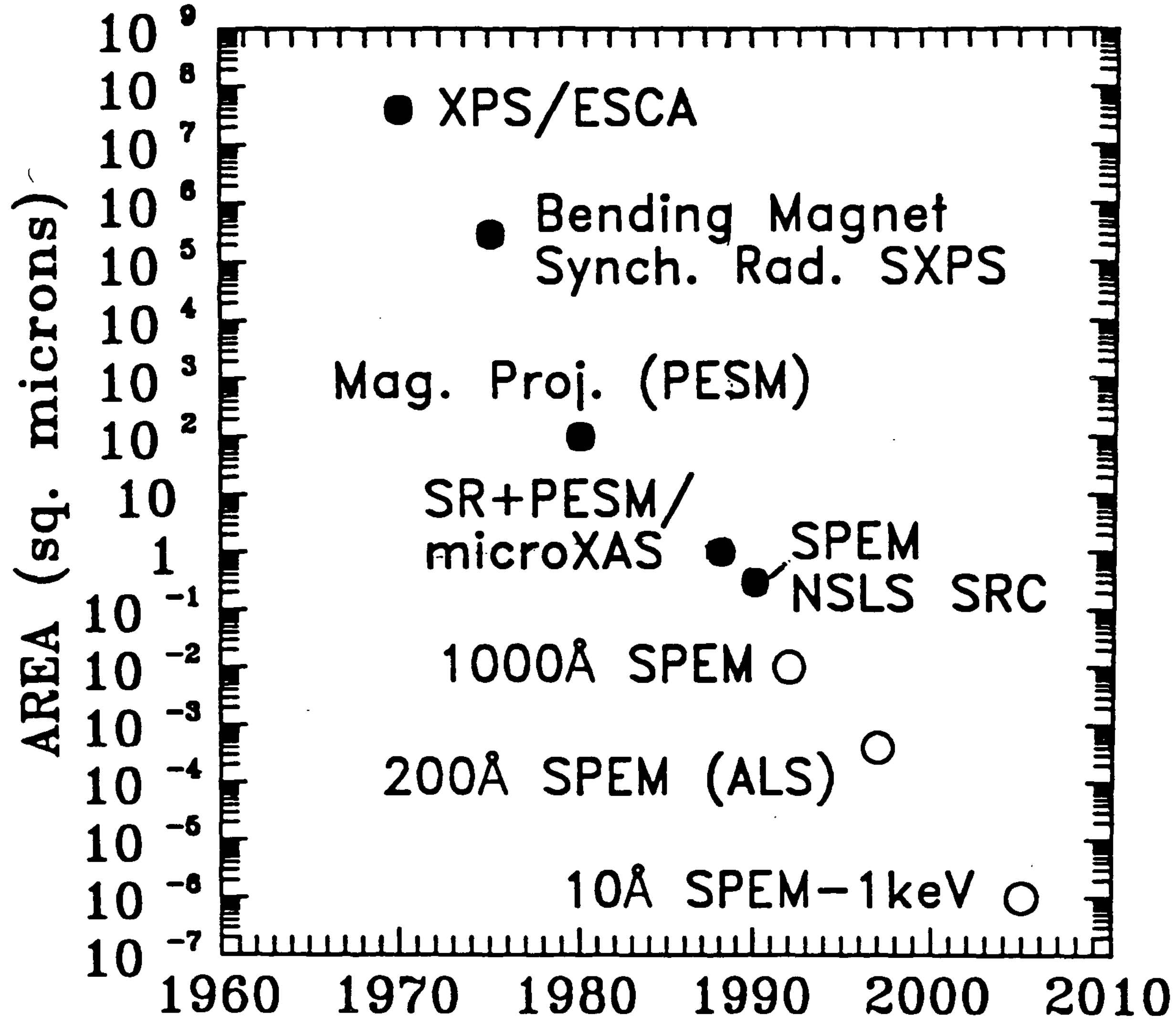


X-ray Absorption Microscopy

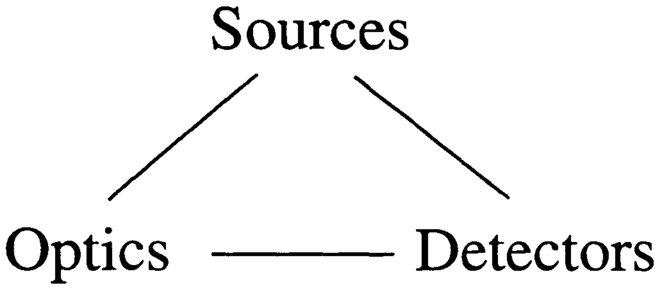
- High sensitivity (secondary yield)
- Spectral resolution of order 0.1 eV
- Spatial resolution limit near 10 nm.
- Compatible with non-UHV processing
- XANES and SEXAFS
  (chemistry and atomic structure)
- Sampling depth is "near surface"


Schwarzschild Objective
Scanning Stage
Sample
Pinhole
Undulator
X
Y
e
Electron Analyzer
Monochromator
Display
Scan Control

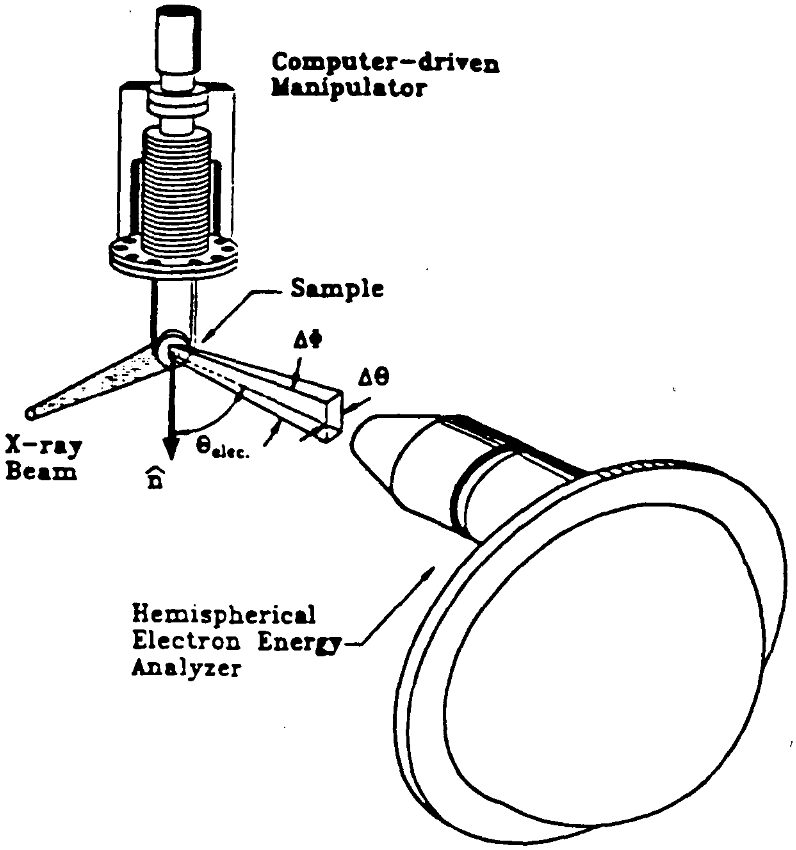
Photoemission Microscopy Spatial Resolution over Time



10^7 improvement in 20 years

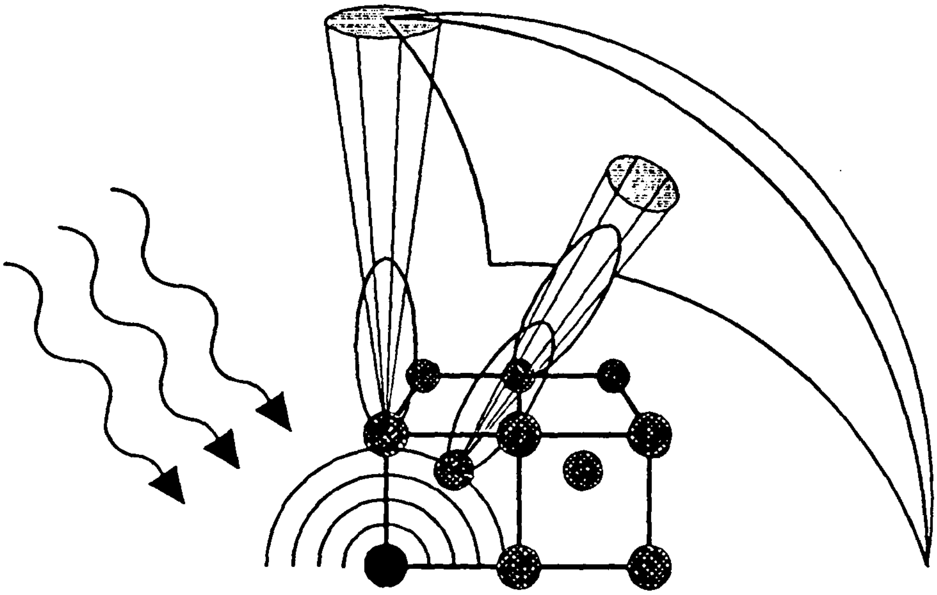

Sources

Optics —— Detectors

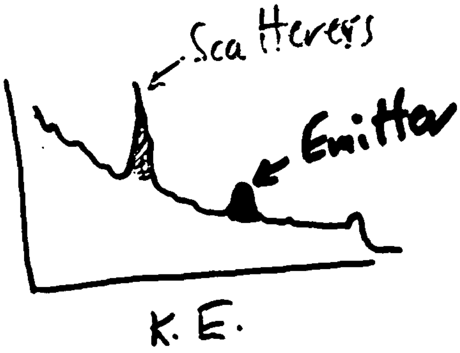


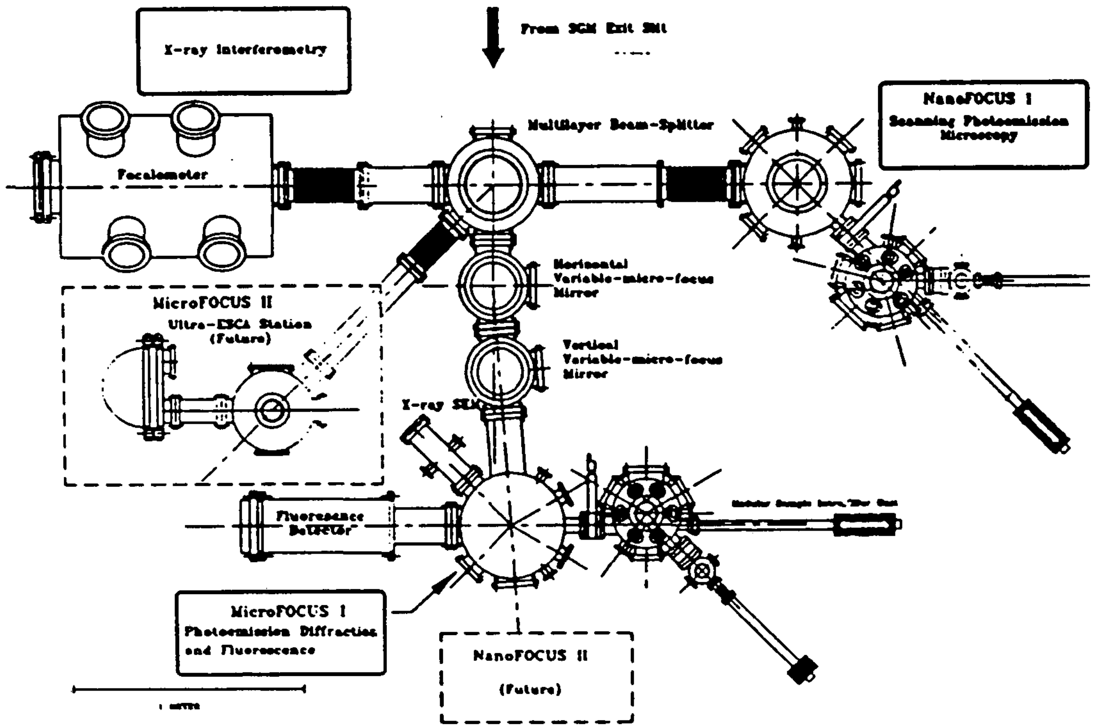
Idealization of the experimental geometry, which maintains a fixed angle between the incident X-ray beam and the ejected electron ($\Theta_{photon}+\Theta_{electron} = \Gamma = const$). For each crystal azimuth (Φ), the electron polar angle (Θ_{el}) is scanned by rotating the sample normal ($\hat{n}$). In practice, the incident X-ray beam illuminates the entire sample surface, and the detector accepts a small solid-angle ($\Delta\Theta\Delta\Phi$) around the emission direction (see text for details).

Photoemission Holography
in
Forward-scattering Geometry



- Buried atoms
- Probes the "core"
- Distinguish emitter by chemical state





ALS-U5.0

Layout of the SpectroMicroscopy Facility, showing the Multilayer X-ray Multiplexer, Variable-focus Mirrors, and 5 Experimental Stations. This drawing is not to scale: the distances from the central axis to the focal point (sample) will be larger in the actual installation.

Advanced Light Source SpectroMicroscopy Facility

Next Generation Source

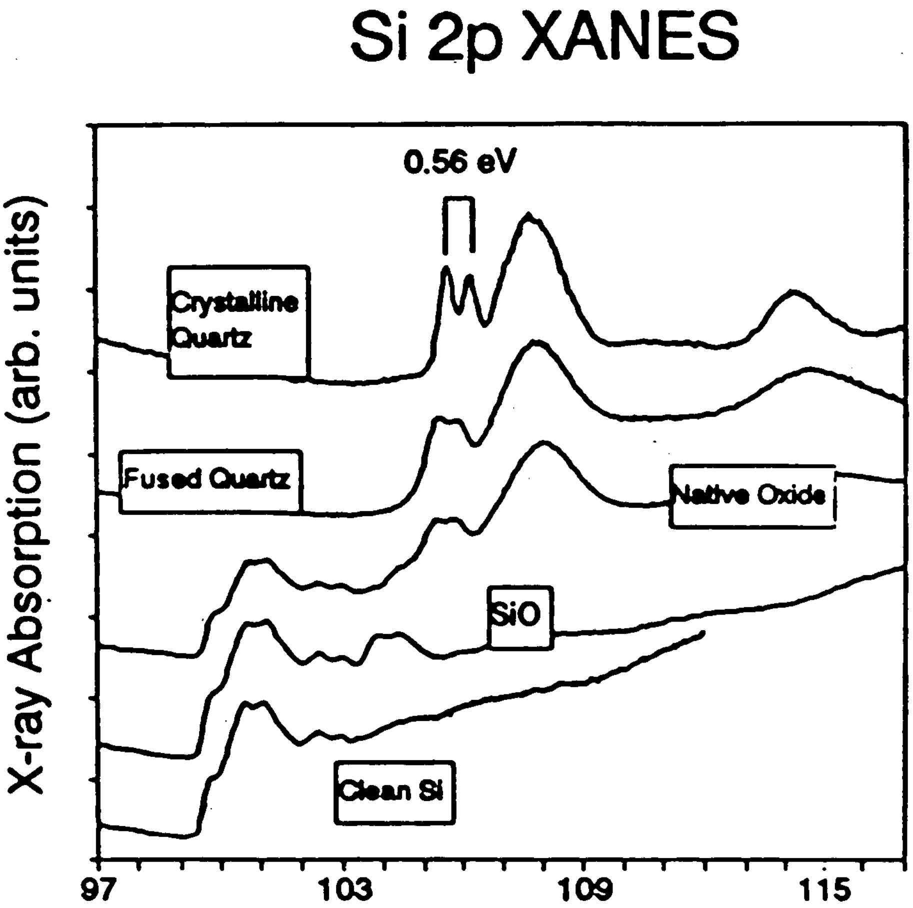
U5 100-1500 eV Soft X-ray undulator

Next Generation Monochromator

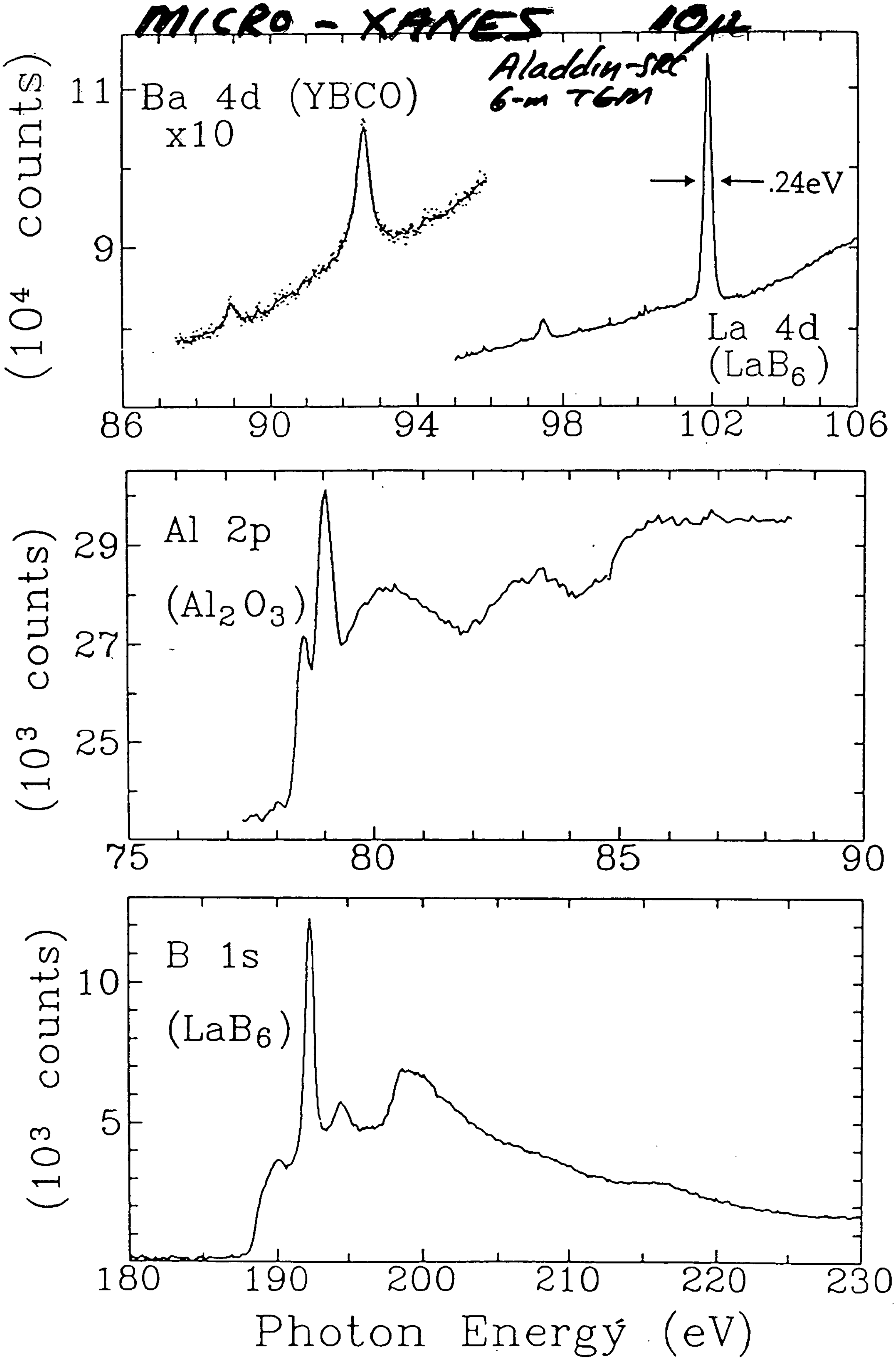
Water-cooled optics small-spot SGM

Next Generation Detectors

Dual-stage diffraction limited microscopes,
Ultra-ESCA XPS diffractometers


Si 2p XANES
0.56 eV
Crystalline Quartz
Fused Quartz
Native Oxide
SiO
Clean Si
X-ray Absorption (arb. units)
97
103
109
115

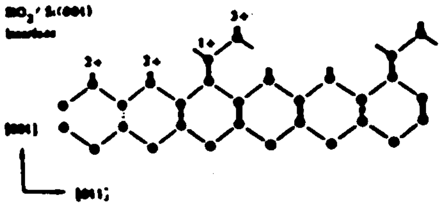
MICRO - XANES 10μ



Aladdin-SRC
6-m TGM

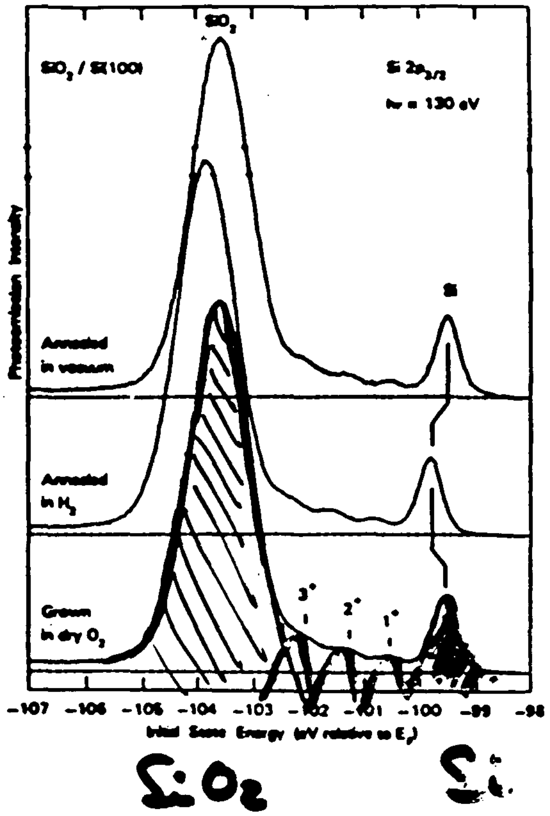
F. J. Himpsel and J. A. Yarmoff

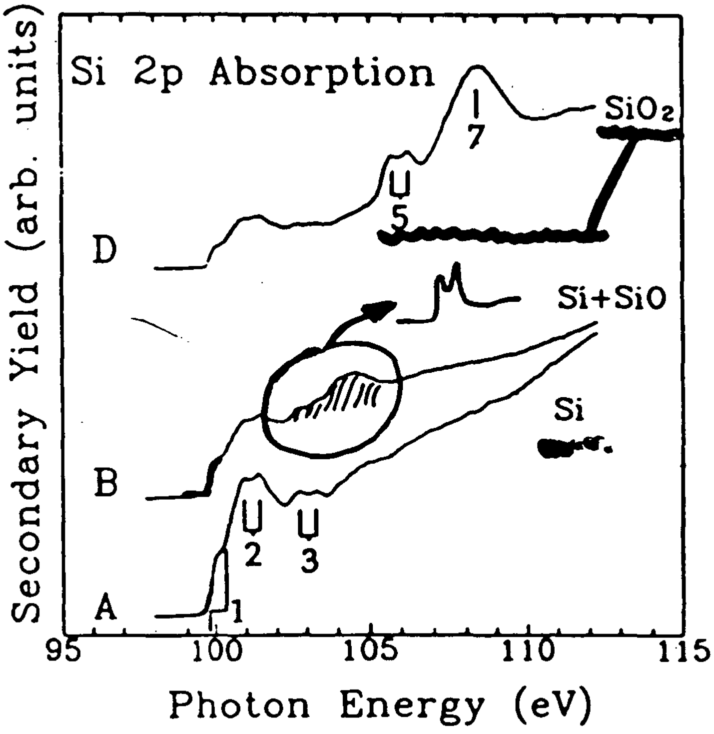
IBM Research Division, IBM T. J. Watson Research Center
Box 218
Yorktown Heights, NY 10598

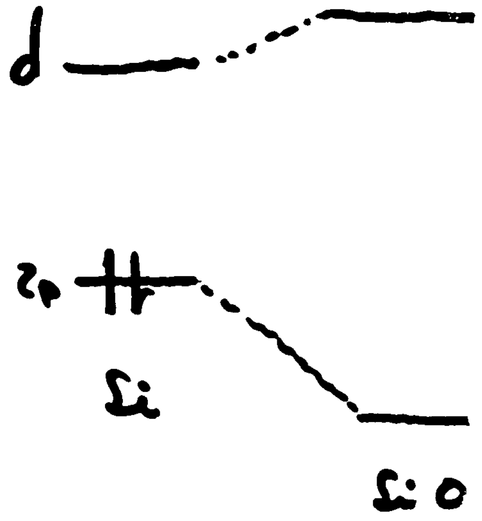


(Above) Structural model for the SiO^2/Si(001) interface derived from core level spectroscopy. The amorphous SiO^2 network (not shown) connects to the broken bonds.

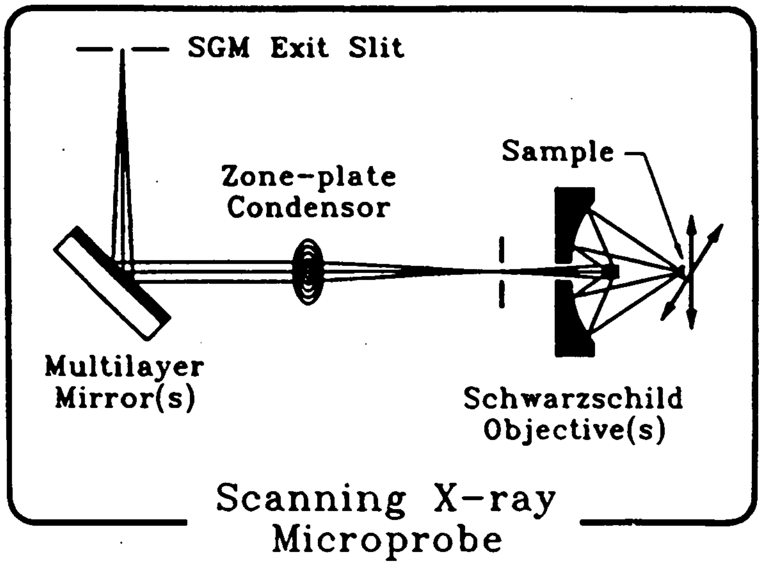
(Right) Distribution of oxidation states at the SiO^2/Si(100) interface. Annealing in hydrogen does not change the distribution but moves the Fermi level to an unpinned position.



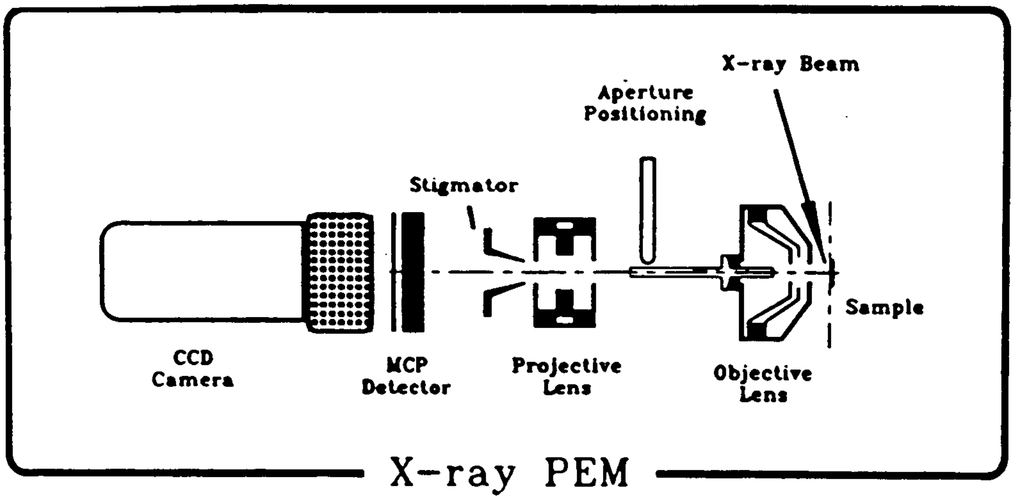




ΔE of XAS
is smaller than PES
⇒ resolve spin-orbit

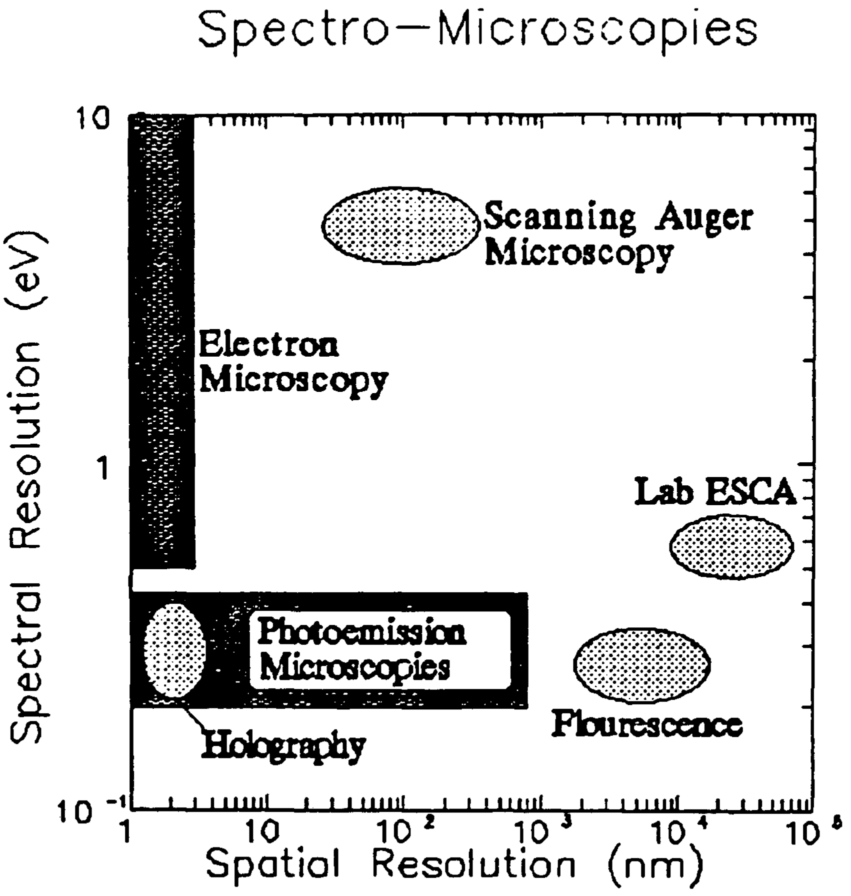


Scanning X-ray Microprobe



X-ray PEM

Schematics of two detectors for the SpectroMicroscopy Facility. A scanning X-ray microprobe using a two-stage condensing optical system with zone-plates and Schwarzschild objectives is shown, as well as a parallel-imaging electron optics based X-ray secondary-electron microscope.


Spectro–Microscopies
10
1
10 ⁻¹
Spectral Resolution (eV)
1
10
10 ²
10 ³
10 ⁴
10 ⁵
Spatial Resolution (nm)
Scanning Auger Microscopy
Electron Microscopy
Lab ESCA
Photoemission Microscopies
Holography
Flourescence

High-Resolution (20 nm) XPS and XANES with the ALS

H. Ade

SUNY/Stony Brook

Nano XPS and XANES imaging with Synchrotron Radiation

Harald Ade, Chen-Hao Ko, and Janos Kirz

SUNY @ Stony Brook

Steven L. Hulbert and Erik D. Johnson

National Synchrotron Light Source, BNL

Erik Anderson

Center for X-Ray Optics, LBL

Dieter Kern

IBM, T.J. Watson Research Center

C. Jacobsen, S. Williams, S. Lindaas, X. Zhang

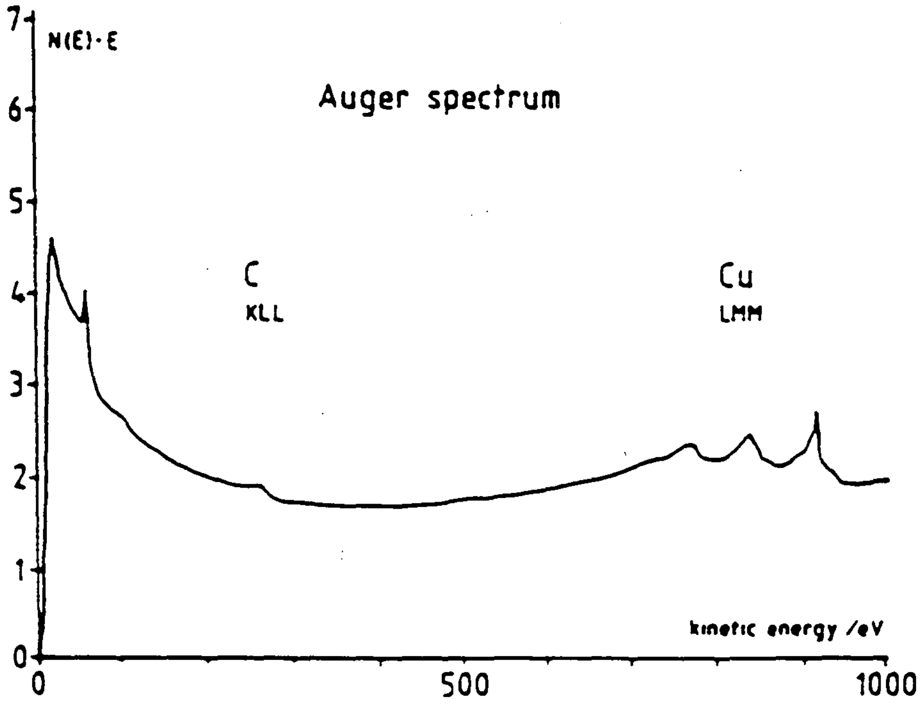
SUNY @ Stony Brook

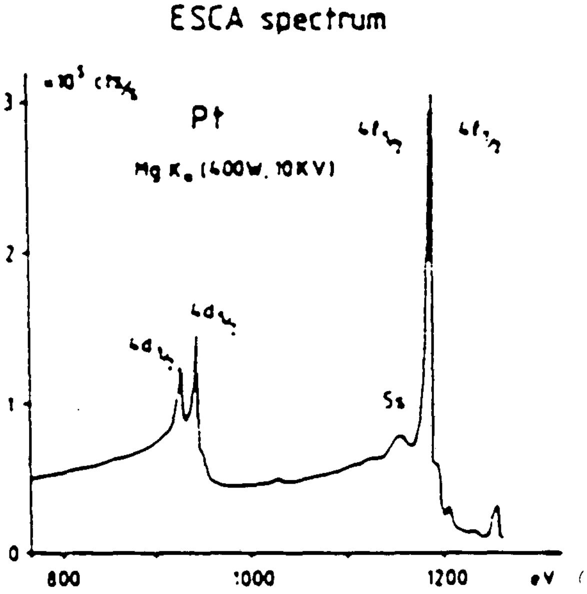
Outline

- Motivation: why tunable X-rays?
- Approaches to Spectromicroscopy
- First results with the X1-SPEM
- C-XANES imaging of polymers with X1-STXM
- Future at the ALS in context with lab instruments

Some issues.

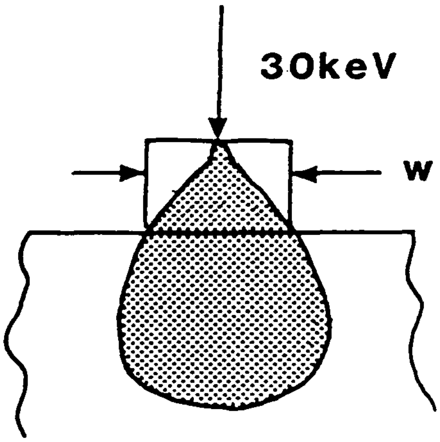
- damage (micro- and macroscopic): S/N, detection efficiency
- Chemical sensitivity: energy resolution
- Quantification
- Matrix effects (BSF, edge enhancement in SAM)
- Spatial resolution
- Charging (always possitive with photons)
- Control over surface sensitivity (tunable x-ray source)

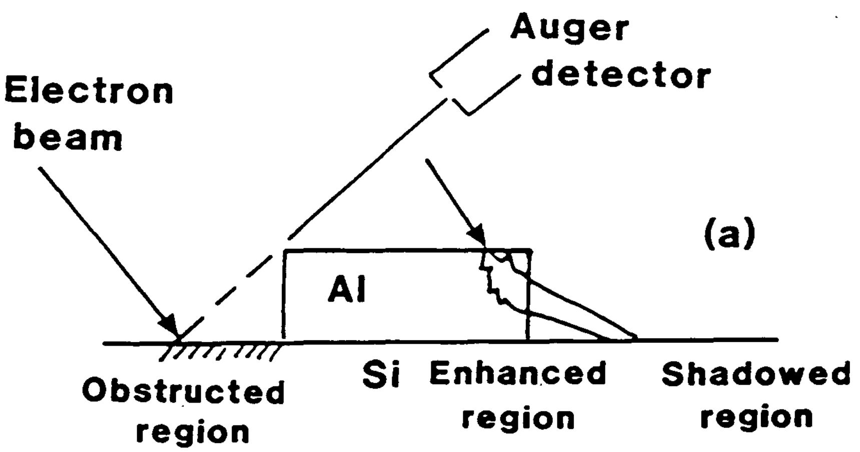




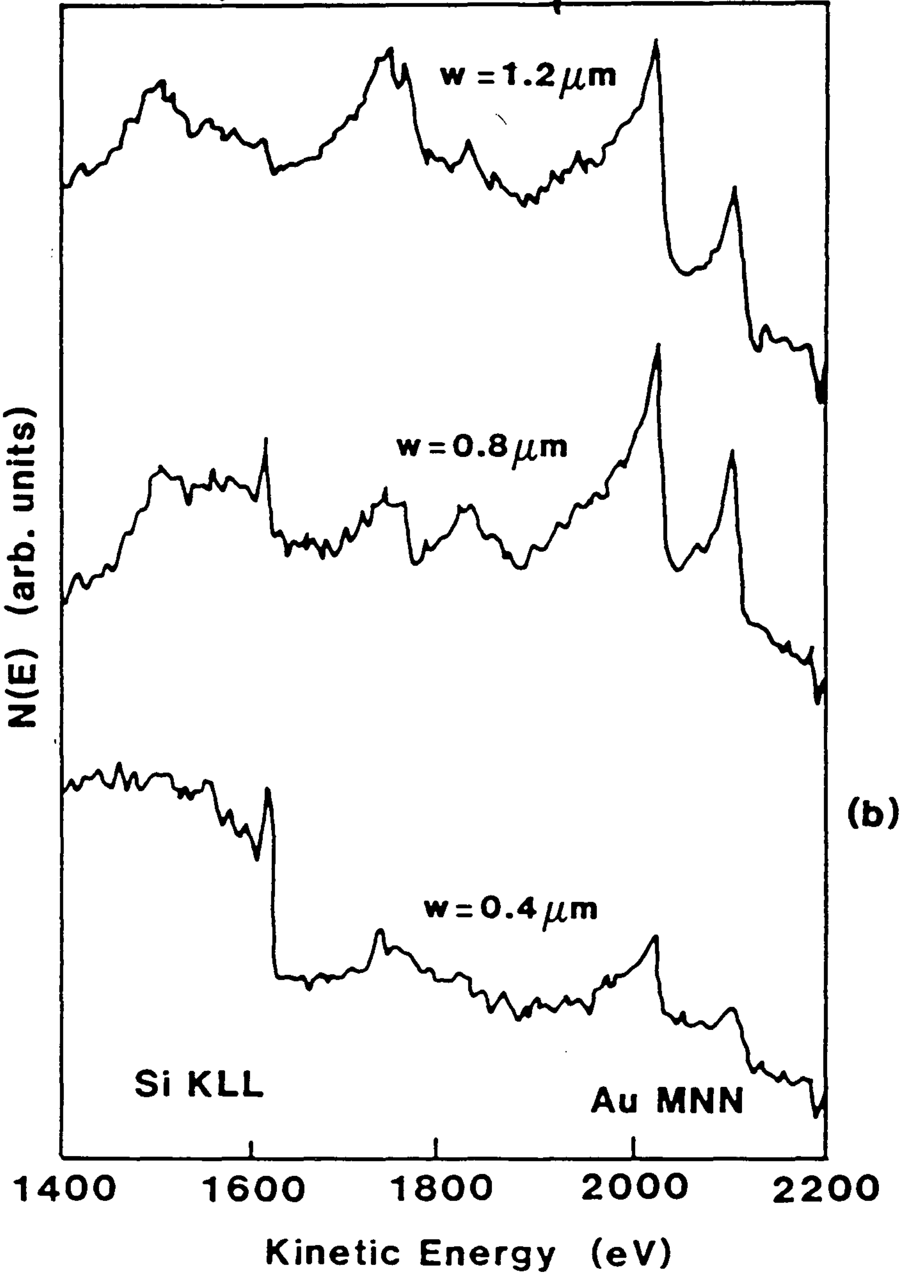
S/B → damage
→ min det. concentr.
→ quantification
→ data ~~aq~~acquisition

Prutton et al
SIA March '92





Umbach et al Surf. Int. Ana 14 (1989)



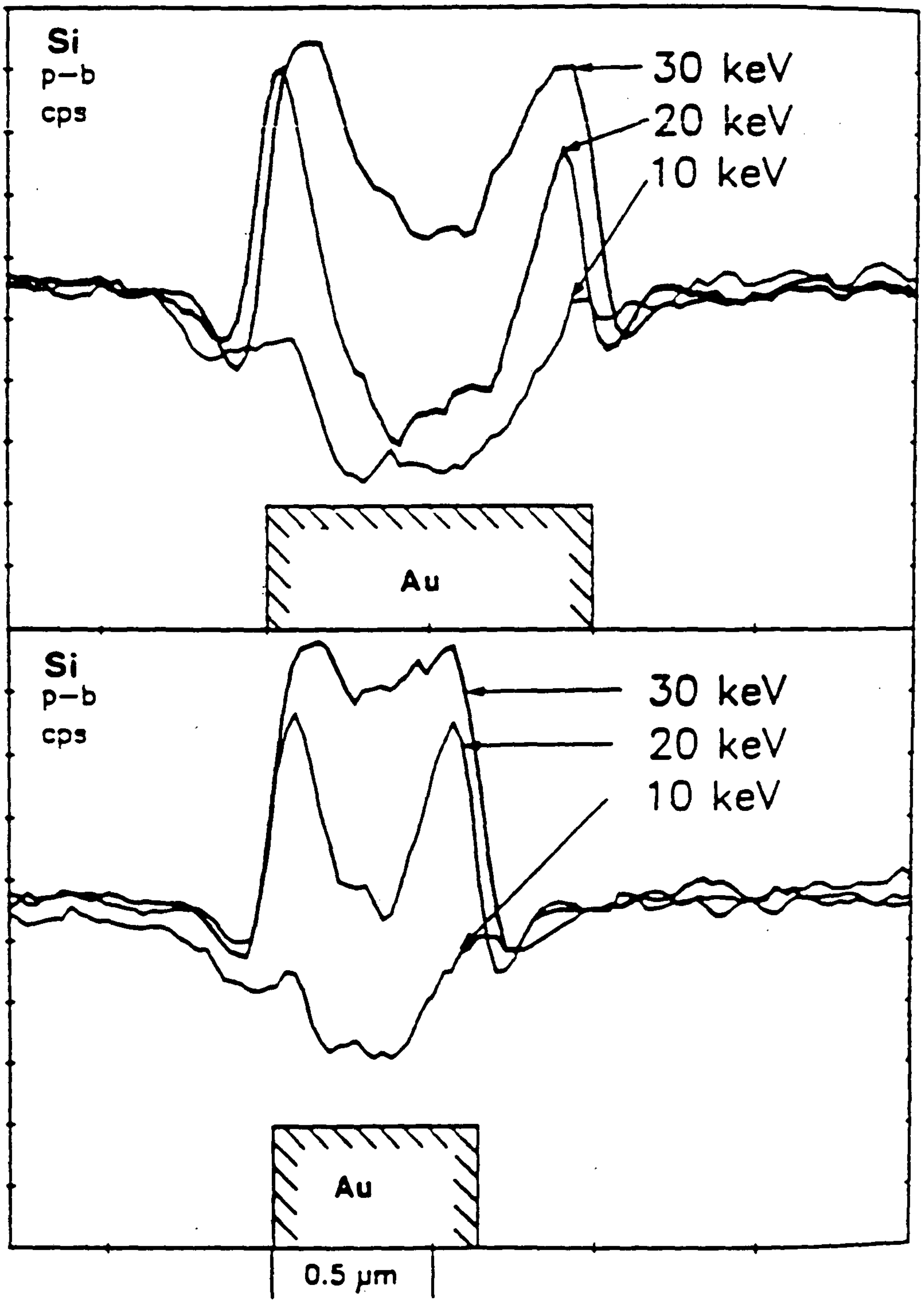
Signal comes from

80%

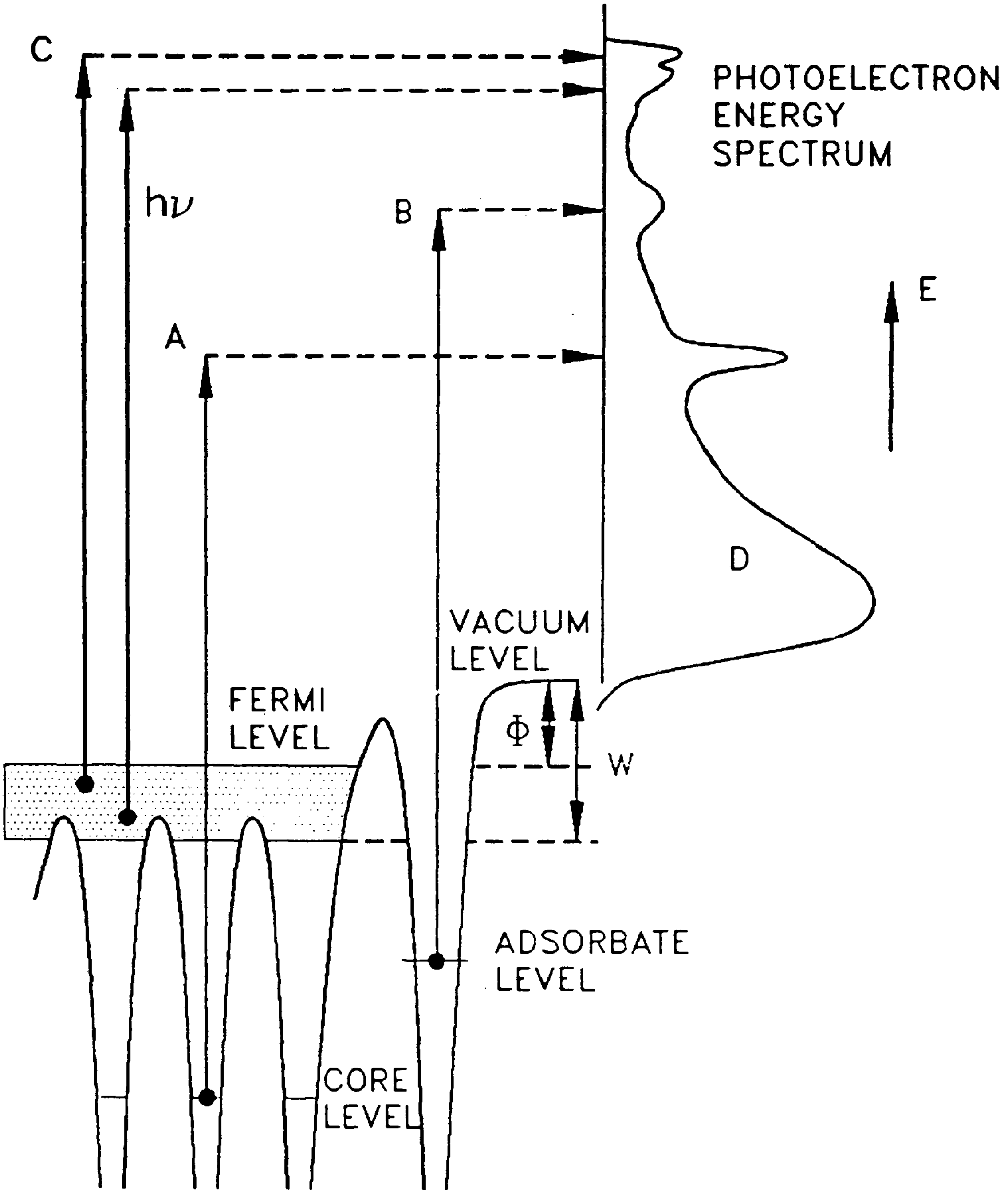
24%

3%

of interaction volume


Si
p–b
cps
30 keV
20 keV
10 keV
Au
Si
p–b
cps
30 keV
20 keV
10 keV
Au
0.5 μm

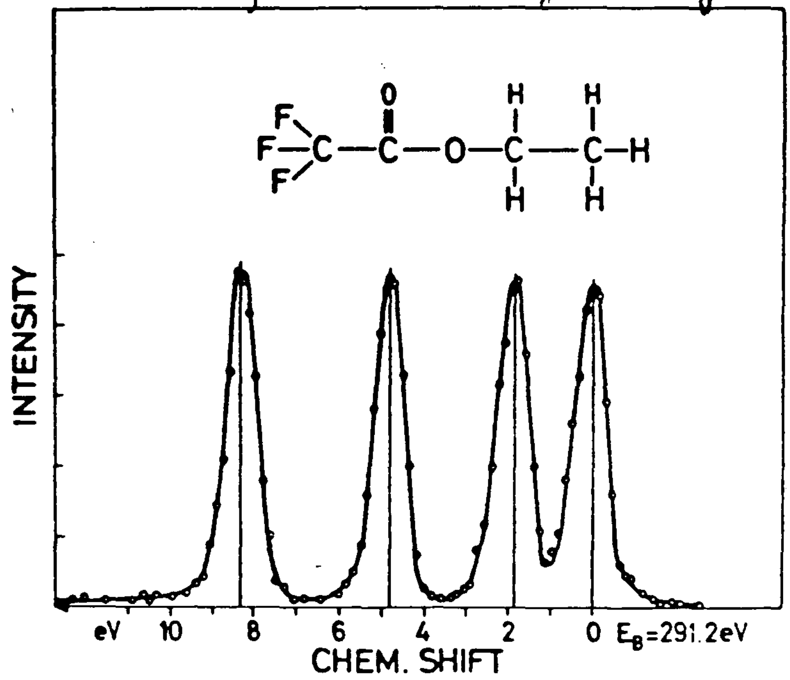
What can we learn from XPS



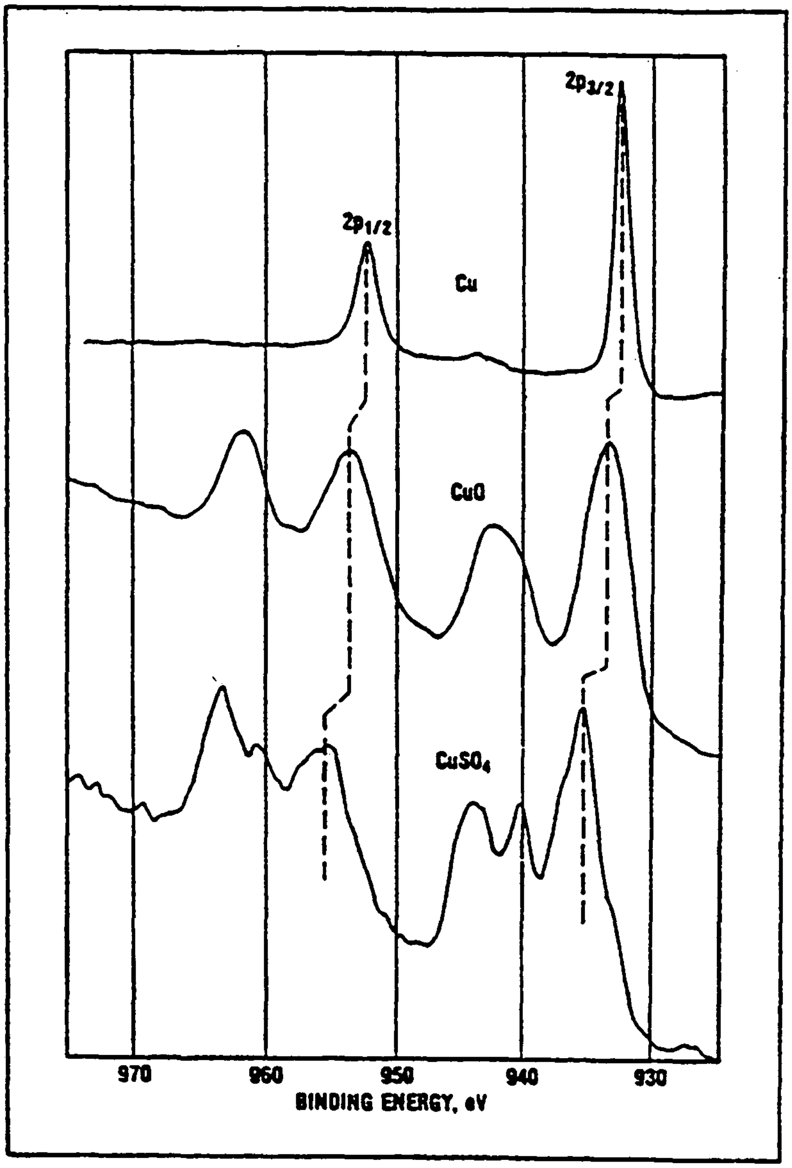
Auger decay of core hole

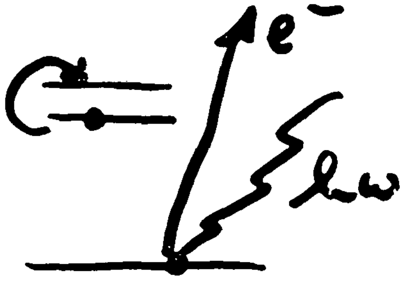
Chemical Shifts

tri fluoro methyl acrylate

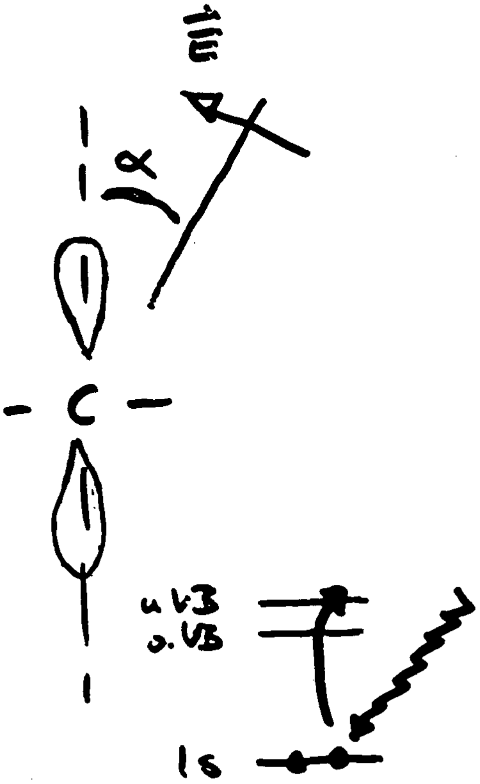


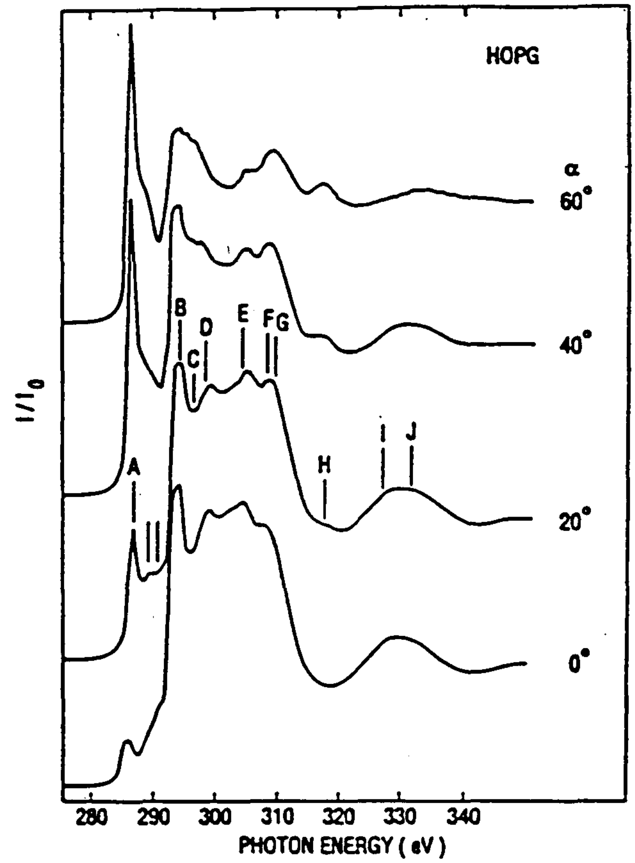
K. Siegbahn et al.

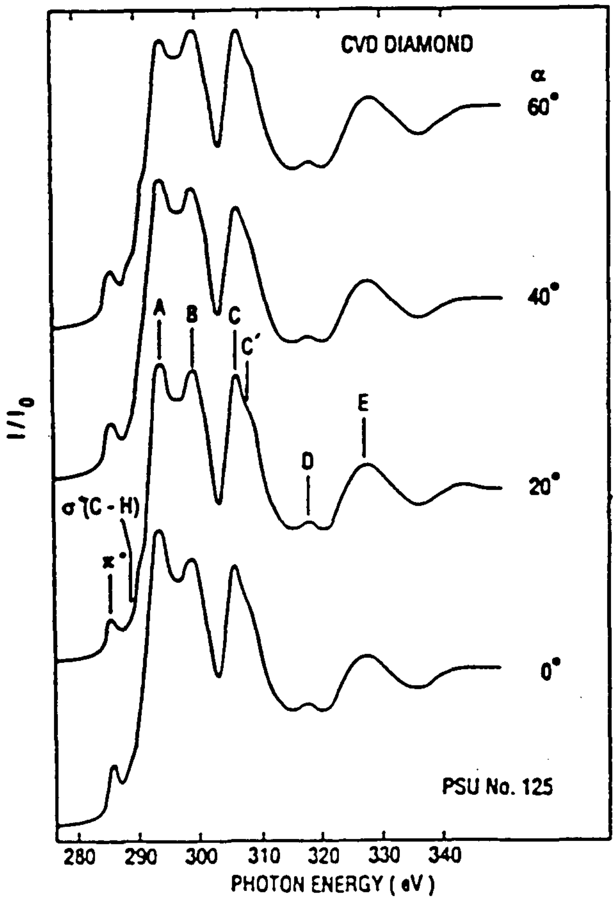

2p3/2
2p1/2
Cu
CuO
CuSO4
970
960
950
940
930
BINDING ENERGY, eV


e⁻
ħω

X-Q Jing et al. J Vac Sci Tech A9 (3) (1991)

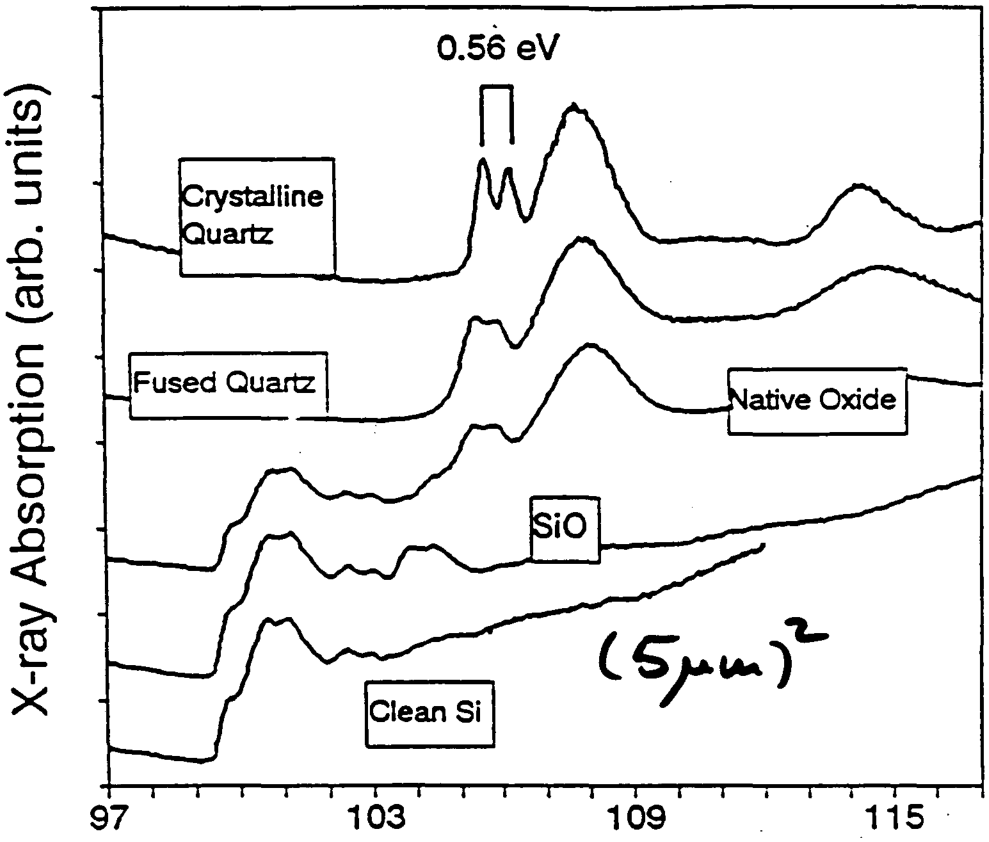


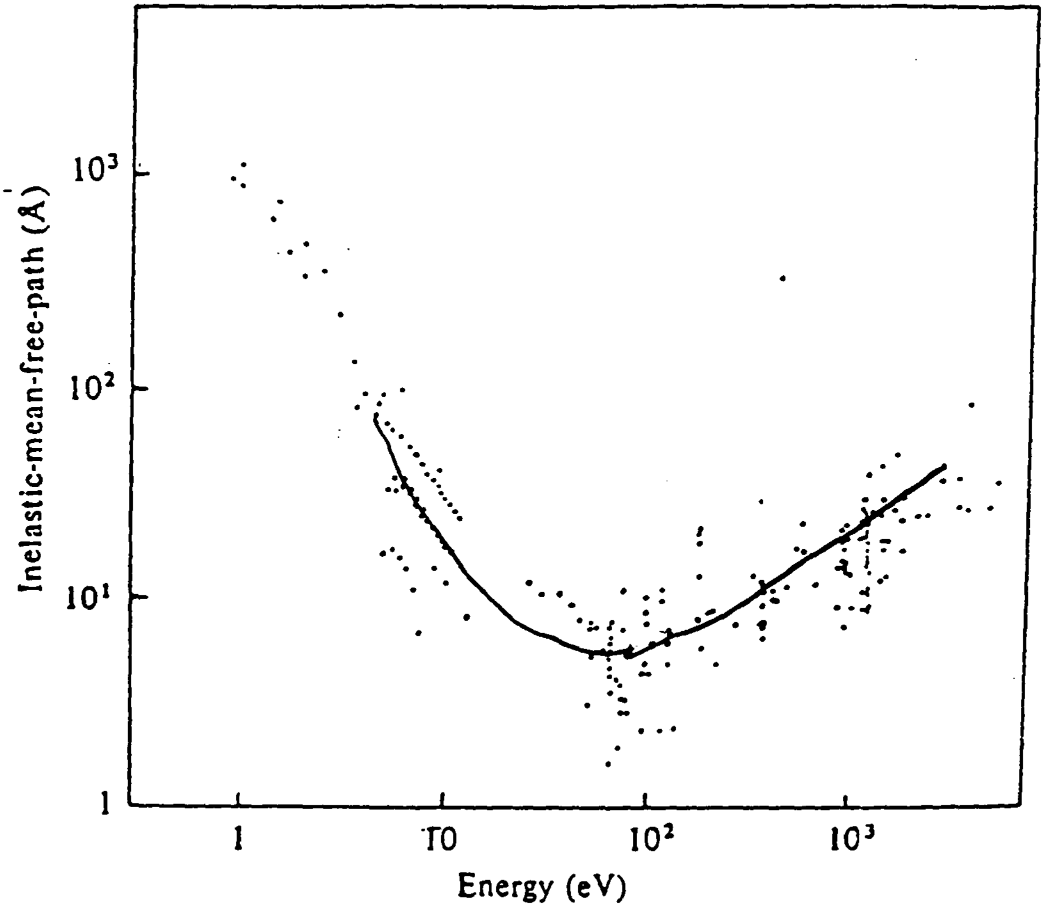




B. Tonner et al.

Si 2p XANES





Inelastic-mean-free-path (Å)
10^3
10^2
10^1
1
1
10
10^2
10^3
Energy (eV)

Why X-ray Spectro-Microscopy?

- **X-ray techniques promise to overcome the limitations of electron probes (damage, limited spectroscopic information) and the STM (virtually no spectroscopic/chemical information)**

- **Photoemission/Soft X-ray Absorption Spectroscopies are**
  Very powerful techniques for studying
  - **Chemistry at Surfaces**
  - **Geometric and Electronic Structure**

- **Many interesting systems are inhomogeneous and/or e-beam sensitive**
  - **Oxides/Oxyhydroxides**
  - **Catalysts**
  - **Thin Films (growth nucleation)**
  - **Semiconductor devices**
  - **Interfaces**

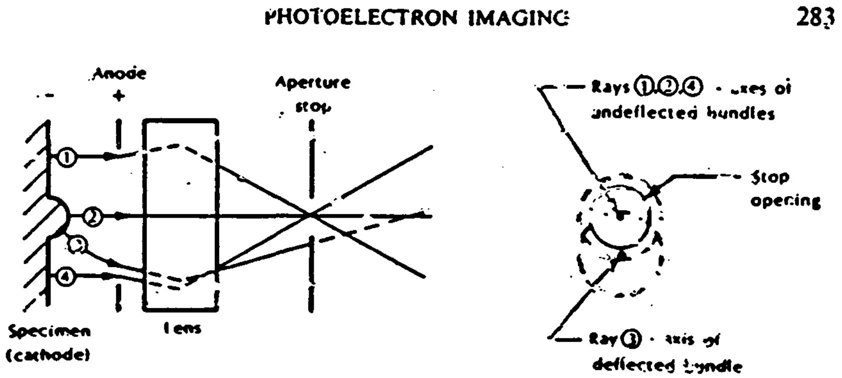
- **PEM contains more information than SAM: primary photoelectron peaks and Auger peaks (can use Auger parameter).**

- **tunable x-ray source: XANES, controlled surface sensitivity**

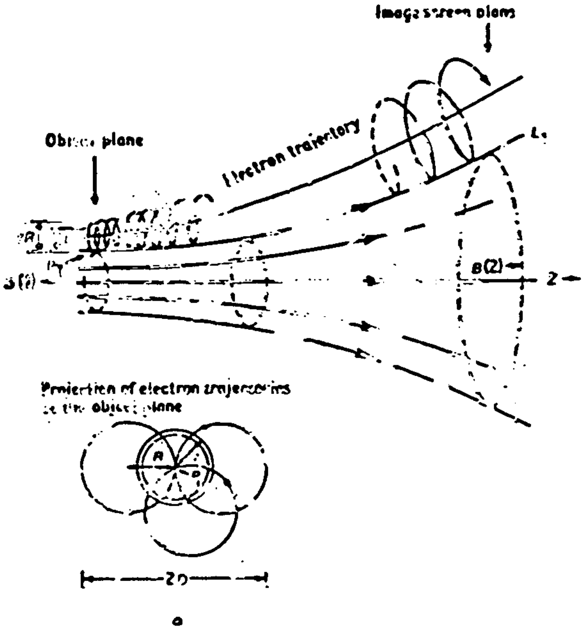
Approaches to Spectromicroscopy

Image e- (Electron Optical Instruments):

- electro-static (Bauer-Telieps, Tonner micro-XANES)



- magneto-static (Beamson, Pianetta)

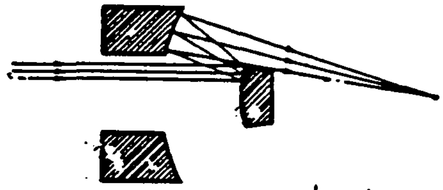


Focus X-rays (Microprobe Instruments):

- **normal incidence multilayer Schwarzschild (F.Cerrina)**

potentially very high spatial resolution

diff limit (3nm) $\approx$ 6 nm



$f \neq f(\lambda)$

WD few cm

but only few % BW tunability

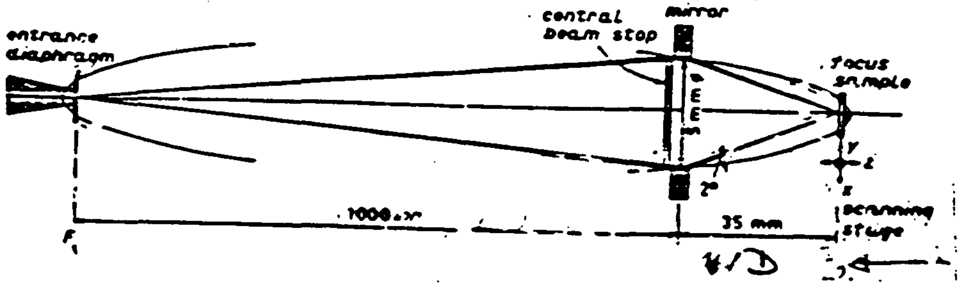
0.3 N.A. Schwarzschild objective

presently $h\nu < 280$ eV

- **grazing incidence ellipsoid (Kunz)**

20 eV → 2000 eV $f \neq f(\lambda)$

inefficient lens 95% obstructed (radius)

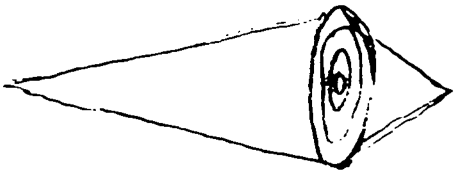


Principle and parameters of the scanning photoelectron microscope under construction at HASYLAB. F_1, F_2 are the foci of the elliptical mirror.

central obstruction → more flux into outer lobes of Airy pattern

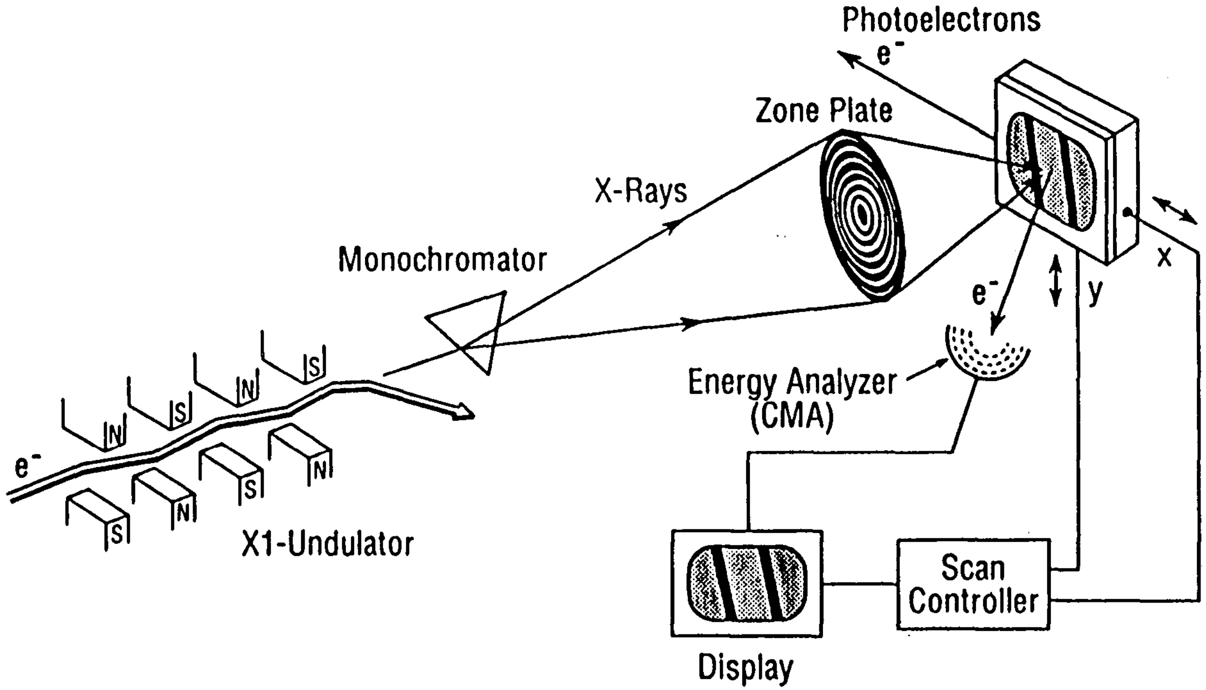
- **zone plate (SPEM)** ~100 eV → ~2000 eV

tunable over ~15% BW (so far)



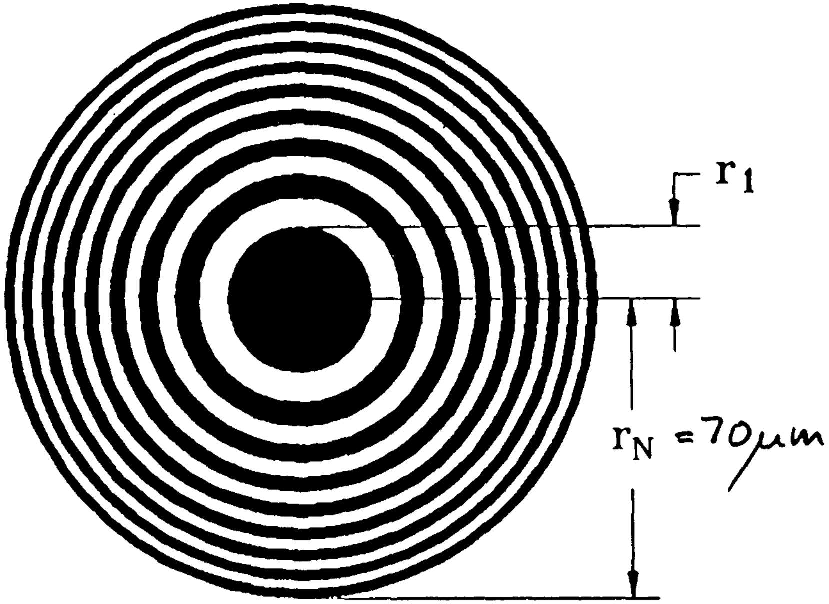
$f \propto E \ (\propto \frac{1}{\lambda})$

WD $\approx$ 1-2 mm

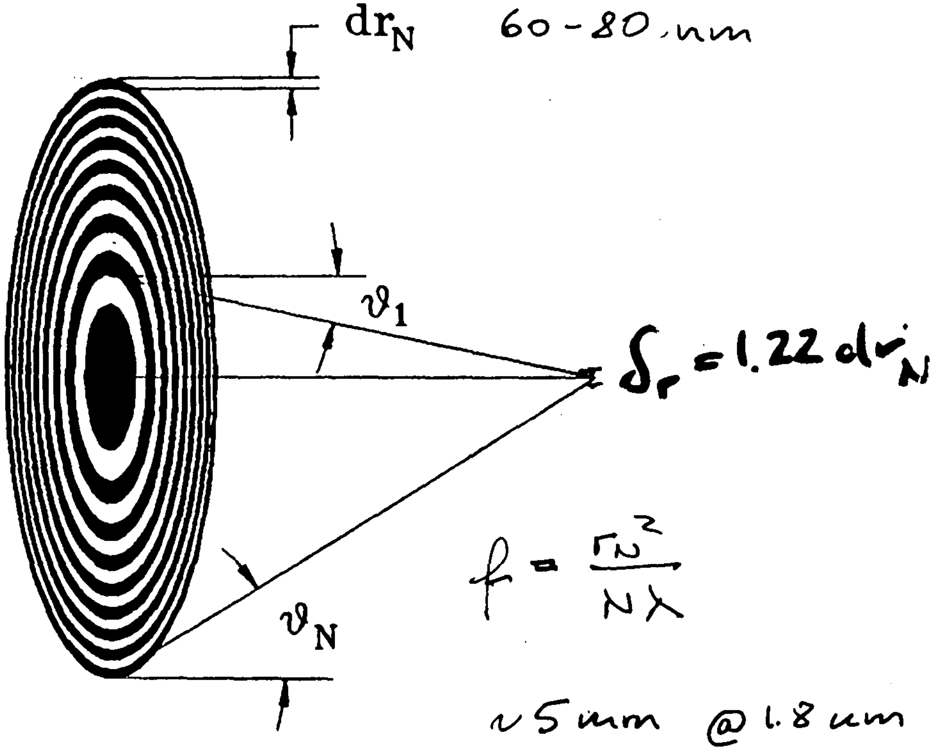


High-Resolution Scanning Photoelectron Microscope

M. Rowe - H. Ade 1a 8/22/91 j.o.



$\delta_1 \leftarrow \frac{\lambda}{2N.A}$



60-80 nm

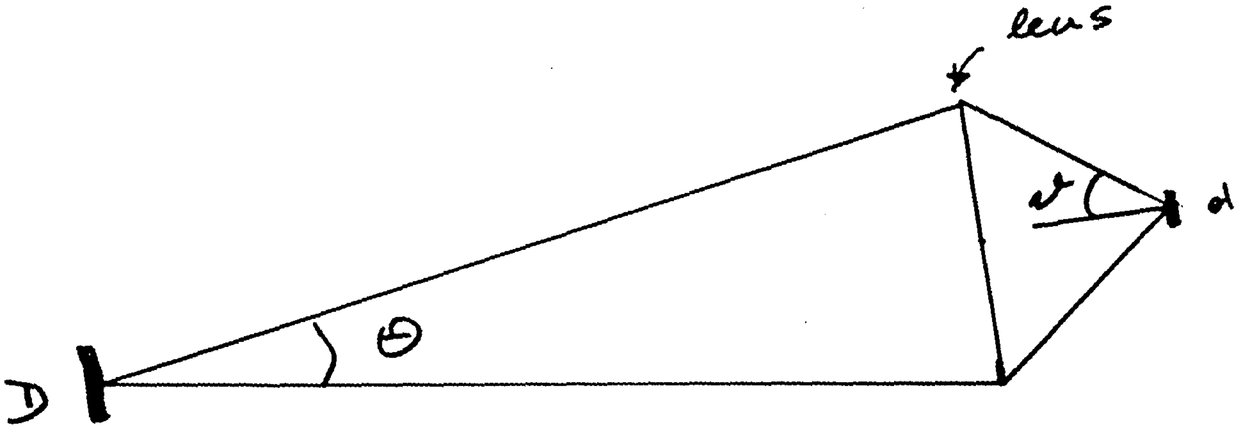
$\delta_r = 1.22\, dr_N$

$f = \frac{r_N^2}{N\lambda}$

$\sim 5\, mm$ @ $1.8\, \mu m$

Diffraction limited resolution

$$d \approx \frac{\lambda}{2\,N.A.}$$



for small angles $\vartheta \approx N.A.$

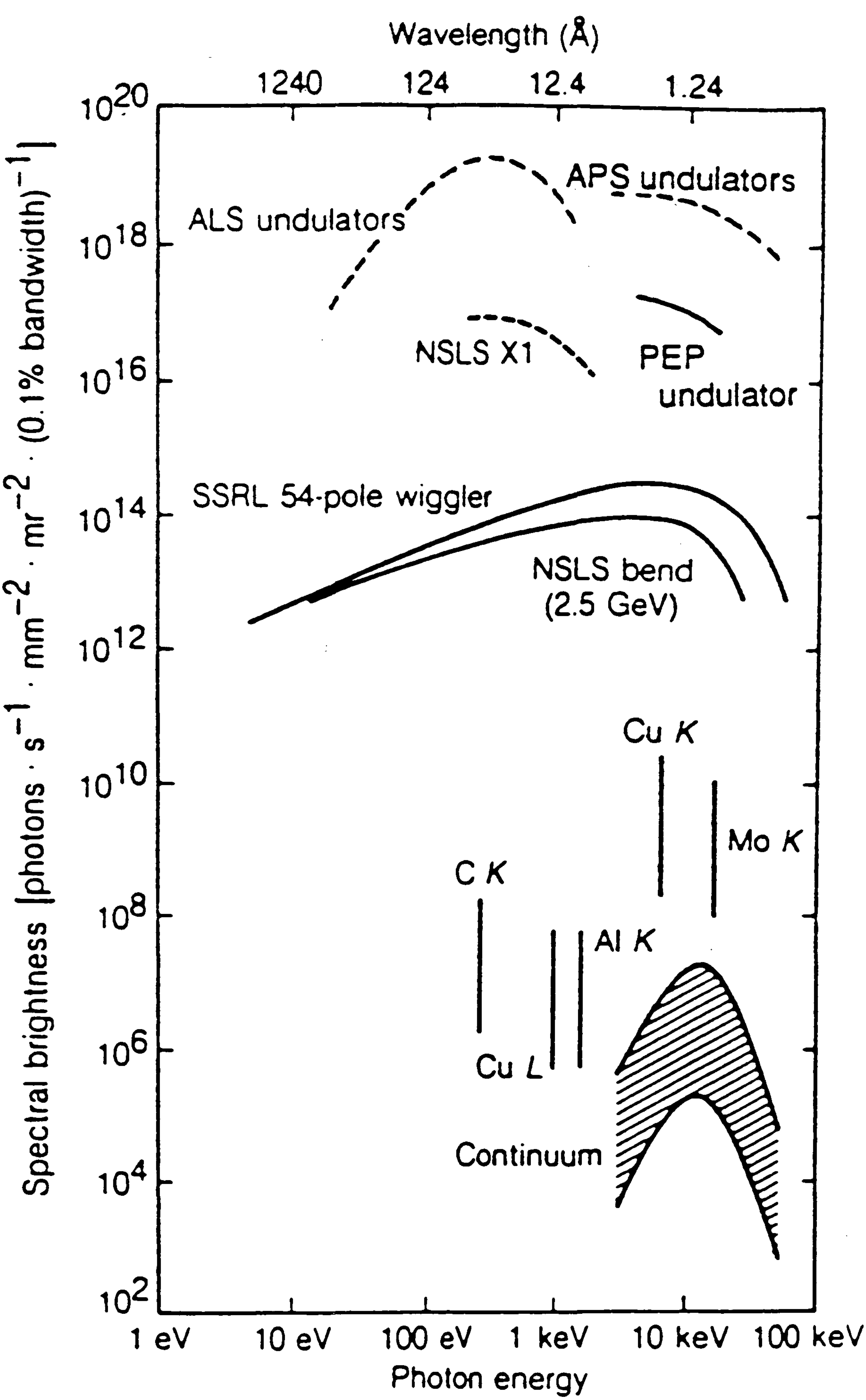
$$\xrightarrow{(1)} 2\vartheta d \approx \lambda$$

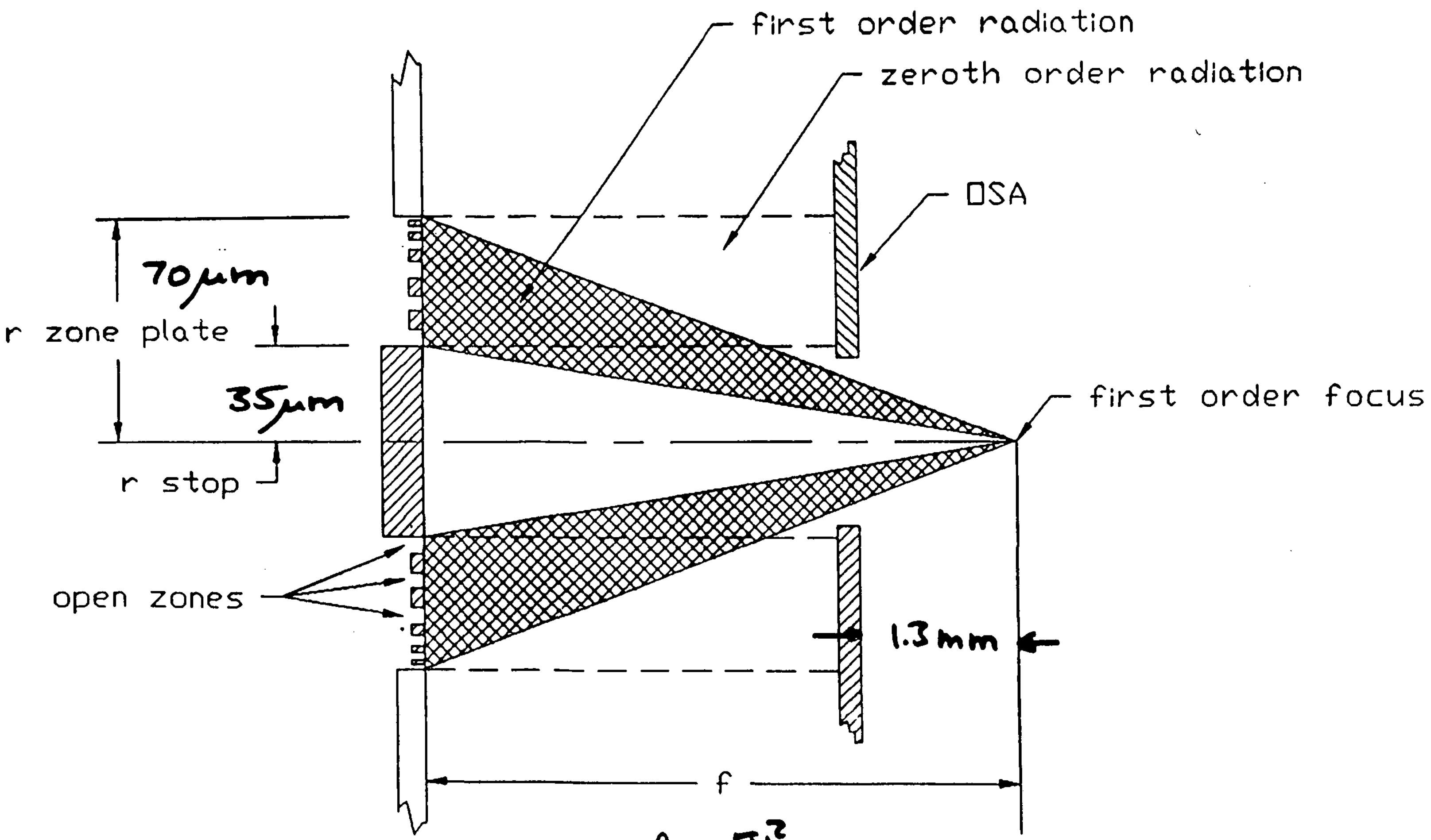
Liouville's Theorem (conservation of photon phase space)

$$D\Theta = 2\vartheta d \approx \lambda$$

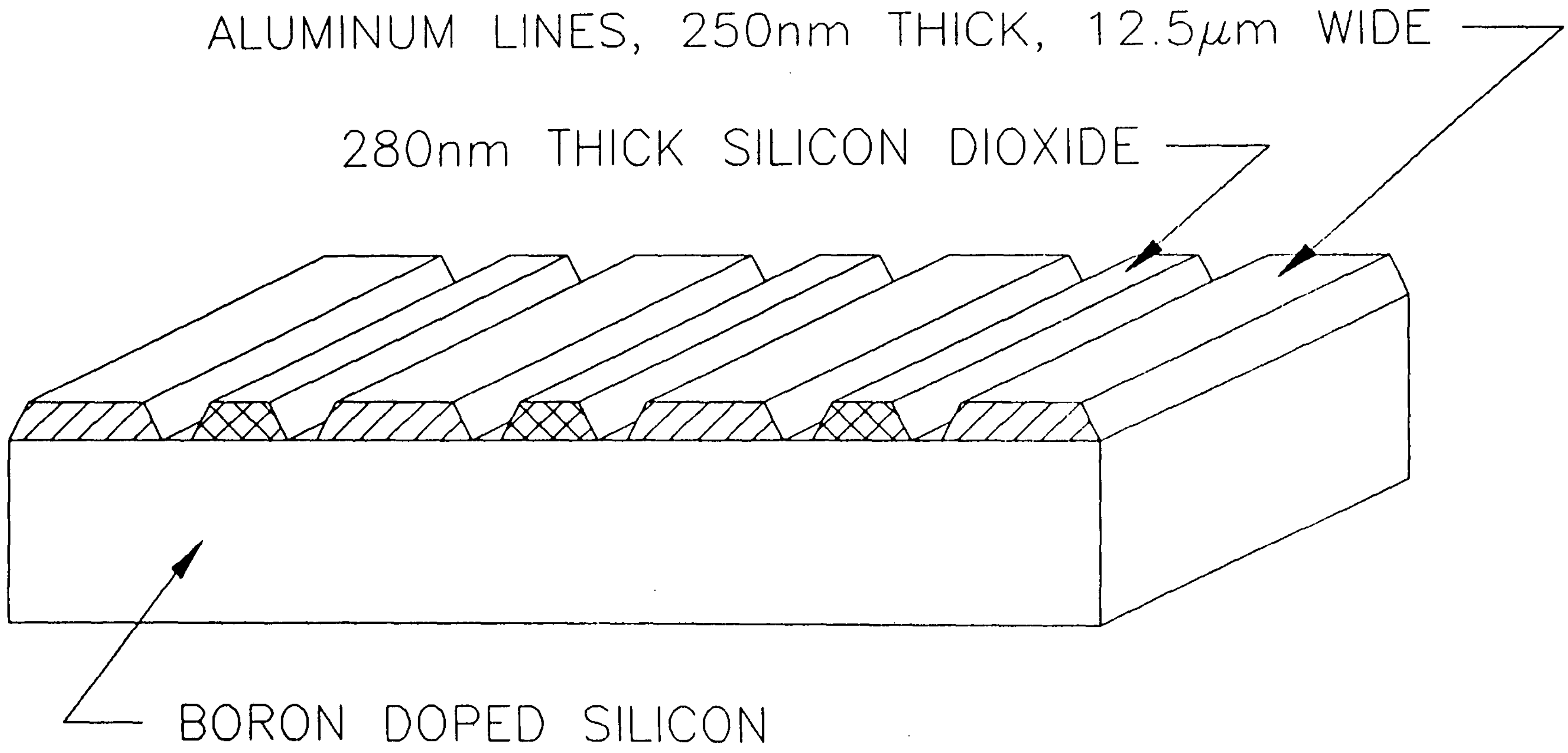
∴ for smallest possible probe size need to limit the accepted source phase space to about λ

i.e. need coherent illumination

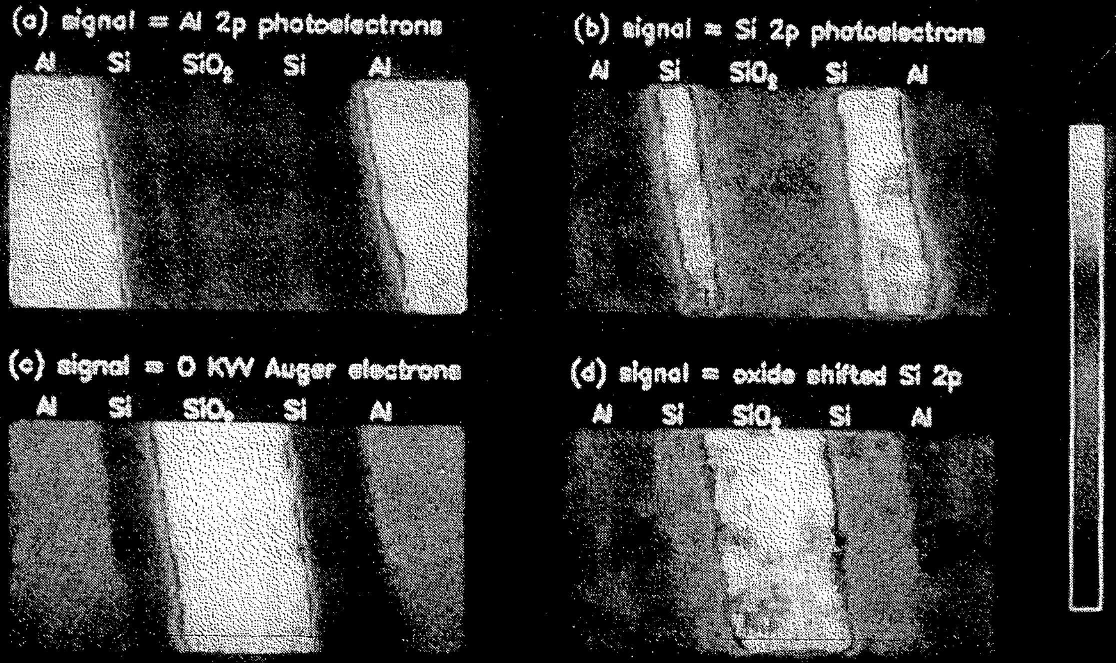

Wavelength (Å)
1240
124
12.4
1.24
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
10^{2}
Spectral brightness [photons · s^{-1} · mm^{-2} · mr^{-2} · (0.1% bandwidth)$^{-1}$]
APS undulators
ALS undulators
NSLS X1
PEP undulator
SSRL 54-pole wiggler
NSLS bend (2.5 GeV)
Cu K
Mo K
C K
Al K
Cu L
Continuum
1 eV
10 eV
100 eV
1 keV
10 keV
100 keV
Photon energy



$f = \frac{r_N^2}{N\lambda}$ → 5.4 mm @ 1.8 nm


ALUMINUM LINES, 250nm THICK, 12.5μm WIDE
280nm THICK SILICON DIOXIDE
BORON DOPED SILICON

Elemental and chemical imaging with the X1-SPEM



(a) signal = Al 2p photoelectrons

(b) signal = Si 2p photoelectrons

(c) signal = O KVV Auger electrons

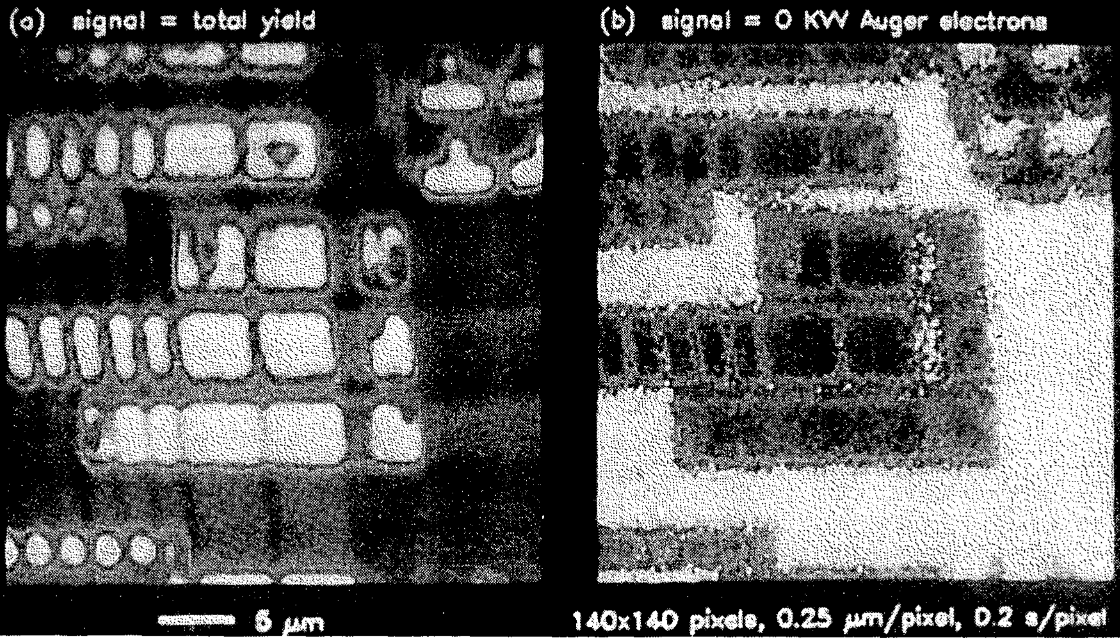
(d) signal = oxide shifted Si 2p

3 μm

120x60 pixels, 0.15 μm/pixel, 0.5 s/pixel

Microelectronic component

(Images acquired simultanously)

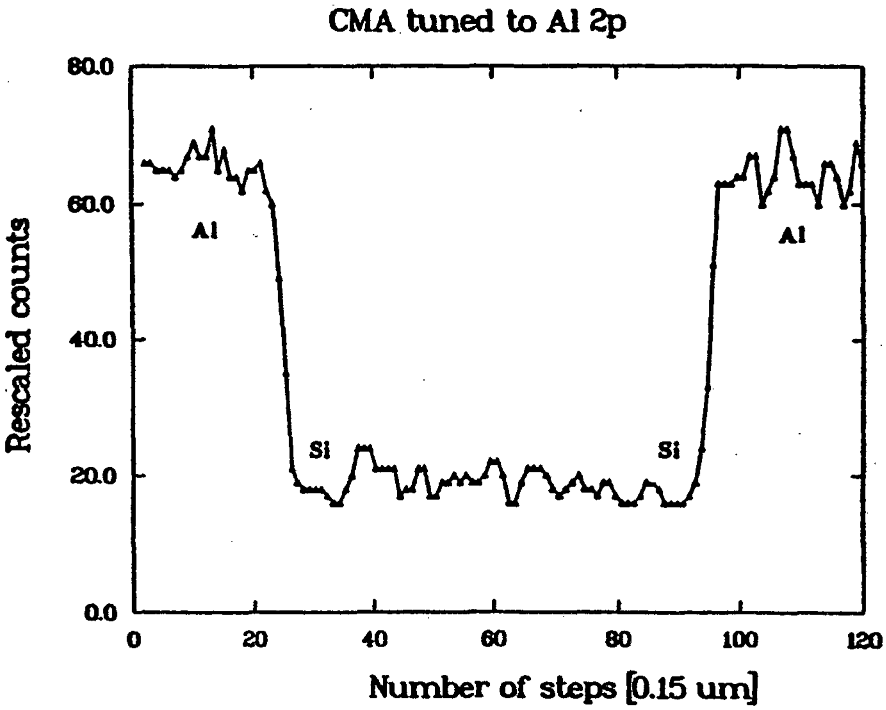


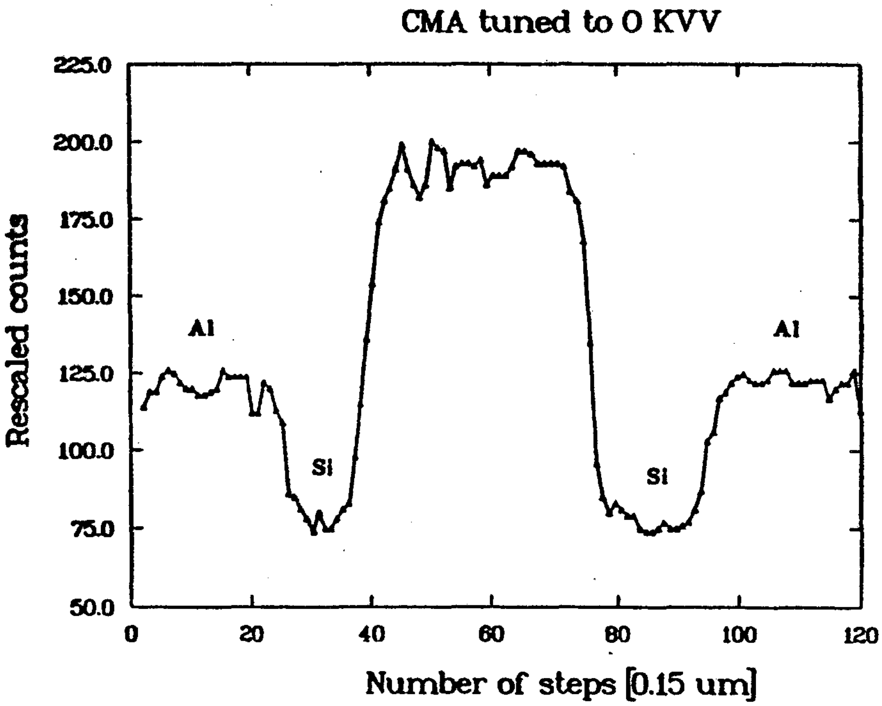
(a) signal = total yield

(b) signal = O KVV Auger electrons

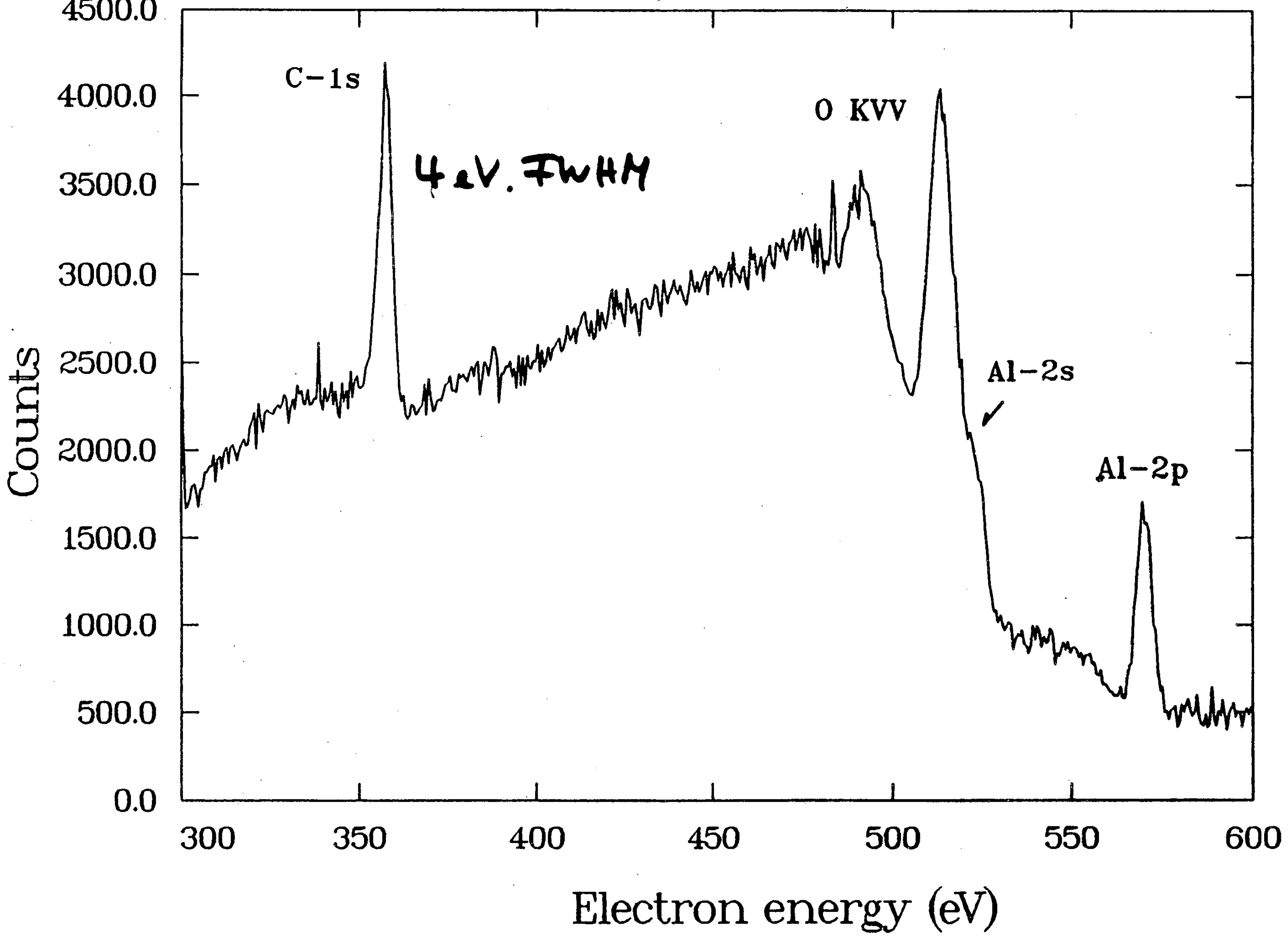
5 μm

140x140 pixels, 0.25 μm/pixel, 0.2 s/pixel


CMA tuned to Al 2p
80.0
60.0
40.0
20.0
0.0
Rescaled counts
Al
Si
Si
Al
0
20
40
60
80
100
120
Number of steps [0.15 um]


CMA tuned to O KVV
225.0
200.0
175.0
150.0
125.0
100.0
75.0
50.0
Rescaled counts
Al
Si
Si
Al
0
20
40
60
80
100
120
Number of steps [0.15 um]

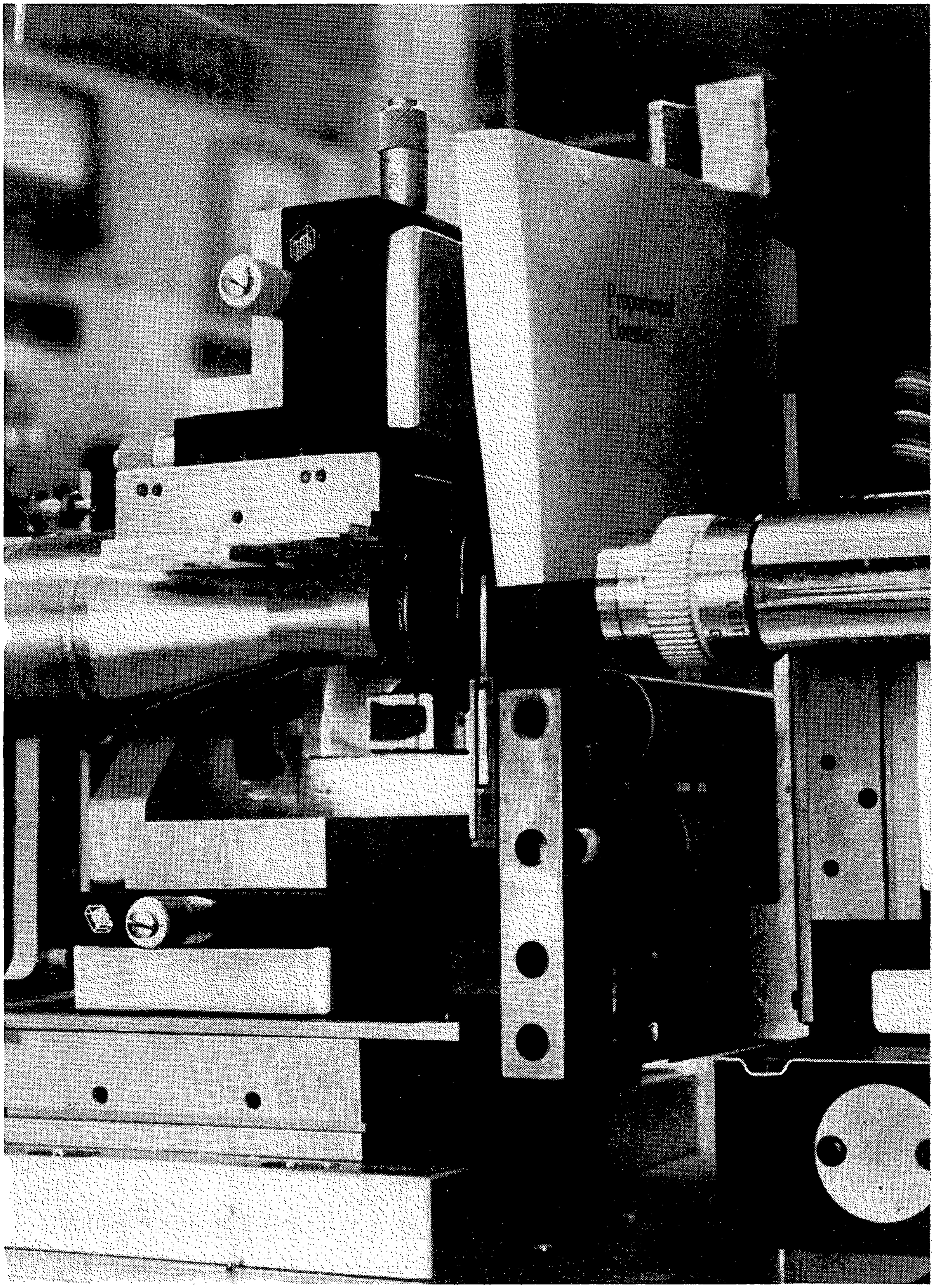
0.2 × 0.15 μm spot



4 eV. FWHM

Instrumental improvements of the X1-SPEM

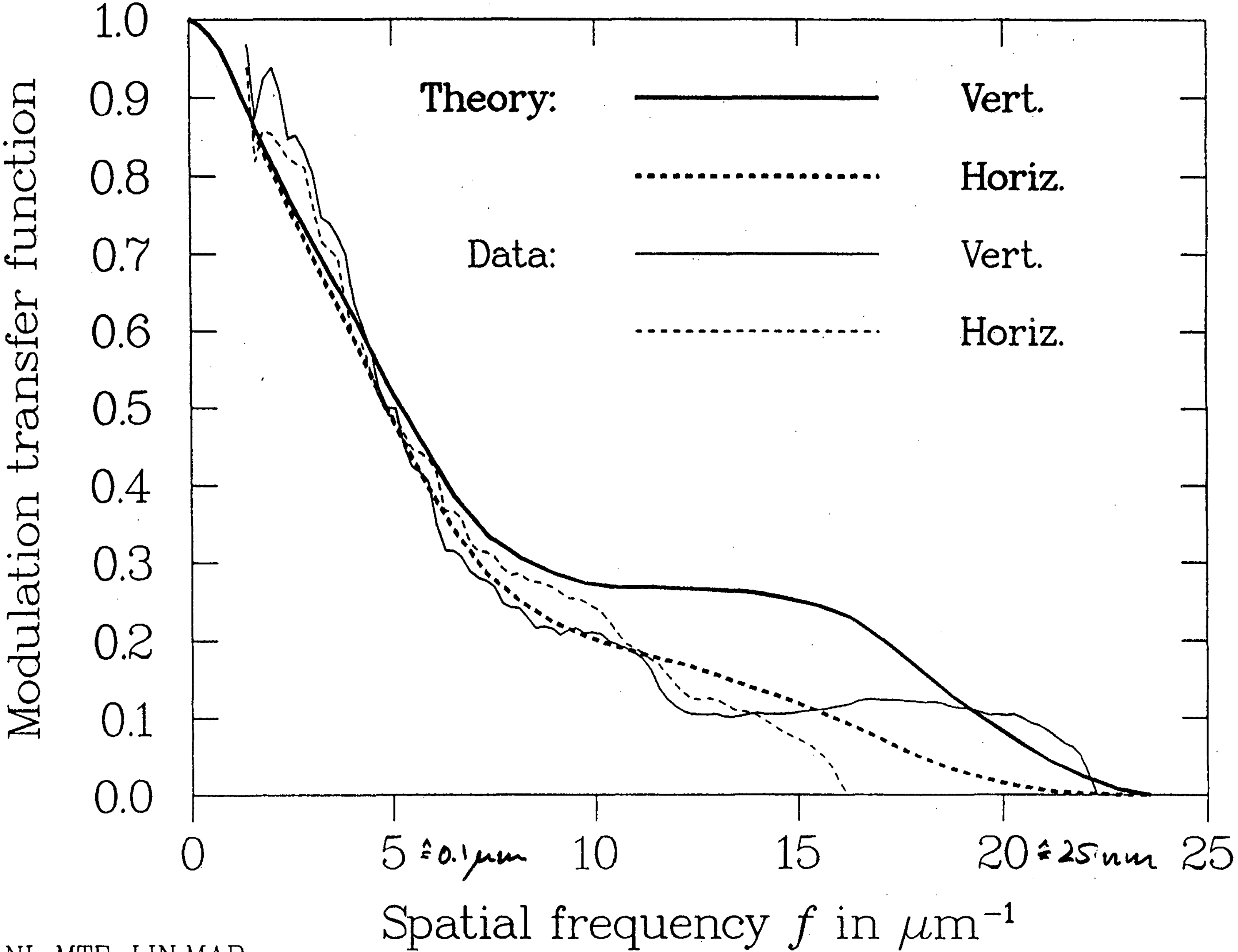
- Add XANES mode with 0.3-1.0 eV photon energy resolution
- Higher spatial resolution (few months: sub 100nm, one year: 50 nm, few years: 20 nm)
- more efficient grating (gain of 2–5 in flux)
- Ni phase zone plates (gain of factor 2 in flux)
- commercial spectrometer (gain of $>$ 10 peak countrate, simultaneously factor 2 in energy resolution, or $<$ 1 eV energy resolution)
- multiple energy (16 channel) detection over 5-20 eV window
- Alternate signals (PSD, fluorescence[ALS], scattering)


Proportional
Counter

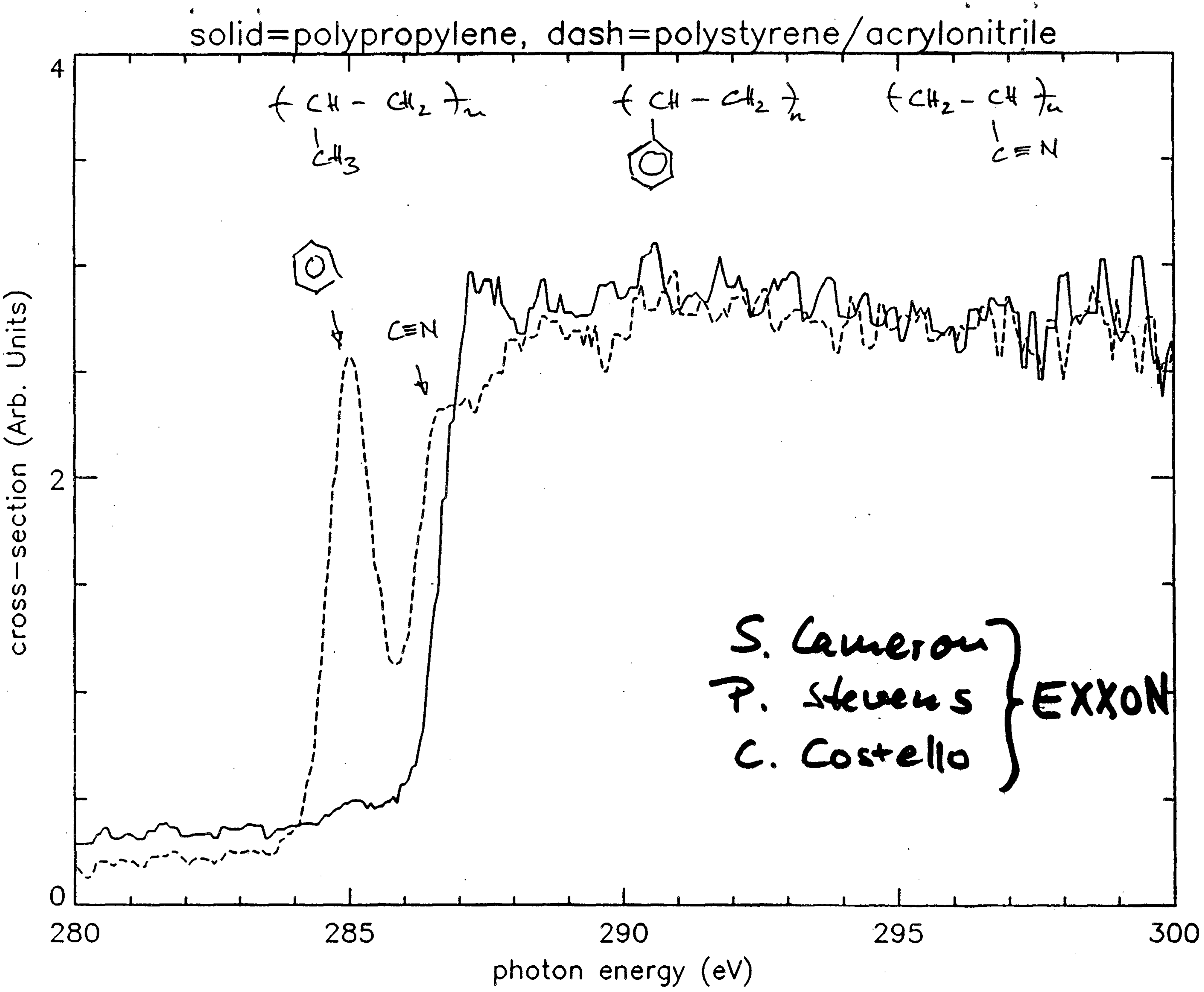
Jacobsen, Zhang et al

GAWE

Zone Plate: 100 nm Ni, δ_{rN}=45 nm

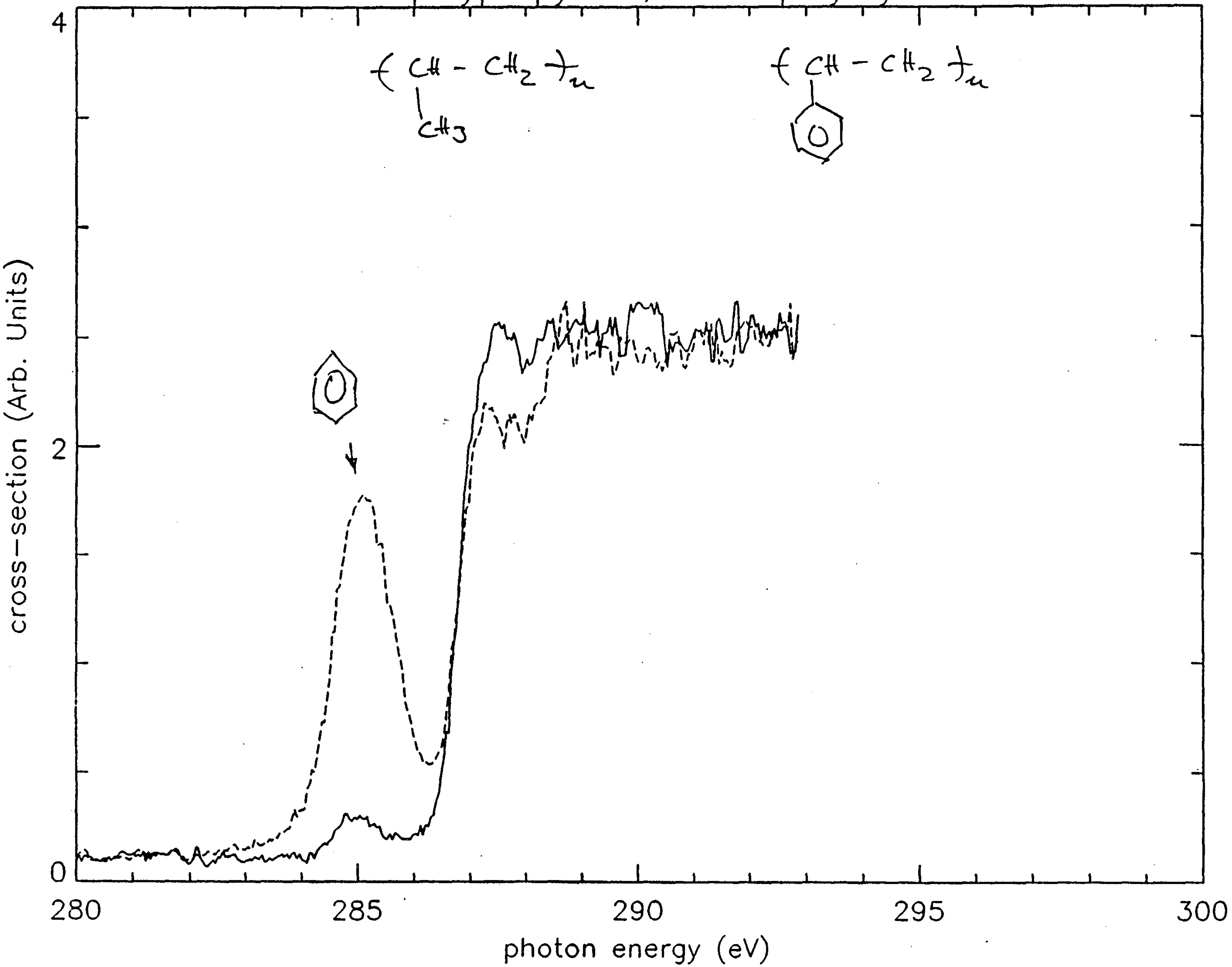


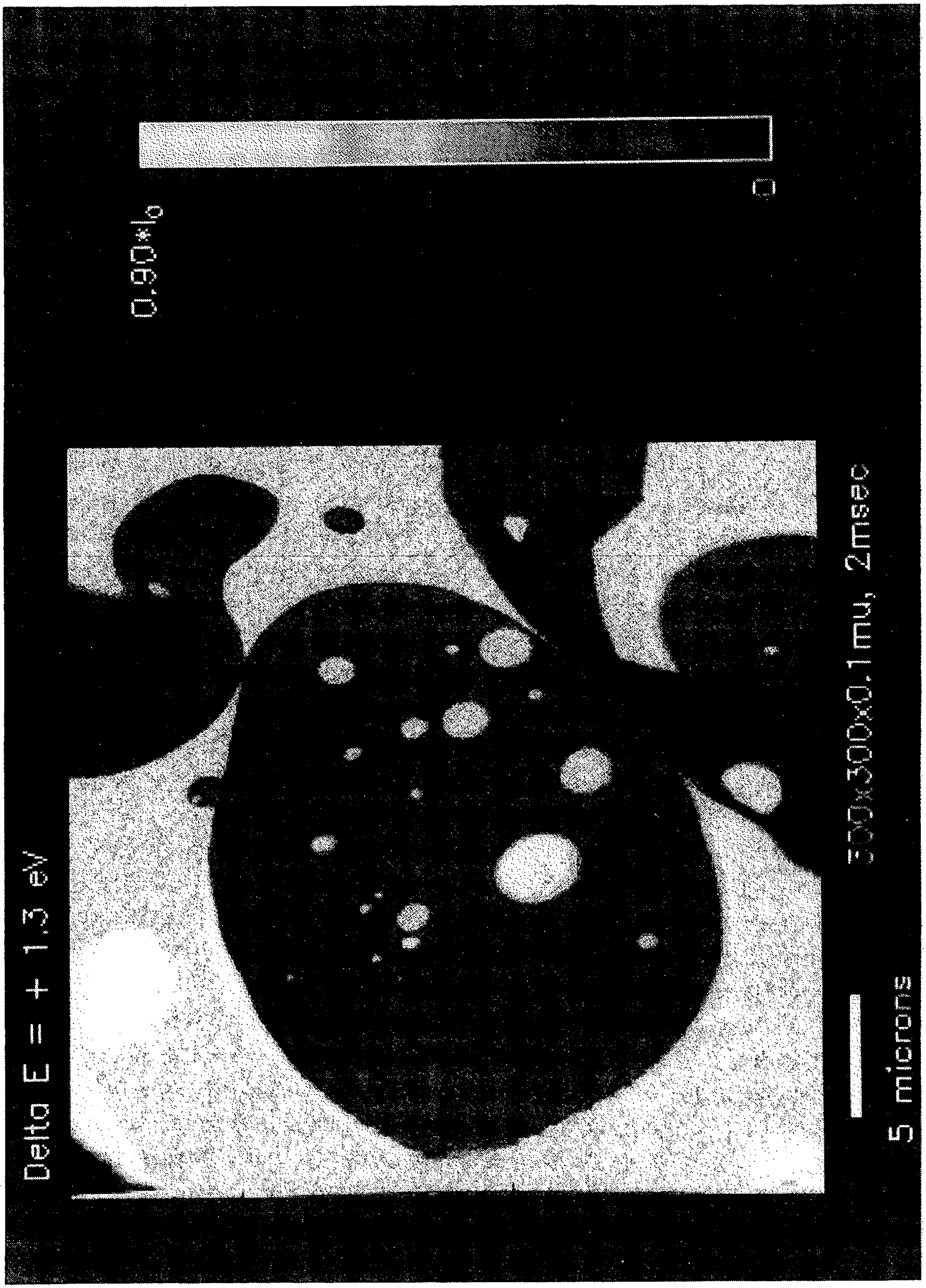
NI_MTF_LIN.MAP

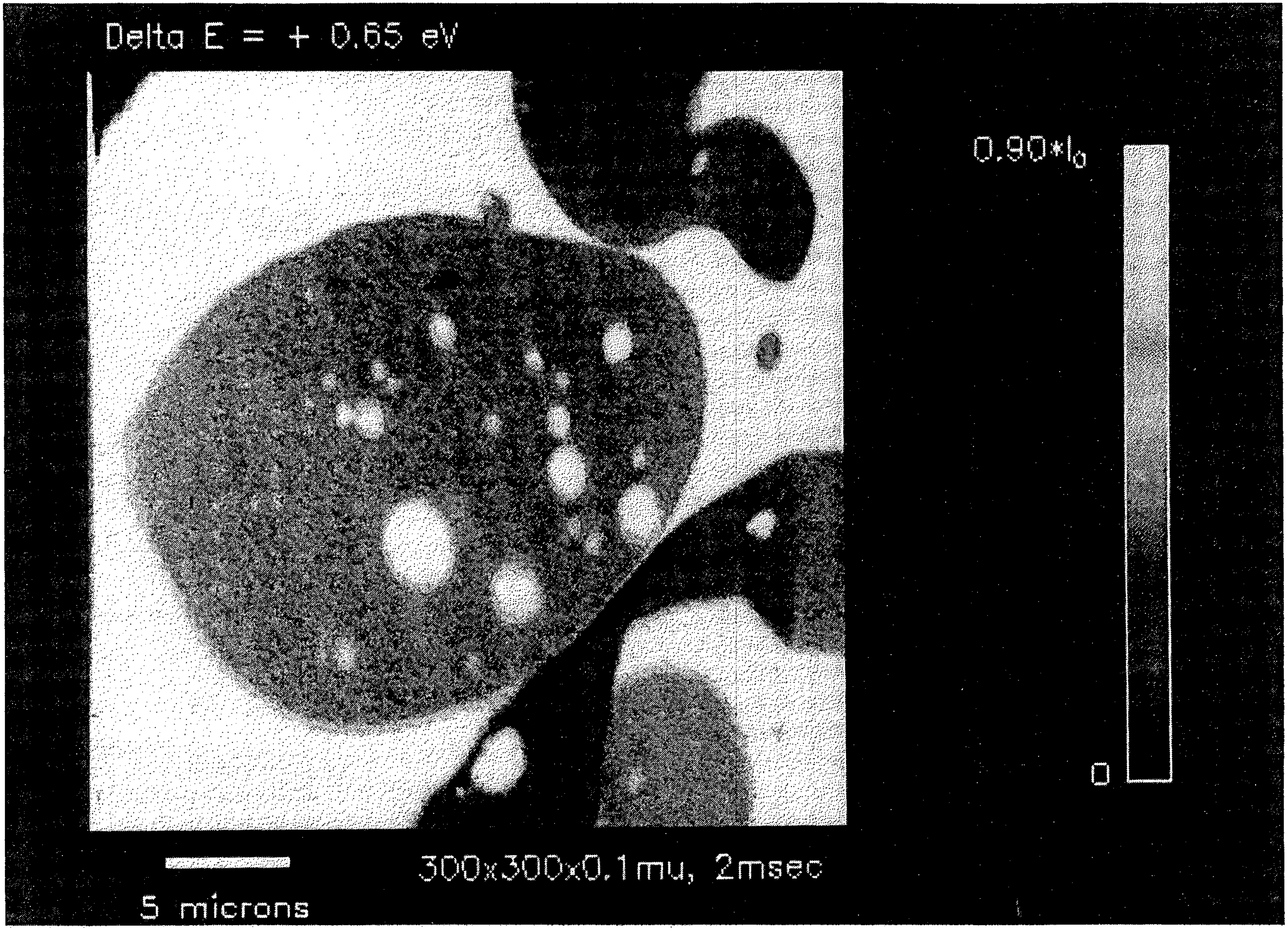


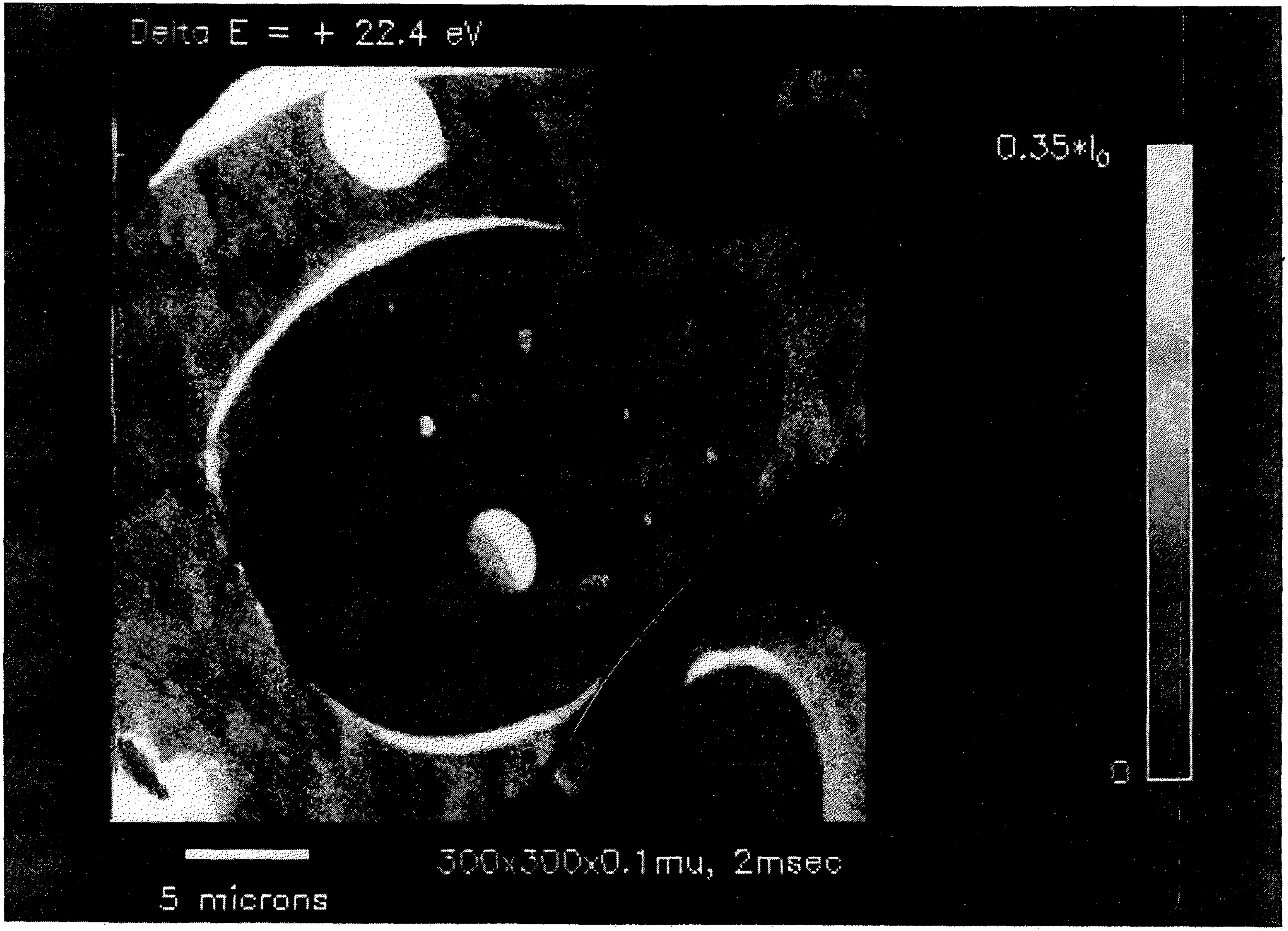
S. Cameron
P. Stevens
C. Costello
} EXXON

solid=polypropylene, dash=polystyrene

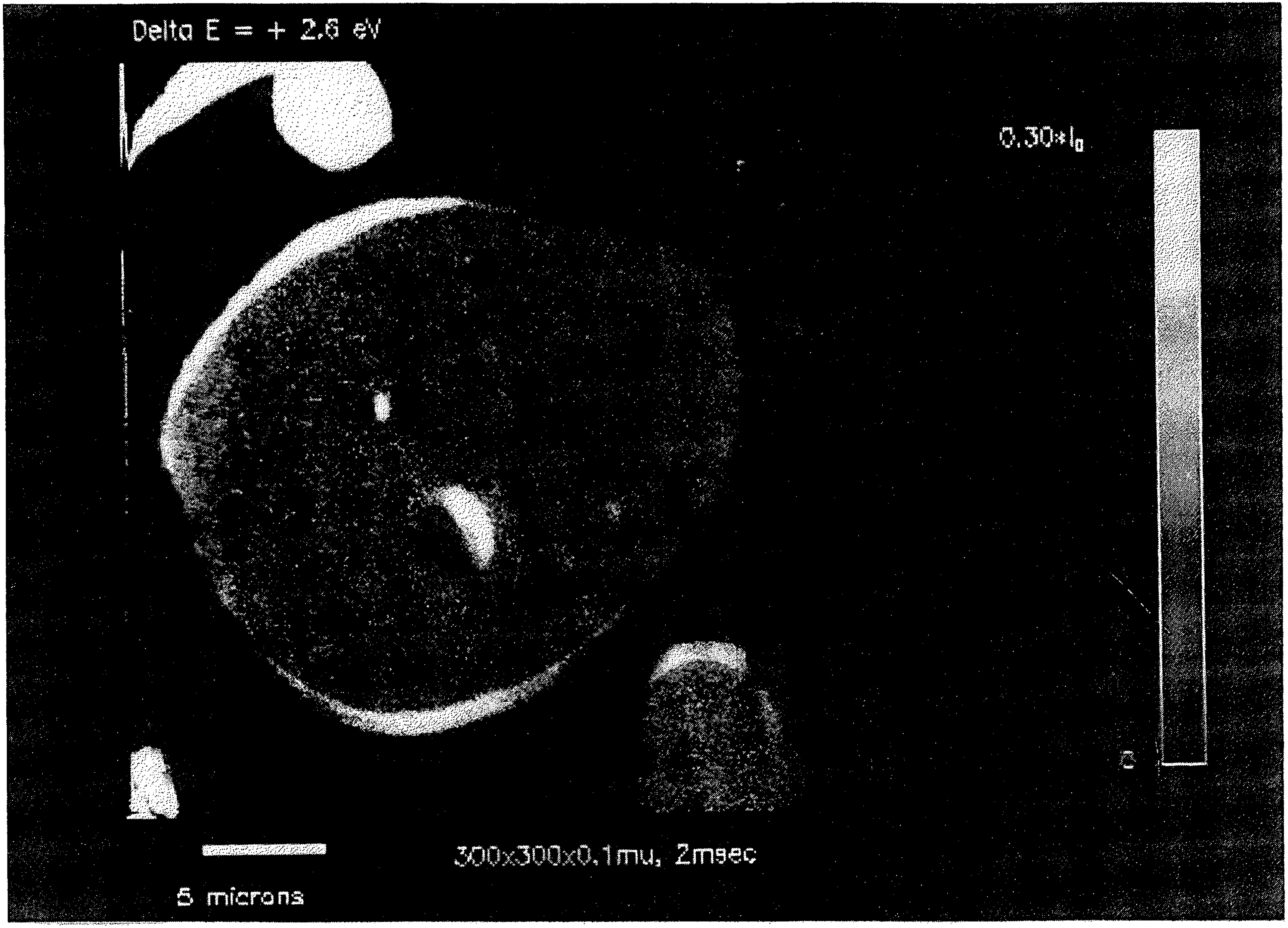



Delta E = + 1.3 eV
5 microns
300x300x0.1mu, 2msec
0.90*I$_0$
0

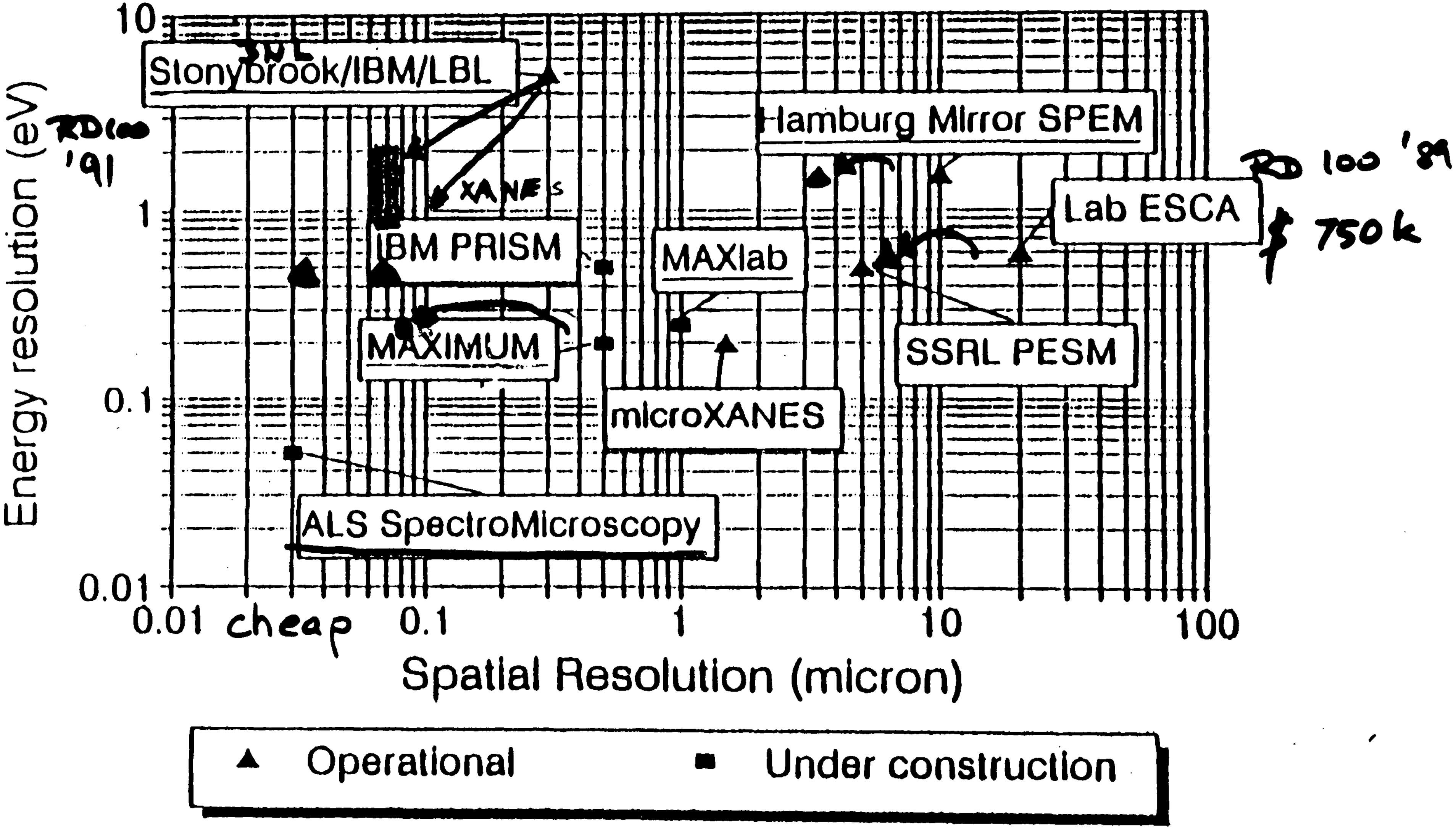

Delta E = + 0.65 eV
0.90*I$_0$
0
5 microns
300x300x0.1mu, 2msec



Delta E = + 22.4 eV
0.35*I0
0
5 microns
300x300x0.1mu, 2msec


Delta E = + 2.6 eV
0.30×I0
0
300x300x0.1mu, 2msec
5 microns

adapted from B. Tonner Jan '91



Photoelectron Spectroscopy in Industry: Current Capabilities, Needs, and Possible Roles for the ALS

M.A. Kelly

Stanford University

Capabilities of Modern XPS Instruments

How XPS is Used in Industry --Examples

Some Possible Roles for the ALS

XPS in Industry

Why it's used —

- Elemental or Chemical Info
- Useful for Insulators, Conductors, Powders, etc.
- Low Sample Damage ← 10^{-3} AES
- Good Quantitation, Easy Interpretation

± 10%

Limitations —

$\times 10^{9}$

- Trace elements: *Use SIMS*

500 Å

- High Spatial Resolution: *Use Auger or SIMS*
- Hydrogen Detection: *Use SIMS*

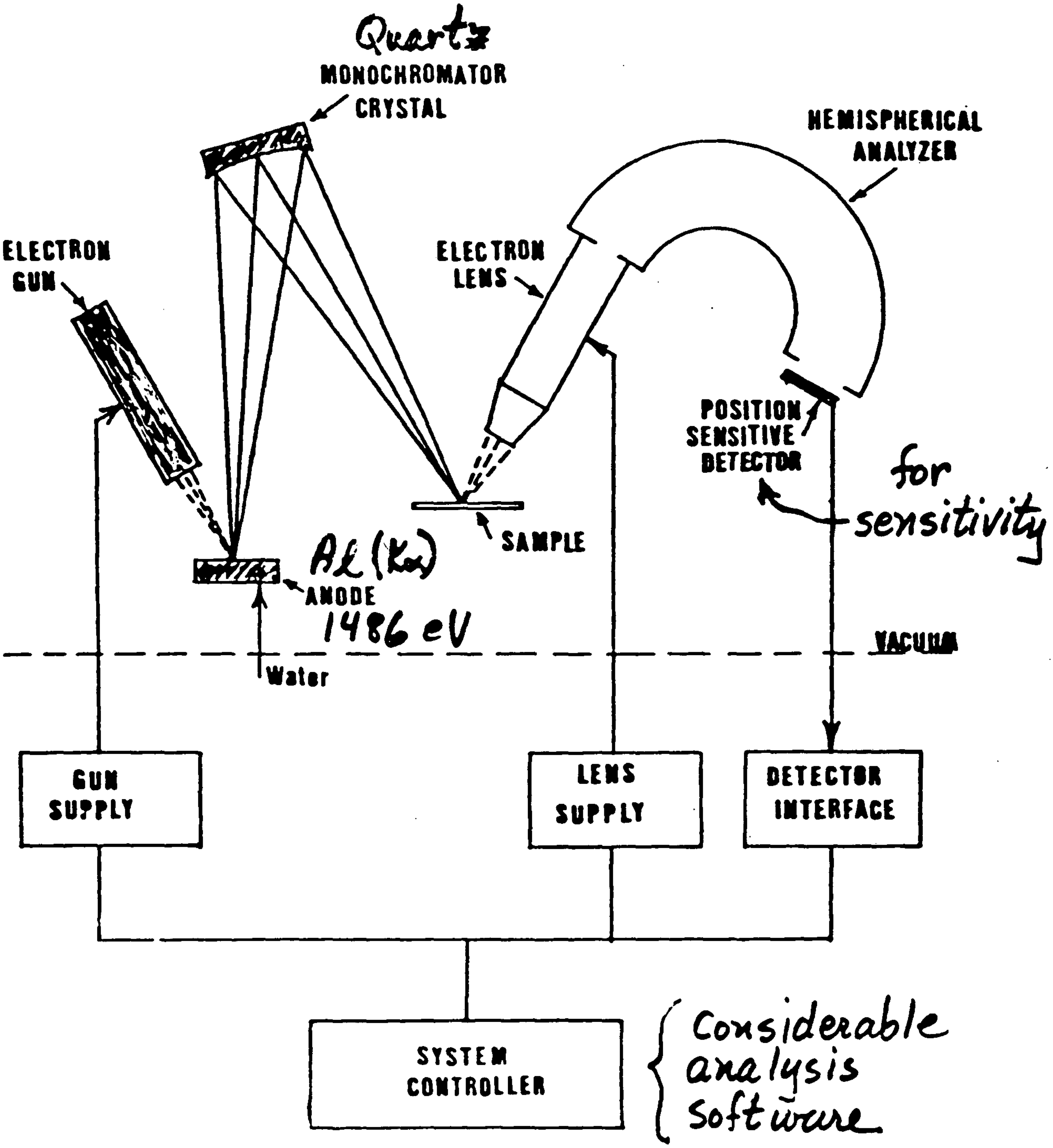
"Standard"
Research Grade XPS Instruments

(Much Improved in the Last Decade)

$400K -- $600K

Perkin Elmer
Fisons (VG, SSI)
Kratos

- great improvements in
  - energy res
  - count rate
  - spatial res
- b orientation —
  more analyt tool than
  research apparatus


Quartz
MONOCHROMATOR
CRYSTAL
HEMISPHERICAL
ANALYZER
ELECTRON
GUN
ELECTRON
LENS
POSITION
SENSITIVE
DETECTOR
for
sensitivity
SAMPLE
Al (Kα)
ANODE
1486 eV
VACUUM
Water
GUN
SUPPLY
LENS
SUPPLY
DETECTOR
INTERFACE
SYSTEM
CONTROLLER
Considerable
analysis
software

Key Instrumental Parameters

- Energy Resolution:
  - *Better Chemical Info.*

Monochromator
e^- Analyzer

- Count Rate:
  - *Time/Cost Effectiveness*
  - *Elemental Sensitivity*

Source brightness
Lens Collection
Parallel Detector

- Spatial Resolution
  - *Point Analysis/Imaging*

↑ "Standard" ↑ "Special"

- Other Important Features
  - *Charge Neutralization*
  - → *Sample Loading /Manipulation*
  - *Depth Profiling*
  - *Vacuum*

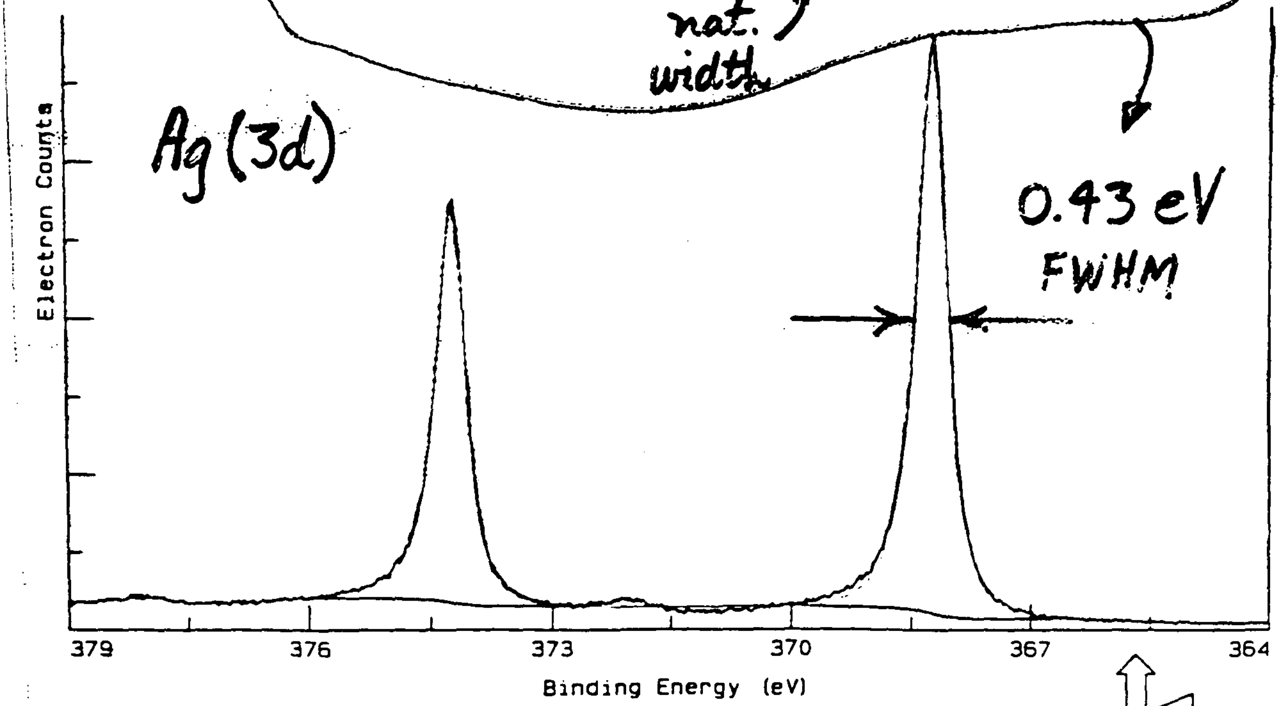
State of the Art Energy Resolution

(Monochromatized Al Kα Source)

for elemental specificity, need ~ 1 or 2 eV

- But better res. helps sometimes for chemical shifts.

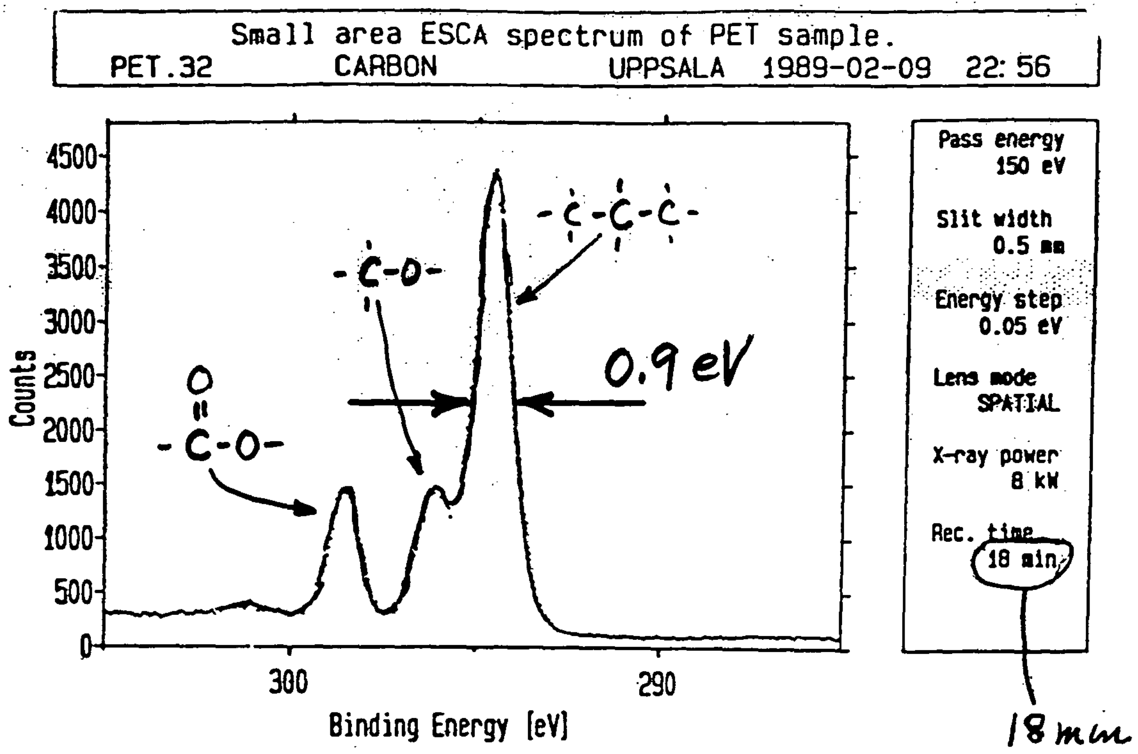
$$\underline{\text{Instr.}}\ \underline{\text{Res}} = \sqrt{(.43)^2 - (\underset{\text{nat. width}}{.35})^2} = \underline{\underline{0.25\,\text{eV}}}$$



Surface Science Instruments

Practical Spectum —

C(1s) Spectrum of Mylar

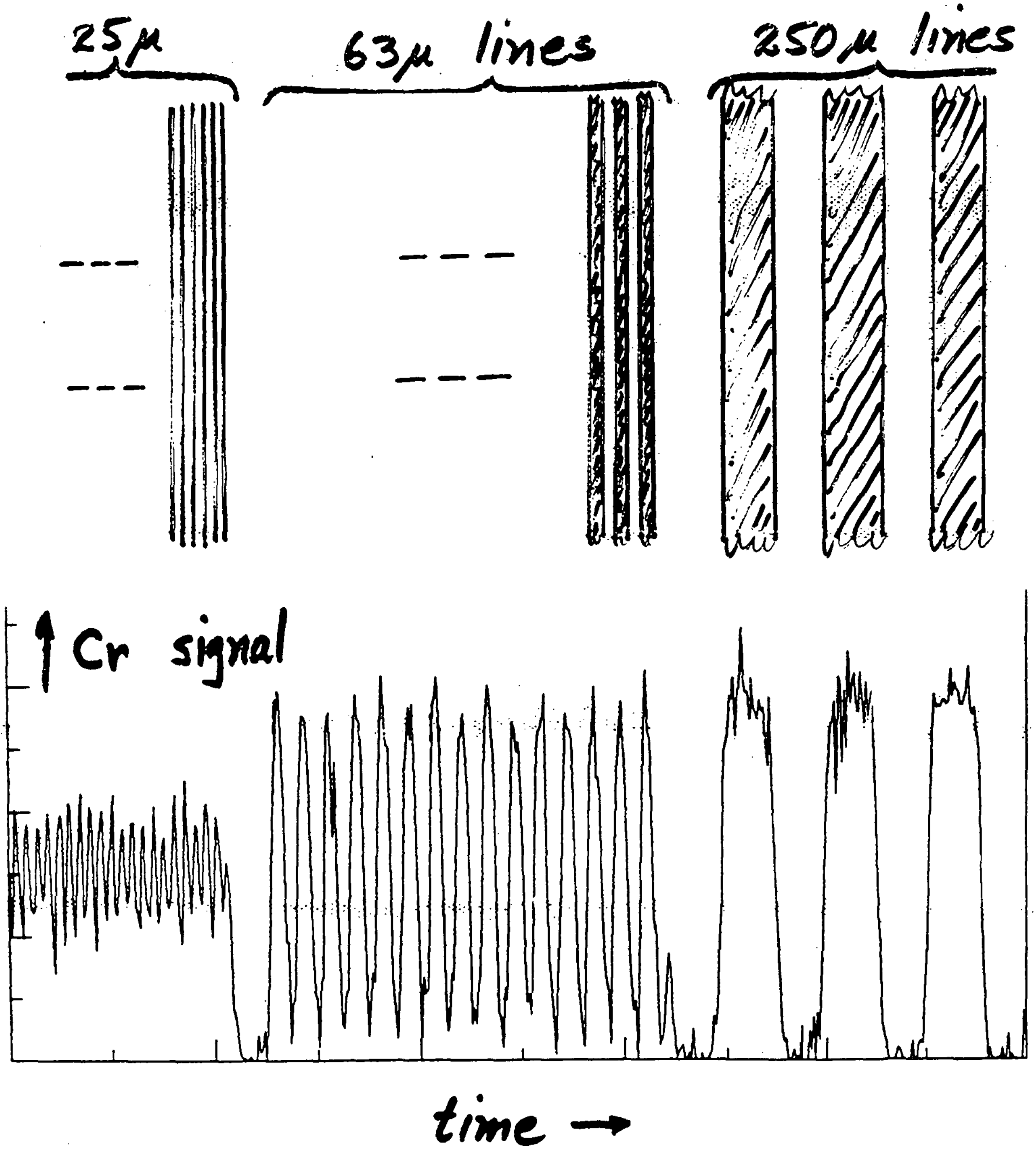


Typical sample-limited widths

~ 0.5 - 2 eV

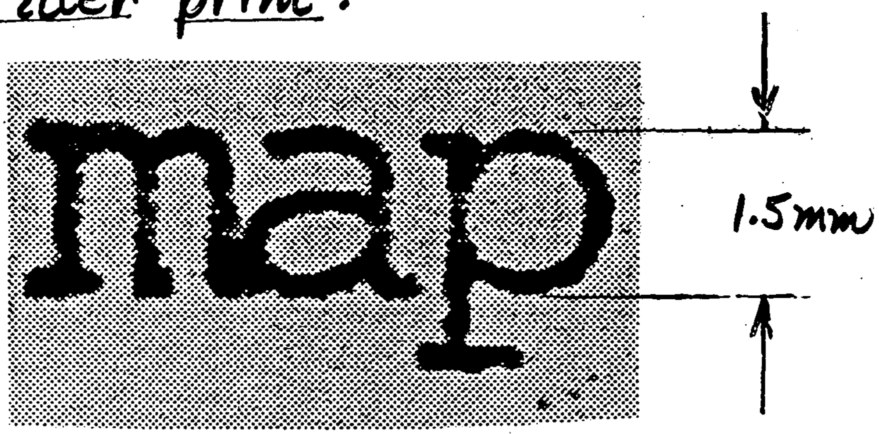
Line Scan

(Spatial Information/Minimum Time)

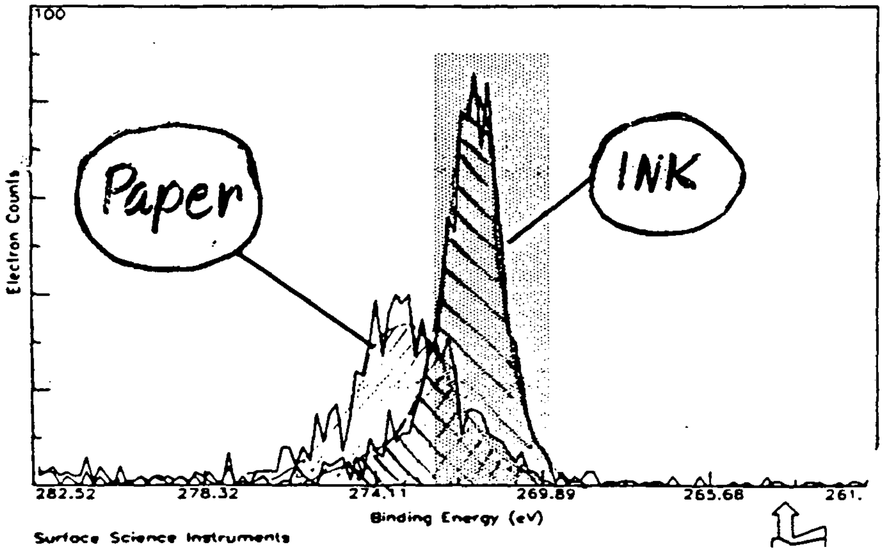


Spatial Resolution:
An Example

Typewriter print:

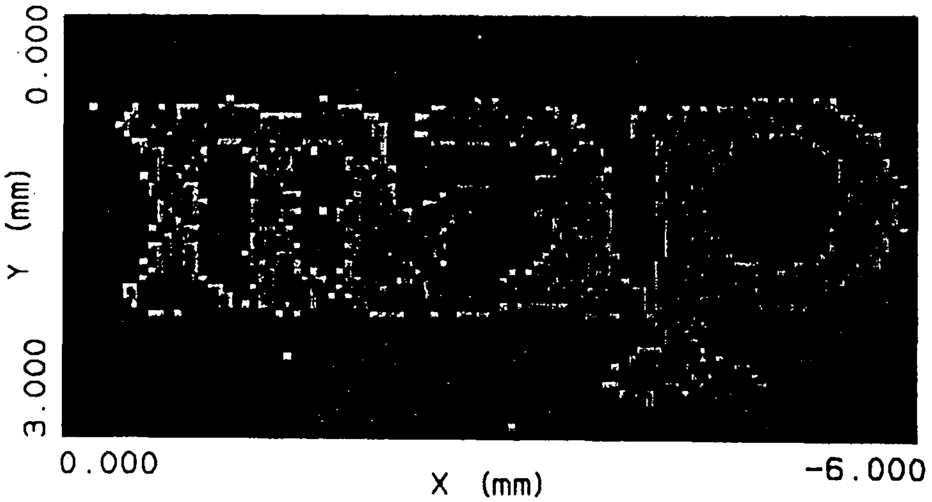


C(1s) Spectrum:



File: COPMAP10 Date: Feb 18, 1991 Operator: rlg

Description: Elemental map of letters on paper, 6um steps, M-Probe.
Region 1 Of 3



Element	O (1s)
Lower BE	515.0
Upper BE	524.0
Seconds	3sec /pt
Floodgun	15 eV
Resolution	4
Spot size	100um
Aperture	None
X nodes	99
Y nodes	49

⇒ 4 hours

■ 100.000 ■ 200.000 ■ 300.000 ■ 400.000 ■ 500.000 ■ unassigned

1 point - all elements ~ 5min
1 point 1 element < 1 min

9eV energy interval
Res ~50μ
Nice "gee-whiz" appl. - but not very useful

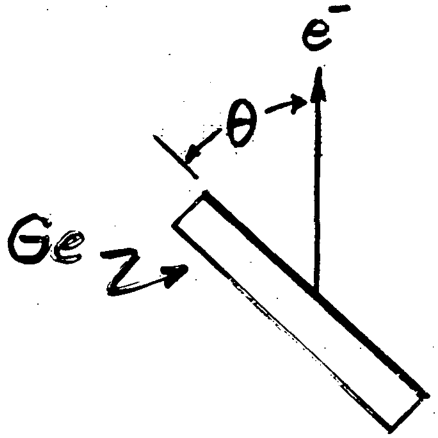
Real use: point analysis
Limit data rate

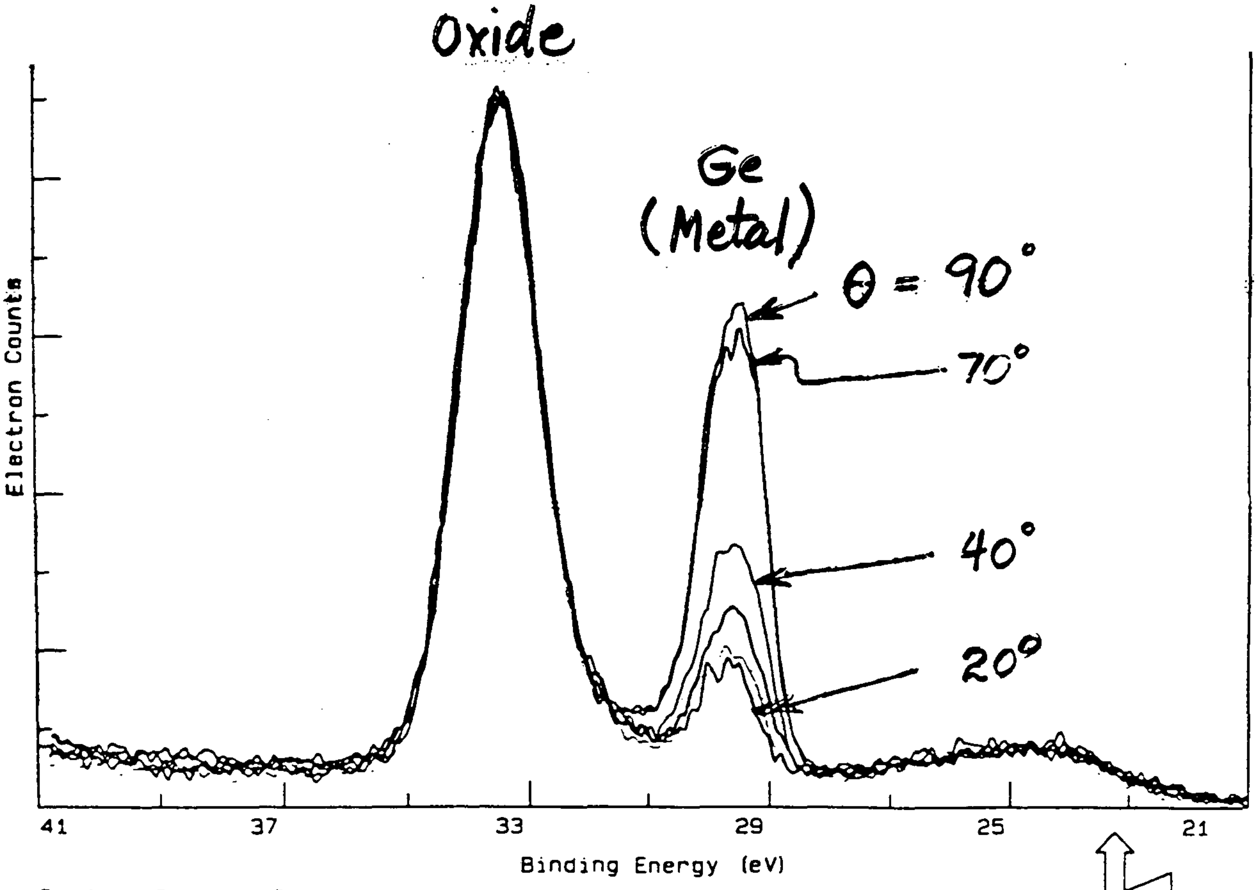
Surface Science Instruments

Depth Info —

Angle Resolved XPS

(Non-destructive Depth Profiling:
Depth < 100Å)





Surface Science Instruments

Special Systems

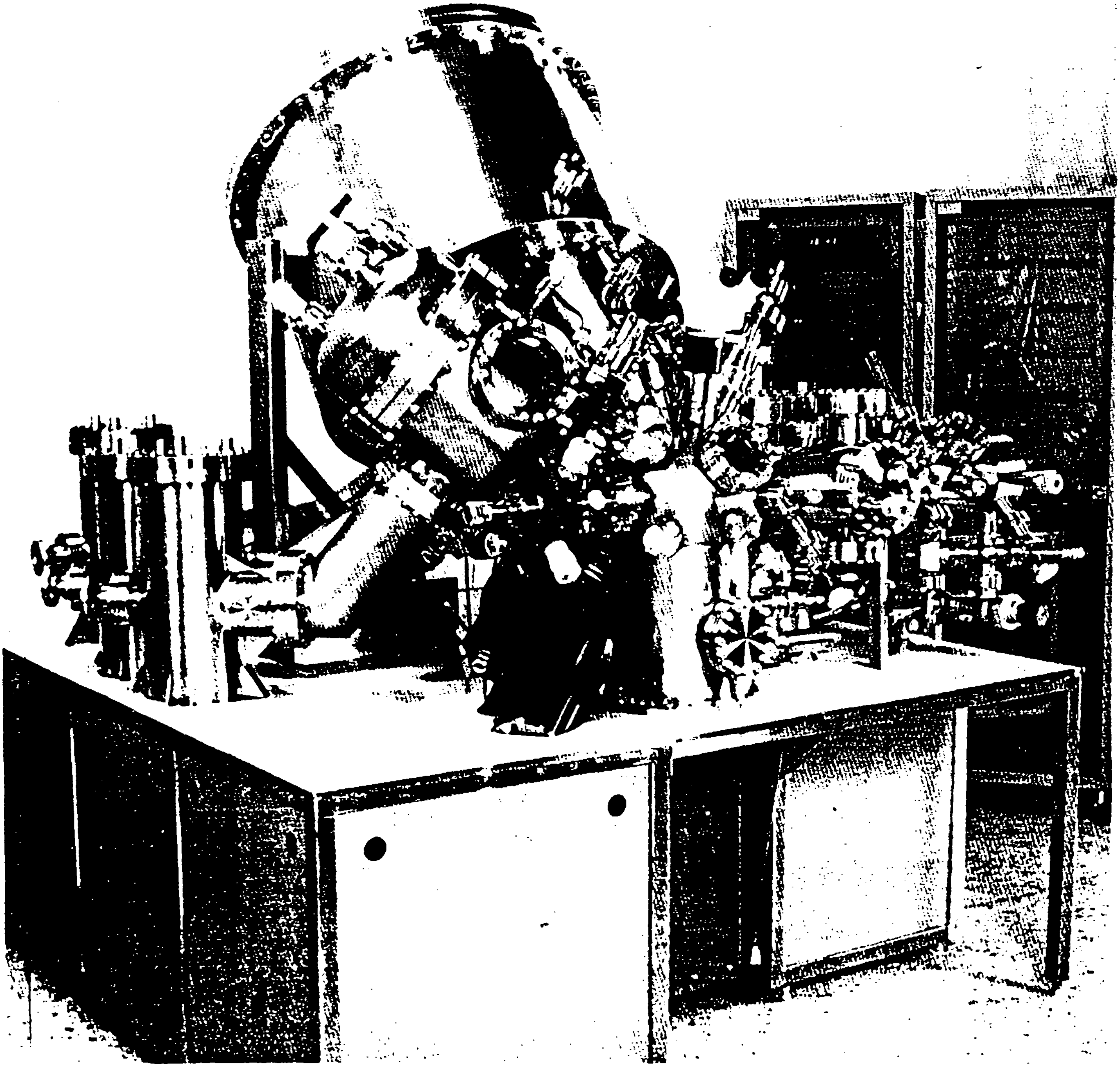
Scienta: Superior Spectroscopy

VG ESCAScope: New Imaging Technique

(VG?): Photoelectron Spectromicroscope

prev - state of art of "std" instr.
- instr that push state of
art in 1 dir or another

ESCA-300

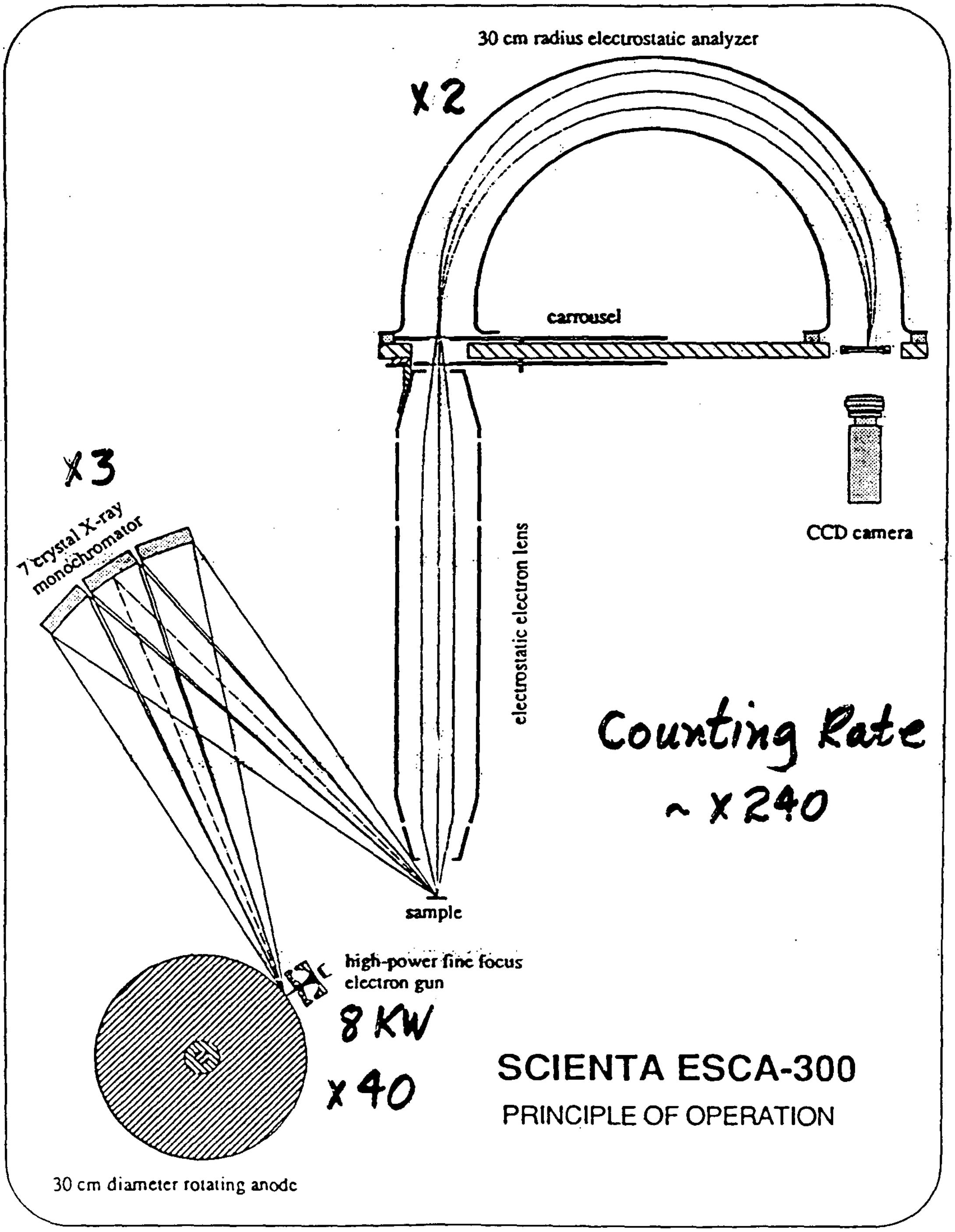


SCIENTA

largest analyzer

SCIENTA INSTRUMENT AB

Seminariegatan 33 H S-752 28 Uppsala, Sweden



x 2

x 3

Counting Rate
~ x 240

8 KW

x 40

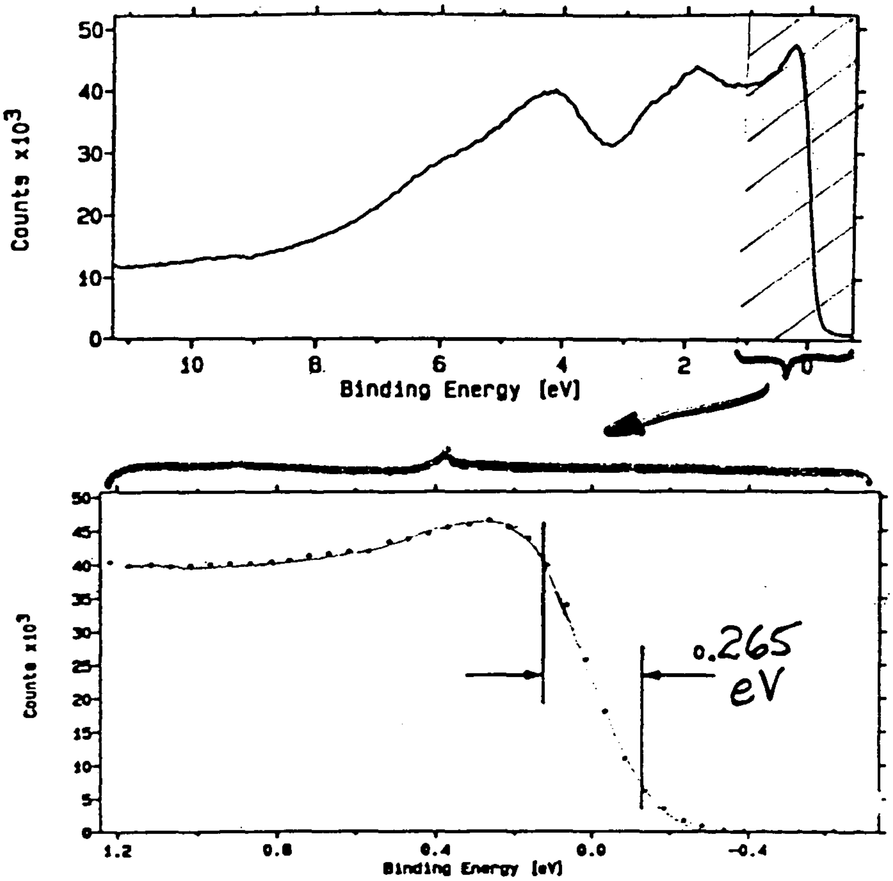
SCIENTA ESCA-300
PRINCIPLE OF OPERATION

Energy Resolution

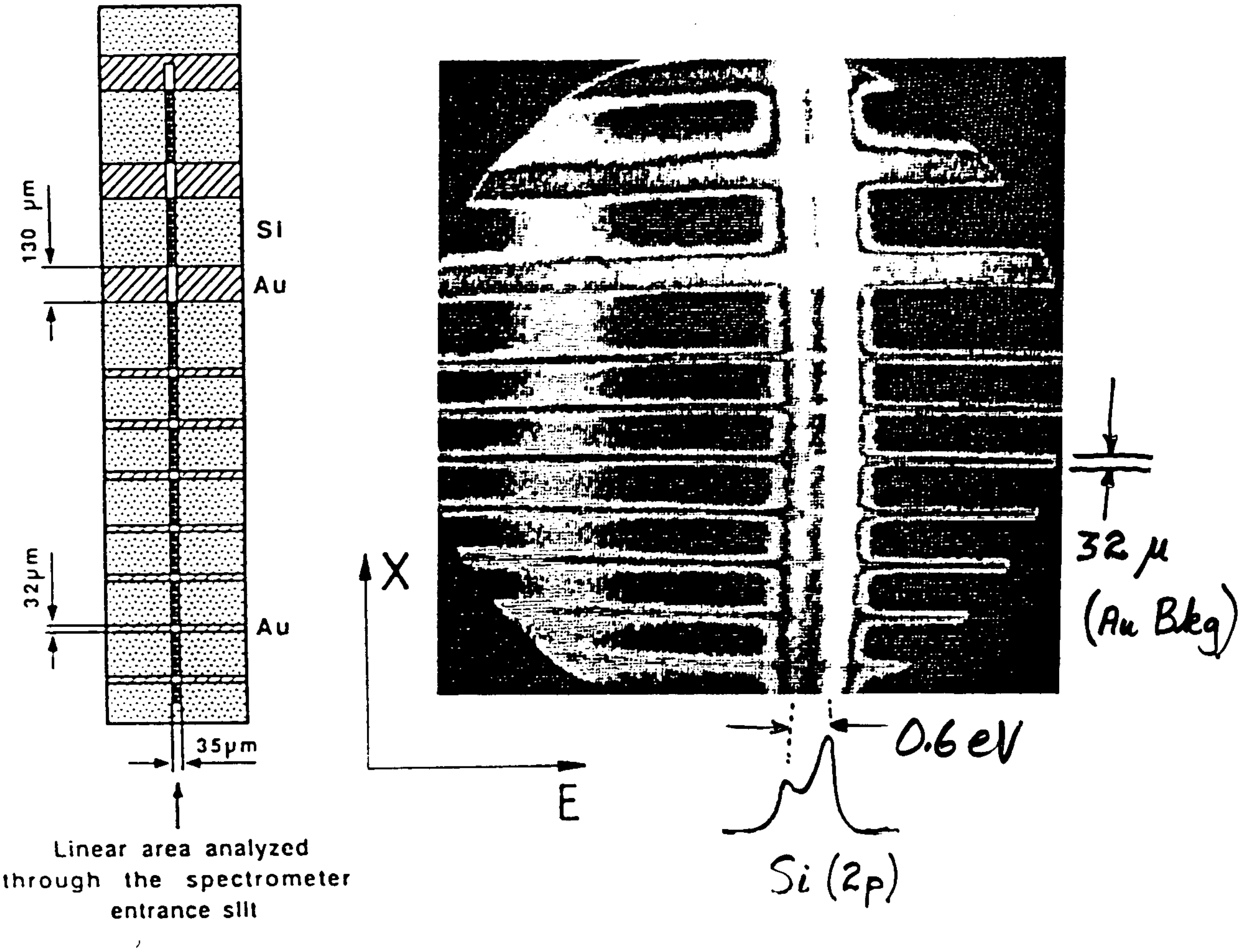
Scienta ESCA-300

from Fermi Edge of Cleaned Pt

(Corrected for kT)



$$.265 = \sqrt{\underset{\underset{\text{source}}{\uparrow}}{(.20)^2} + \underset{\underset{\text{analyzer}}{\nwarrow}}{(.17)^2}}$$

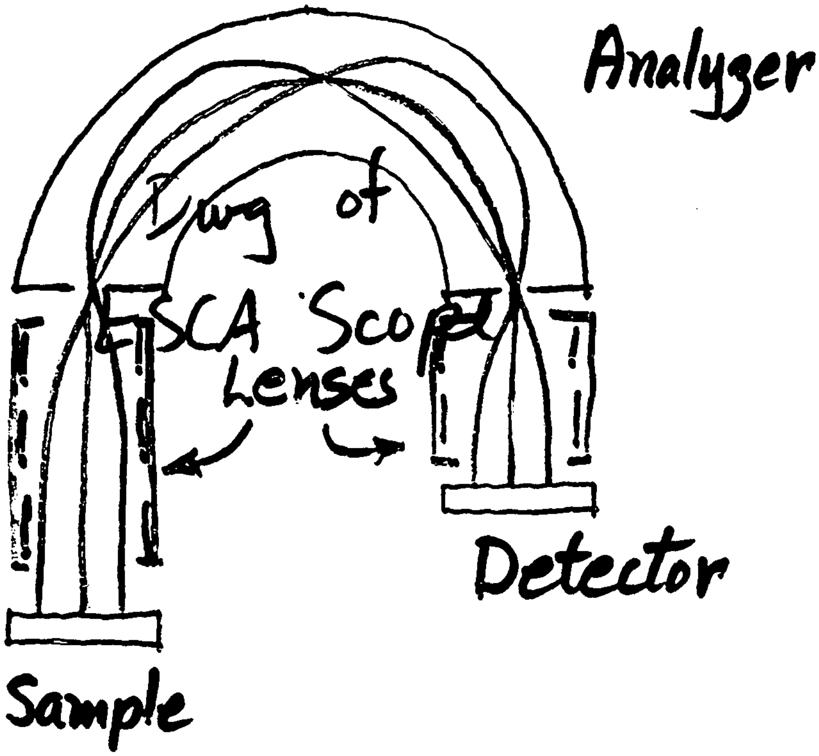


ESCA-imaging with high spatial and energy resolution is demonstrated in this photograph of the color-coded intensity distribution on the detector. The sample is a silicon wafer with evaporated gold stripes. The wide gold stripes are 130 μm and the narrow stripes are 32 μm wide, with a periodicity of 400 and 200 μm, respectively. The pass energy of the spectrometer was in this recording 150 eV, and a 10 eV wide region around the Si 2p energy is detected simultaneously. With the analyzer slit width chosen, 0.5 mm, and a lens magnification of 15x, the observed area on the sample is 35 μm x 2.3 mm, with the long direction perpendicular to the gold stripes, as shown schematically to the left. The backgrounds from the gold spectra extend throughout the displayed energy region. In the intervening silicon regions, the Si 2p doublet is seen clearly resolved, and the SiO_x signal is also very evident. The intensities are high enough to allow the simultaneous collection of high resolution ESCA spectra from 100 separated surface elements along the observed line, with a spatial resolution of about 25 μm.

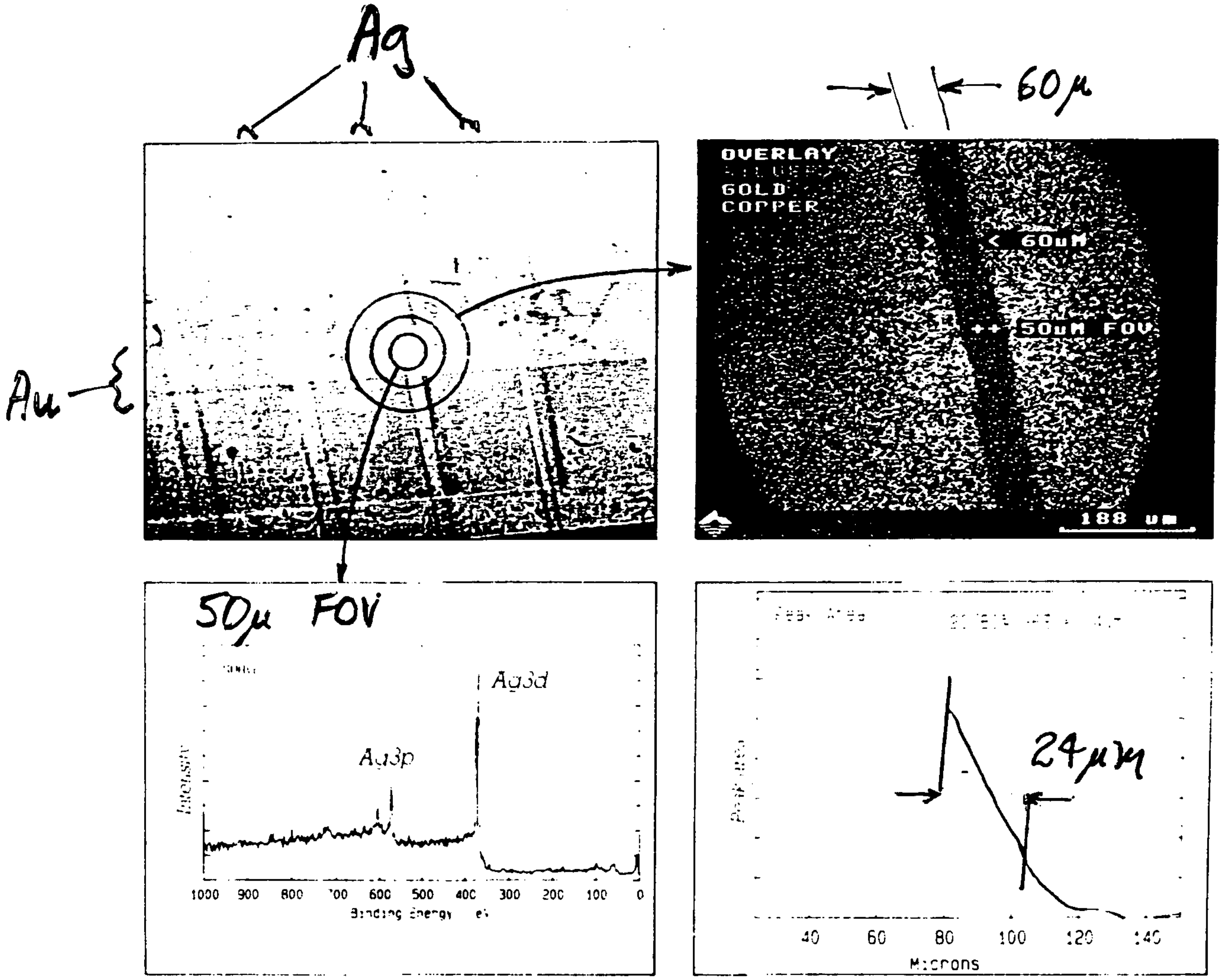
upr: turning e lens —
get good spatial res
~ 25μ

ESCA Scope

VG / Fisons



innovative imaging concept
positions converted to ∡ at entrance
slit ; preserved, re-converted

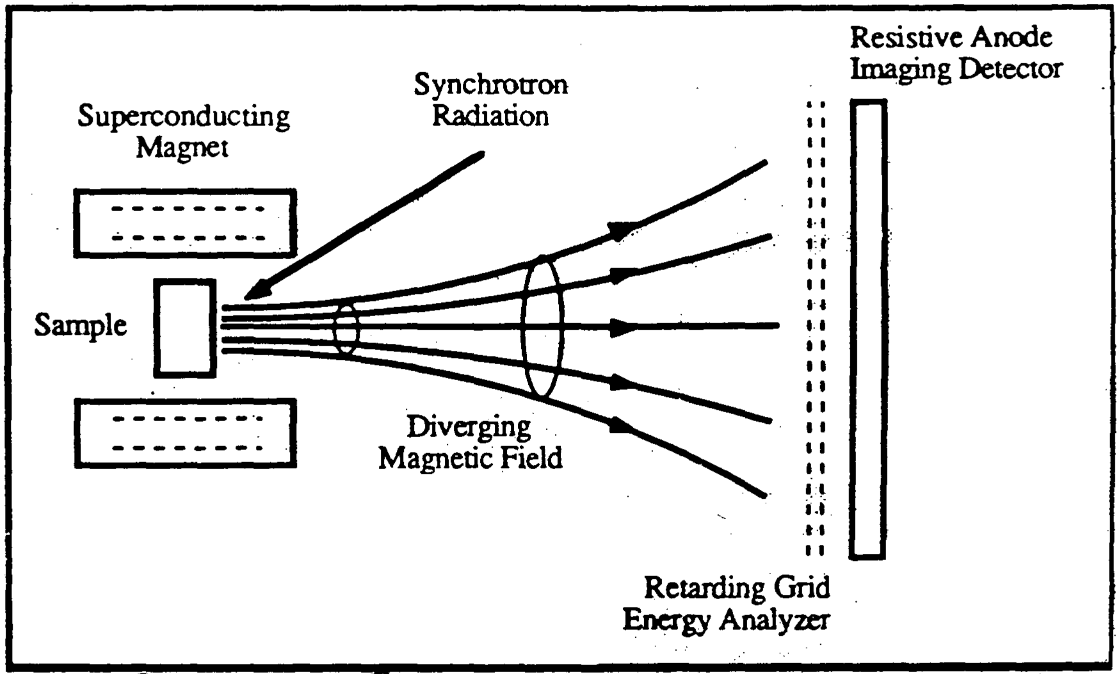


eg of performance

- prob - intensity -
  in std instr e^-s from
  1 point fill analyzer

so I (Total picture) = I (1 pt) std

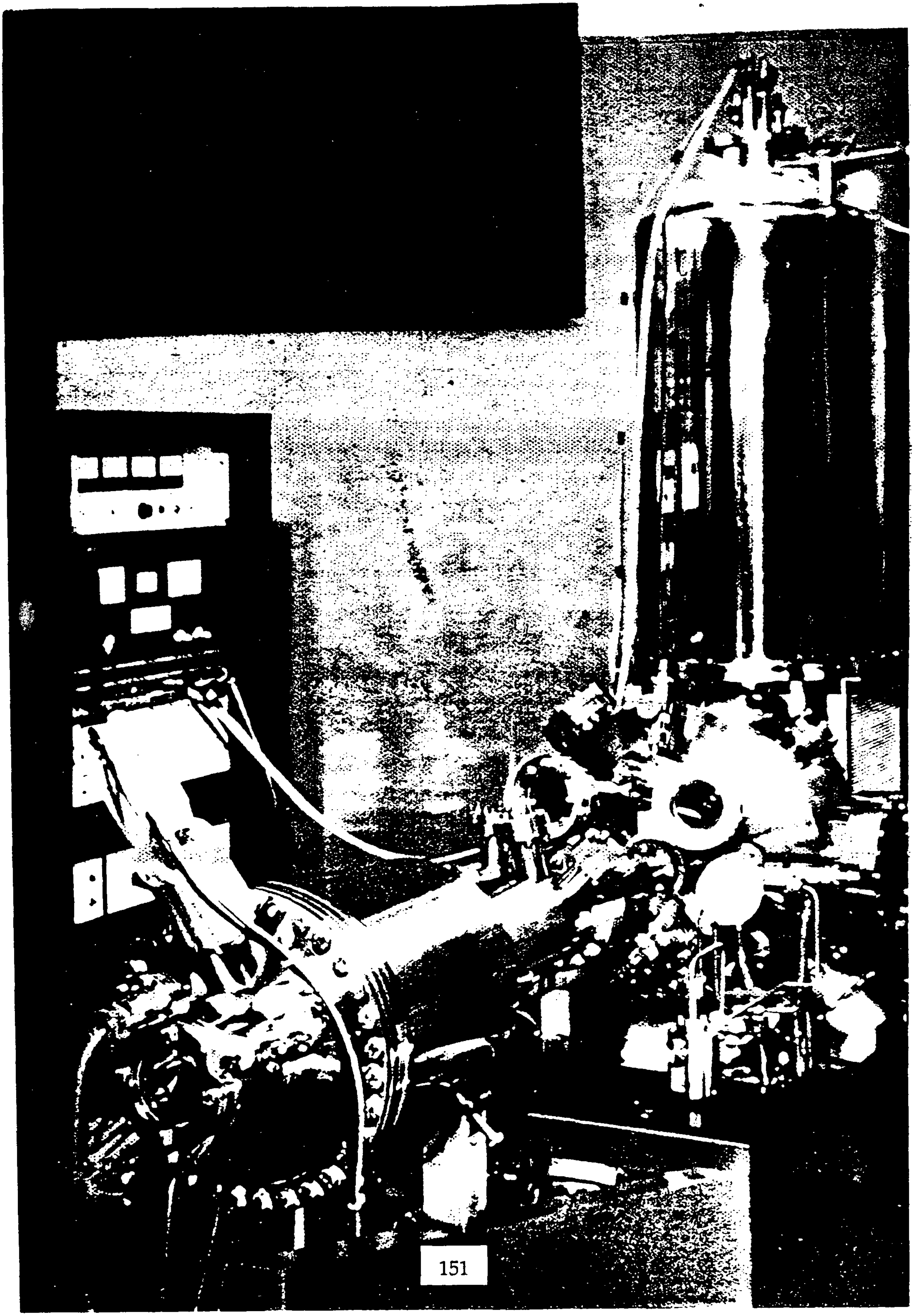
⇒ need brighter source.

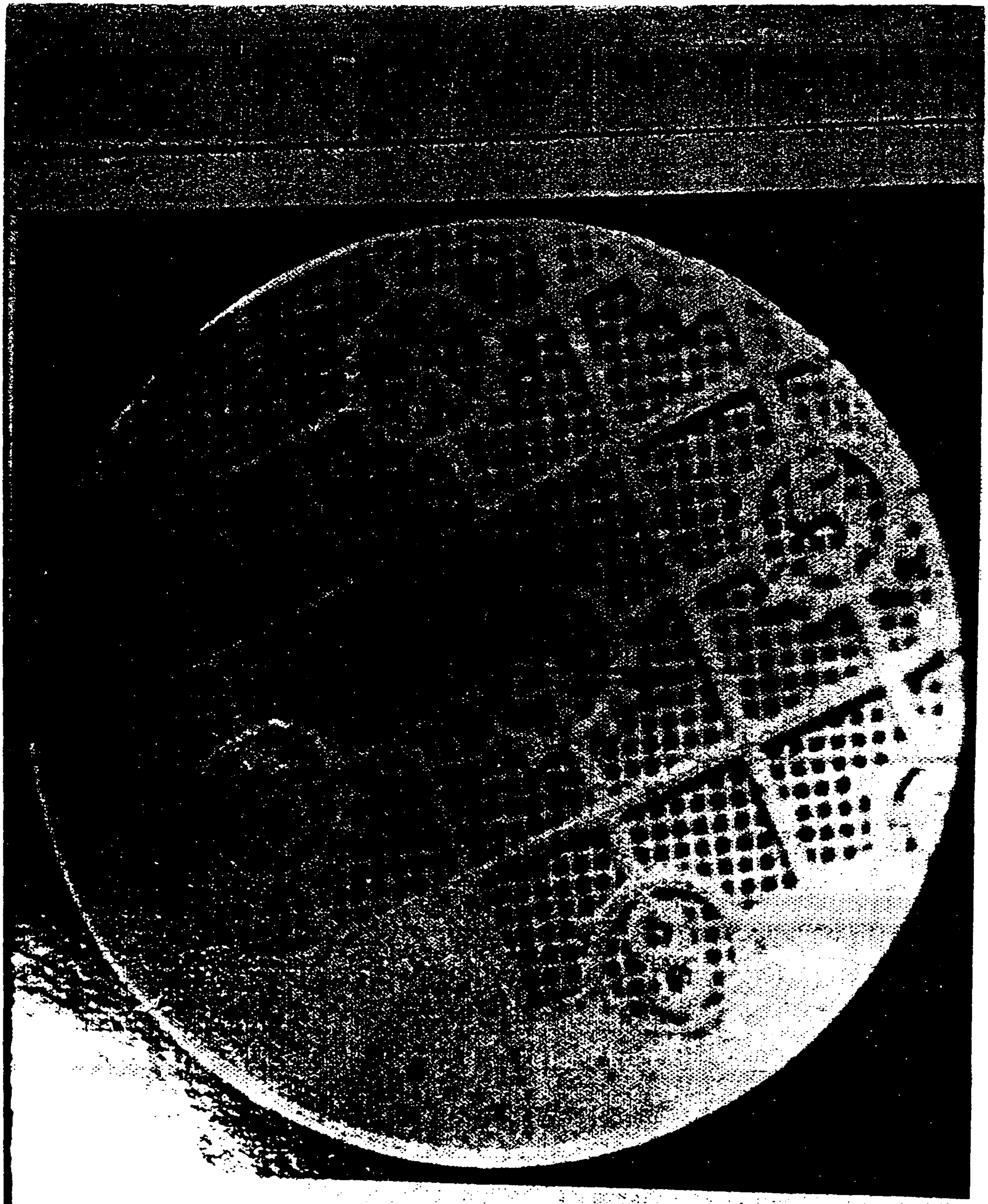


BEAMSON, PORTER, TURNER (1981)

- Photoelectrons projected along Magnetic Field -----> Imaging
- Magnification -----> $(B_{sample}/B_{detector})^{1/2}$
  ≈ 70X @ B_{sample} = 7T
  ZOOM: +2X/-4X
- Spatial Resolution -----> Rmax ∝ $E^{1/2}B^{-1}$
  Standard: 1-10 μm
  Future: 0.2-1 μm
- Pixel Size -----> Determined by detector
  Range: 0.4-3.2 μm
- E/momentum conserved -----> Spectroscopy with Retarding Field Analyzer.
- High efficiency ⟶ collect 2π

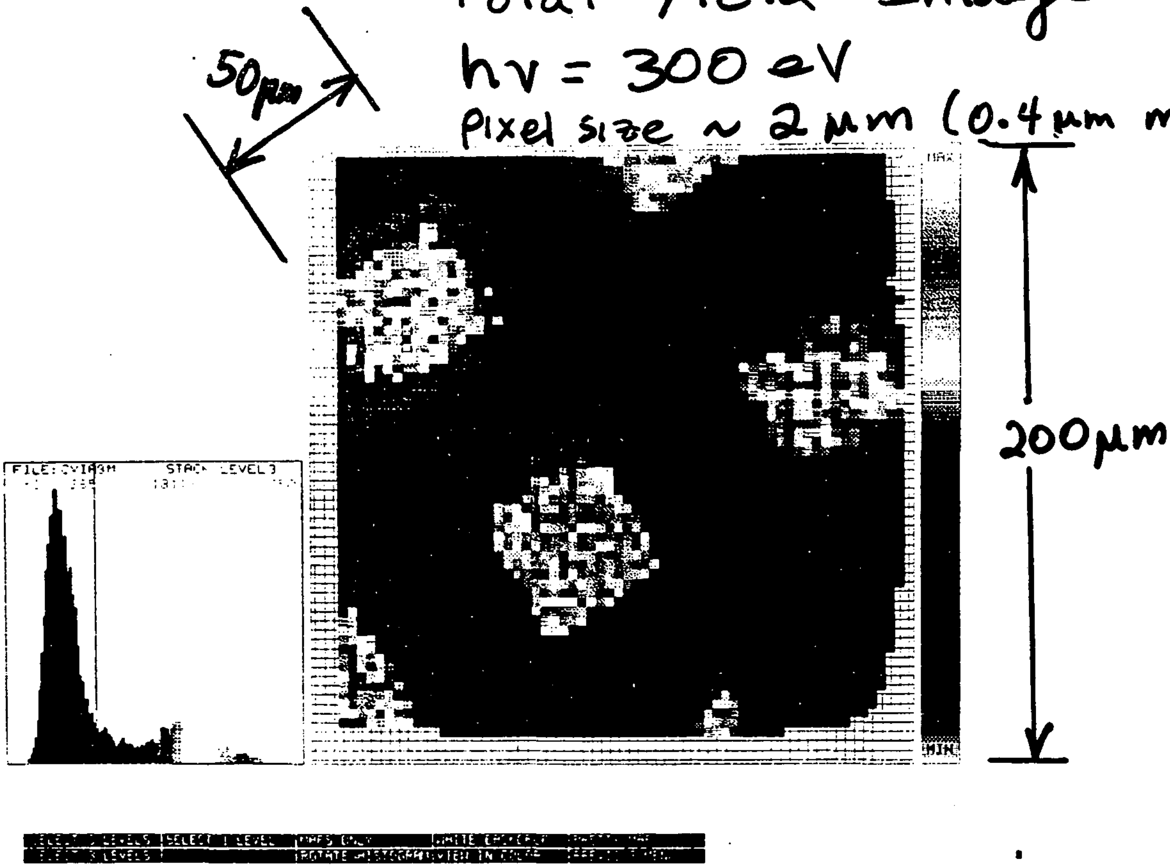
C.W.R.



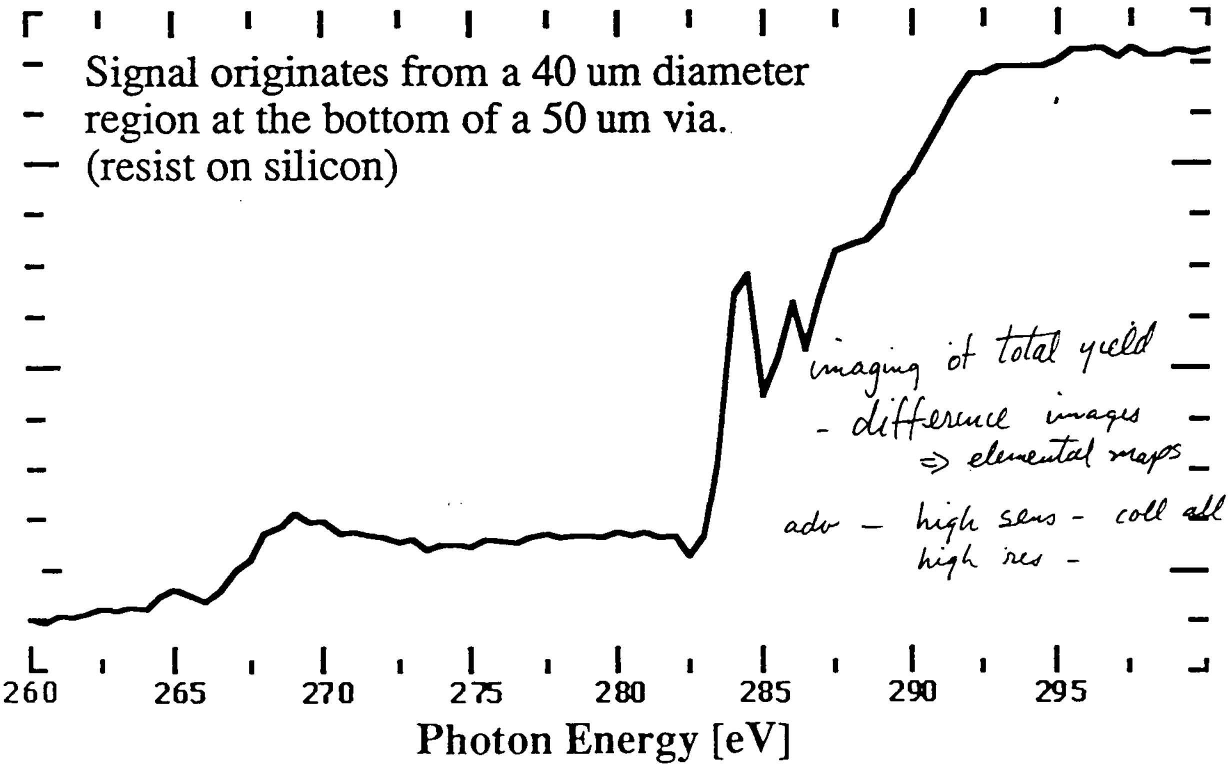


VIAS IN RESIST

Total Yield Image
hν = 300 eV
pixel size ~ 2 μm (0.4 μm min.)



Total yield spectrum at carbon 1s edge

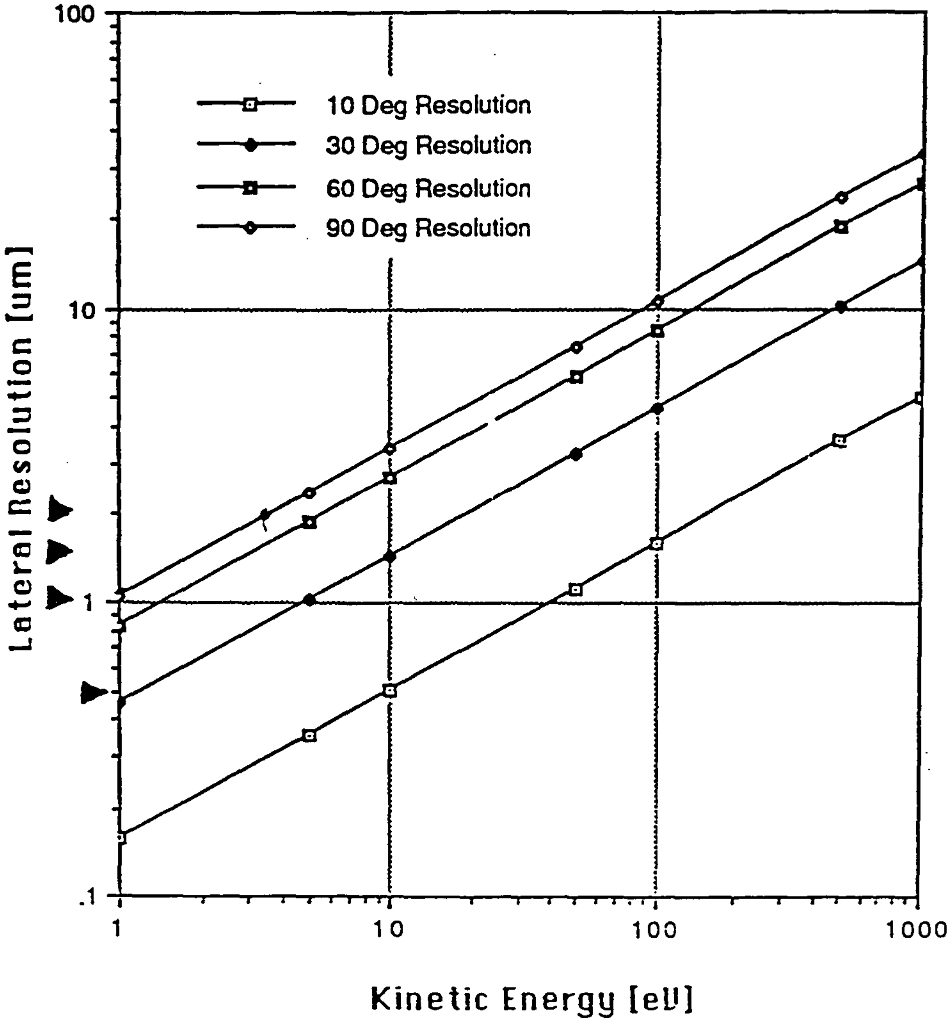


Signal originates from a 40 um diameter region at the bottom of a 50 um via. (resist on silicon)

imaging of total yield
- difference images
⇒ elemental maps

adv – high sens – coll all
high res –

Resolution vs. kinetic energy at various skimming angles



Σ - Promising tech w/ var photon energy.

- imaging energy analyzer

probs {
- chg neutralizing
- sample in 9T field

Summary of Commercial Instruments

- Wide Variety of Uses
- Resolution adequate
- Pressure for more speed, Spatial Resolution
- Limited Use of Angular Info; Other Photon Energies

Industrial Uses of XPS

- o ***Troubleshooting:***
  Finding the
  Unexpected

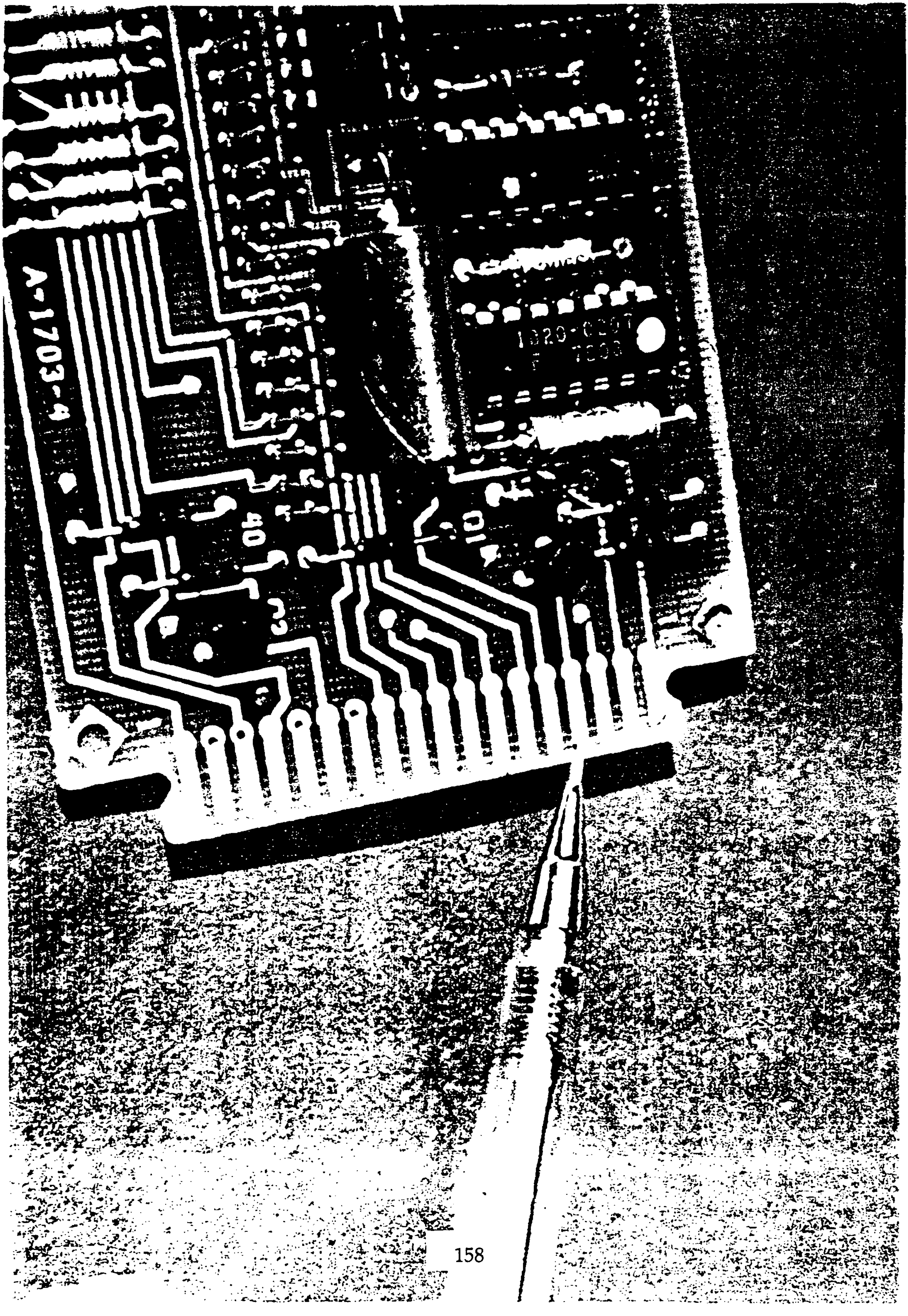
- *o* ***Process Fingerprinting:***
  Monitoring
  Deviations
  From a Standard

- *o* ***Research/Development:***
  Tracking Theory
  With Experiment

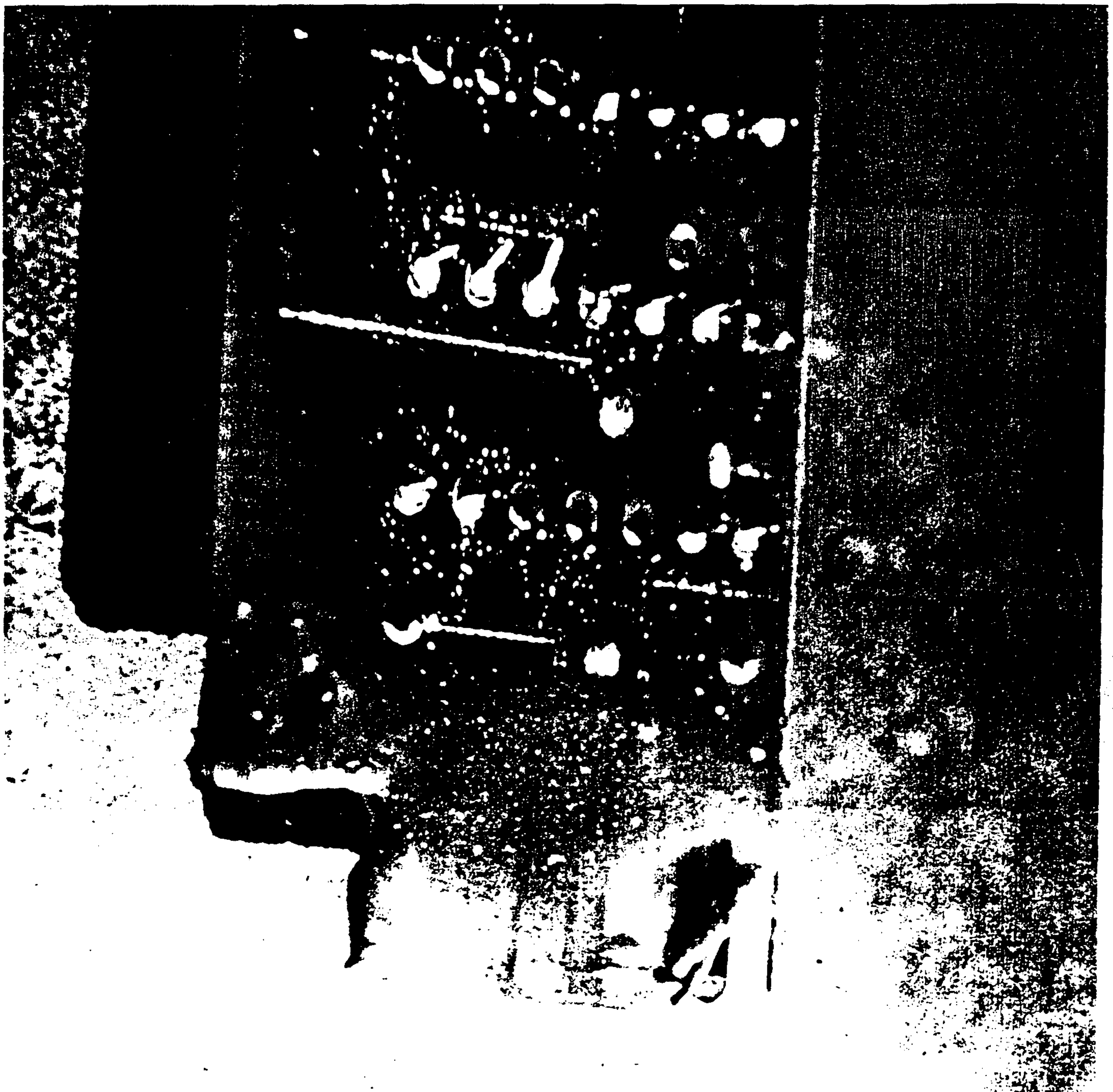
Most non-ind uses are last
categ - look through journals
to find egs

	Trouble-shooting	**Finger-printing**	**Research/ Develop.**
Time	Urgent	Routine	Planned
Task Definition	Low	High	Complex
Analysis	Broad	Specific	Custom
Looking For	Clues	Deviations	Understanding
Important Features	Breadth	Repeatability	Flexibility

eg of each –

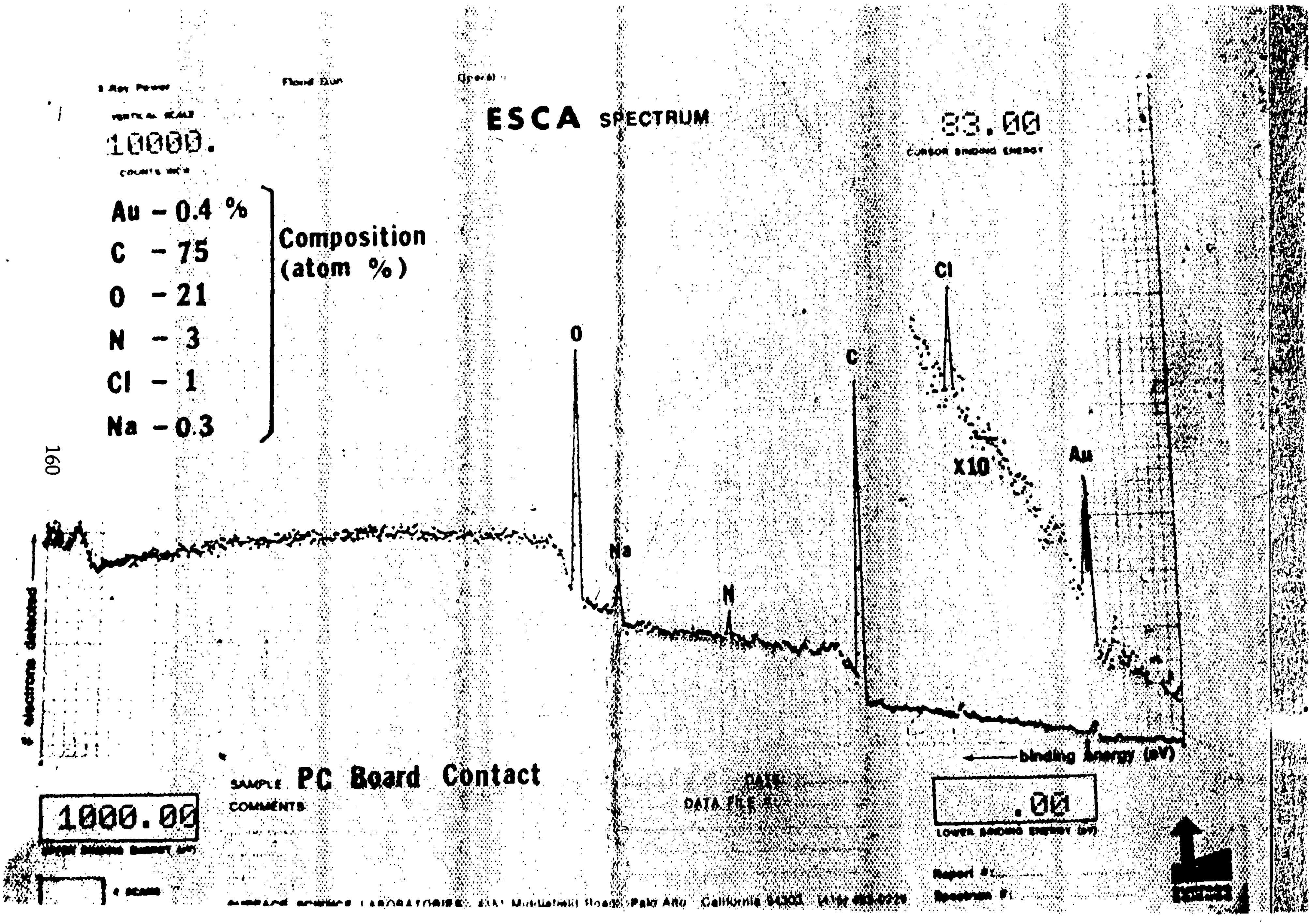


A-17703-4
40



5 min scan
elem't rel abund

High res scans –
look for C-O bonds
– not specific answer –
– spectra of cleaners,
resists, etc used to
fab board

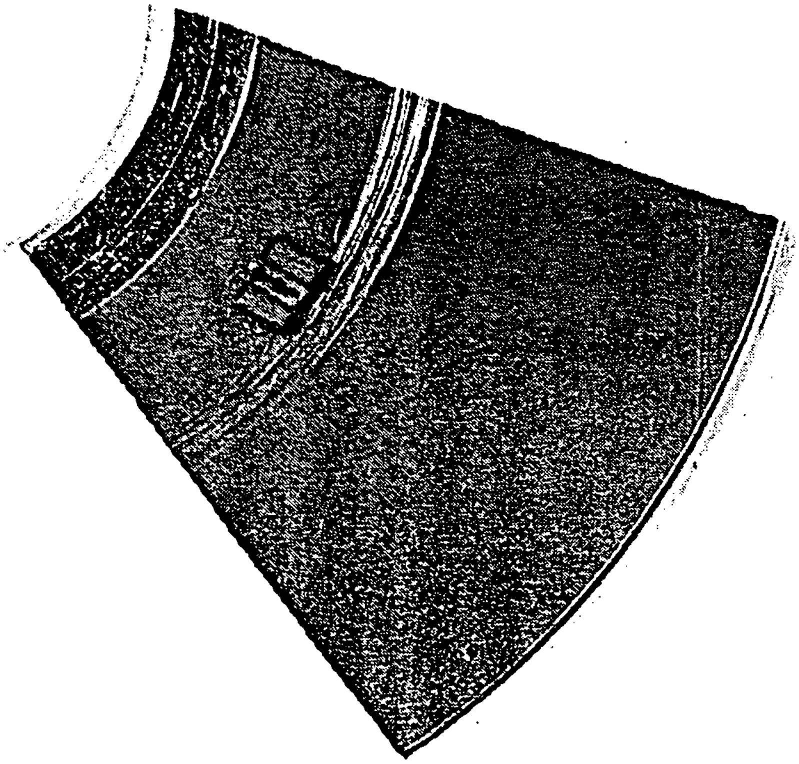


Au - 0.4 %
C - 75
O - 21
N - 3
Cl - 1
Na - 0.3

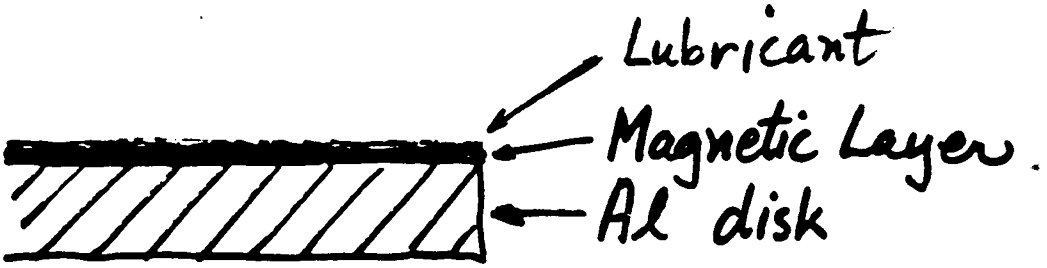
Composition (atom %)

SAMPLE PC Board Contact

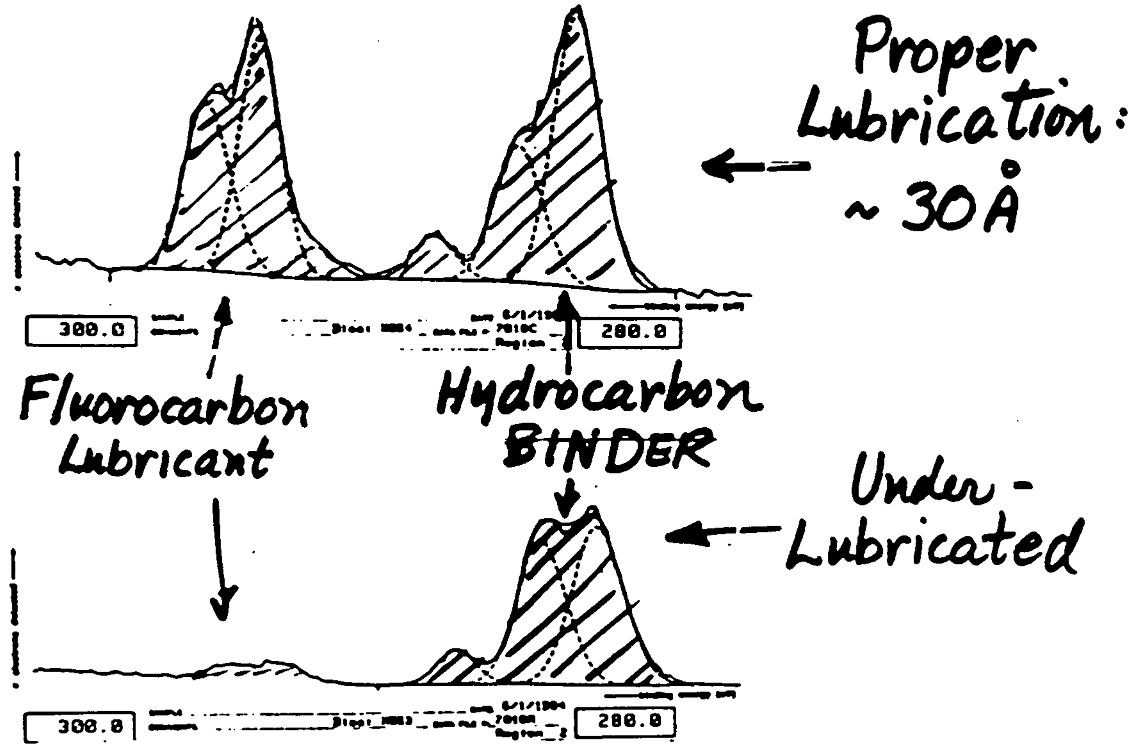
Process Fingerprinting



Lubricant Thickness



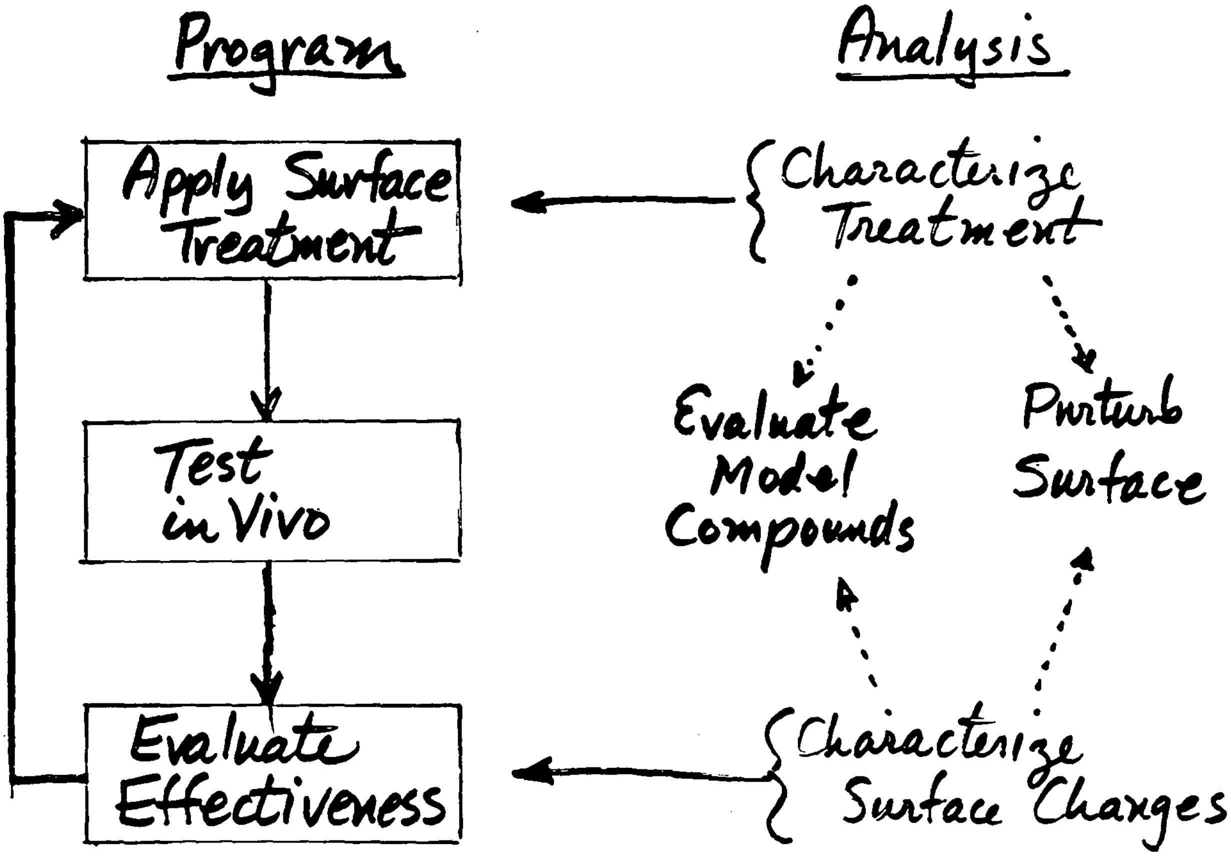
C(1s) Spectra :



Analysis Time: 15 sec/sample

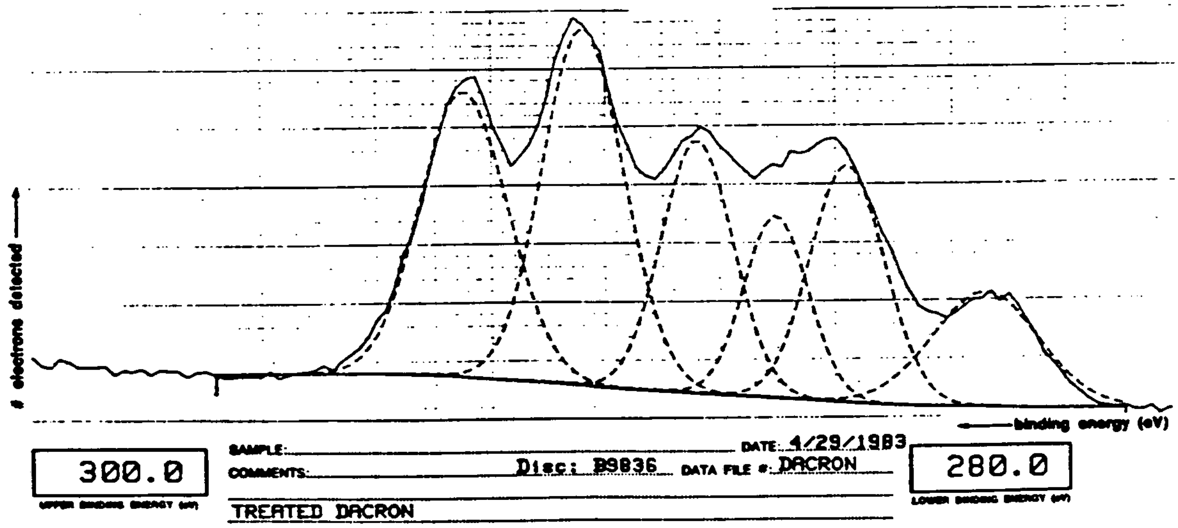
A Research Application:
Development of a Polymeric Implant

- Synthetic Dacron Artery



invest considerable time in understanding
complicated analyses
develop special processes —
eg analyze wet materials

C(1s) Spectrum of plasma treated surface:



300.0

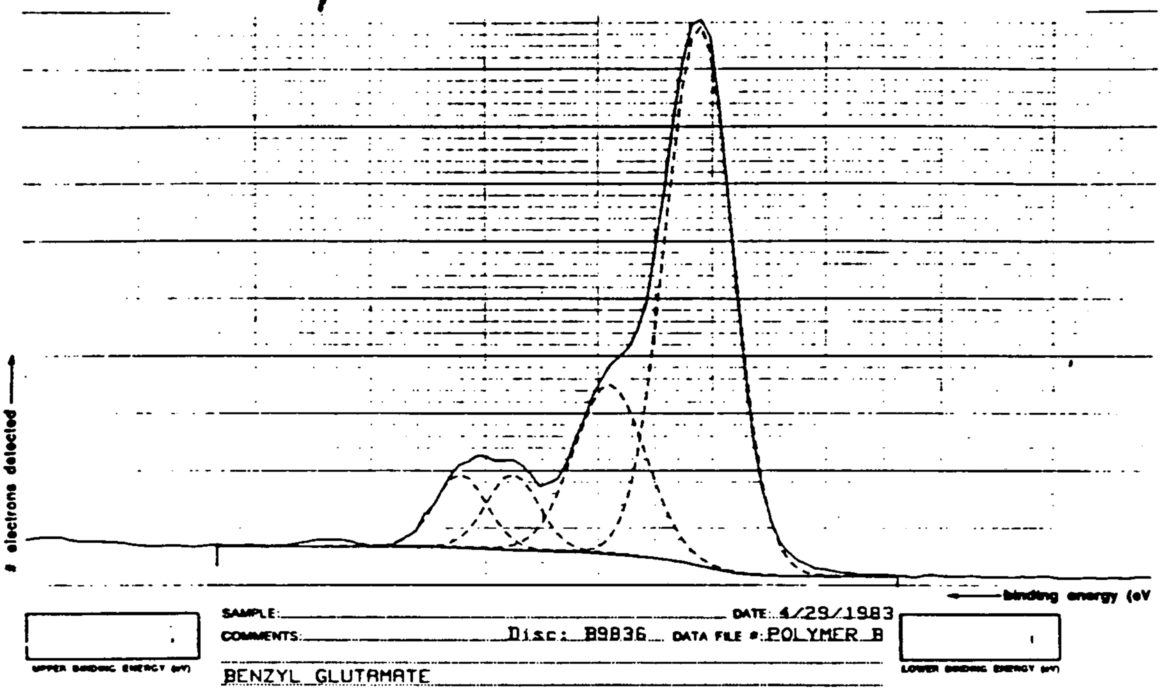
SAMPLE: DATE: 4/29/1983

COMMENTS: Disc: B9836 DATA FILE #: DACRON

TREATED DACRON

280.0

Model Compound ?



SAMPLE: DATE: 4/29/1983

COMMENTS: Disc: B9836 DATA FILE #: POLYMER B

BENZYL GLUTAMATE

- Much machine time
- Special features needed
  - analyze hydrated surfaces
  - spectral synthesis software

Economics

Equipment Depreciation..........	$100K
Operator + Overhead.............	$120K
Facility, Services, Supplies.......	$100K
Total:	$320K

2000 hrs/yr $160/hr

Simple Problem:

3hrs $480

Research Problem:

6 weeks $38,400

Information has to be worth its cost

easier to throw-out
plating bath than
to understand contaminant

Areas of Opportunity

- Variable Photon Energy
  - --Diffraction Effects
  - --Deep Depth Profiles

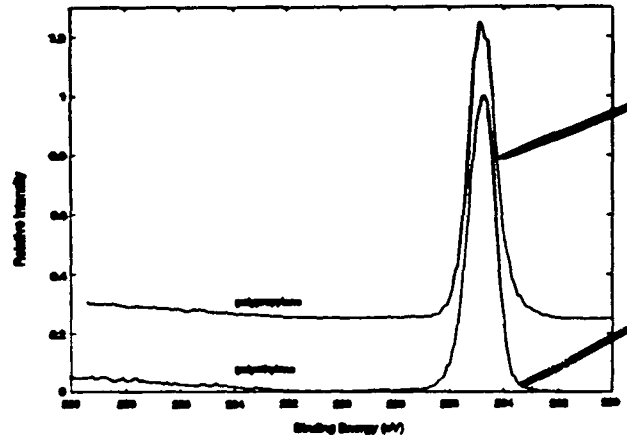
- Sub-micron Imaging

- Valence band Characterization

– time resolved
– 2 photon
XANES

Distinguishing Polymers

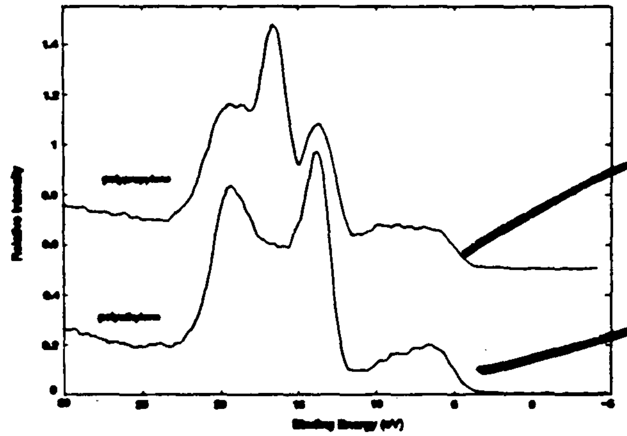
Core level:



Polypropylene

Polyethylene

Valence band:

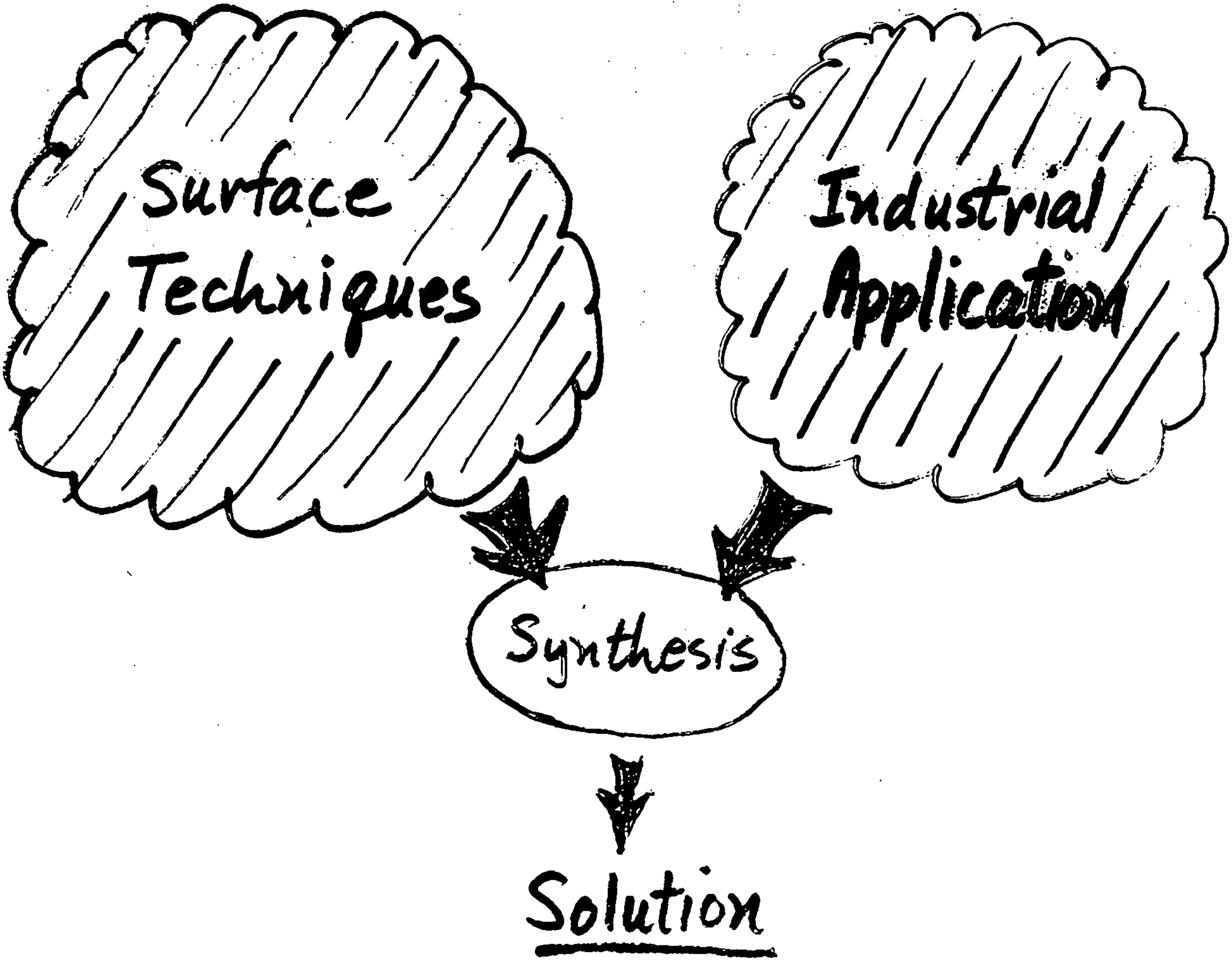


Polypropylene

Polyethylene

– from Mike Edgell

Relating Surface Measurements to Commercial Problems



Materials Analysis by Photoemission: Is This Practical at ALS?

R. Brundle

IBM Almaden Research Center

PRACTICALITY OF "REAL WORLD" ANALYSIS AT THE ALS ?

PHOTOEMISSION

Ⓐ WHAT ARE THE TECHNICAL ISSUES ?

Ⓑ WHAT ARE THE PRACTICAL ISSUES ?

FIRST : WHAT IS MEANT BY "REAL WORLD" ?

- Problems presented to the analyst every day in the "trenches" — NOT A RESEARCH PROGRAM
- What is there — Qualitative Identification
- How Much is there – Either Quantification or comparison of one sample to another (reference)
- How Is it Distributed — Position, thickness, depth, etc.
- Wide range of chemicals from large organic molecules and polymers through to metals.
- Wide range of materials forms – particles, thin films, patterned (rough) structures, engineered (processed) parts

TECHNICAL ISSUES

PHOTOEMISSION — XPS OR ESCA

- USUALLY CORE-LEVEL WORK. ALMOST NEVER VALENCE LEVEL WORK (but see Kelly)

→ SURFACE OR NEAR-SURFACE INFORMATION

→ ELEMENTAL IDENTIFICATION
Sensitivity (sometimes resolution)

→ CHEMICAL STATE IDENTIFICATION
Resolution (sometimes sensitivity)

→ DISTRIBUTION → LATERAL
DEPTH
DEPTH PROFILING

What do you get at ALS (or other synchrotron) ~~that~~ in the above areas that

(a) You can't get by XPS in your lab?

(b) You can't get well enough / easily enough in your lab? (is it a practical proposition?)

(c) You can't get by some other technique? (eg electron impact, such as Auger, EDX).

Only if one of these is strongly positive will people come to ALS to do materials analysis, and then only if conditions are favorable
— cf commercial analytical labs.

— CAN YOU ACCESS IT ?
— CAN YOU SEE IT ?

ELEMENTAL IDENTIFICATION

- ALS expected to operate with "usable" flux over the 100 eV – 1000 eV hν range. Would like at least to 1486 eV (Al Kα standard source : known cross-sections)

— Actually seems that ALS works fine to well above 1486 eV

— Expected available monochromators die well before this however

SO • ALL USEFUL CORE-LEVELS "AVAILABLE" IN LAB AVAILABLE AT ALS ?

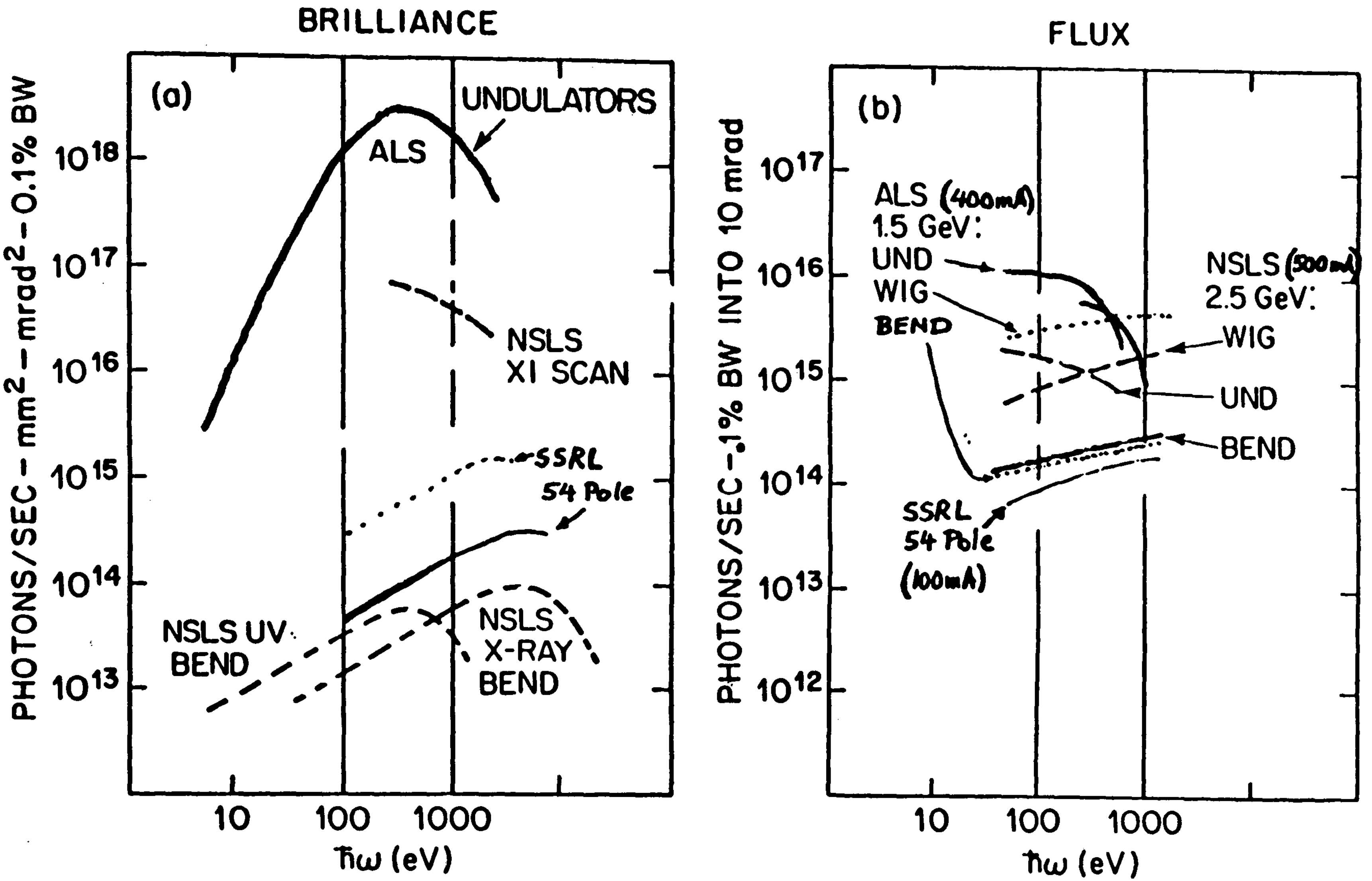
Na 1s 1072

Zn 2p 1021

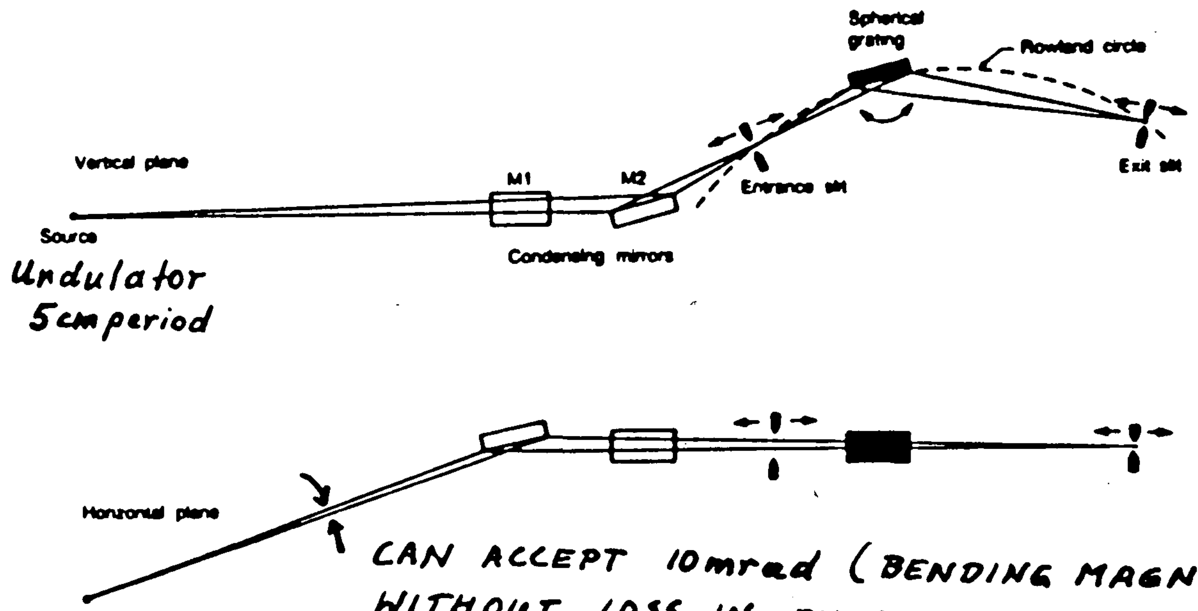
• WHAT EXACTLY IS THE SIGNAL STRENGTH COMPARED TO AVAILABLE COMMERCIAL XPS INSTRUMENTS ? — ie WHEN IS SENSITIVITY / SPEED SIGNIFICANTLY INCREASED ?

Usual Approach ⟶ Wait and see if it works

NOT WHAT ALS WANTS !

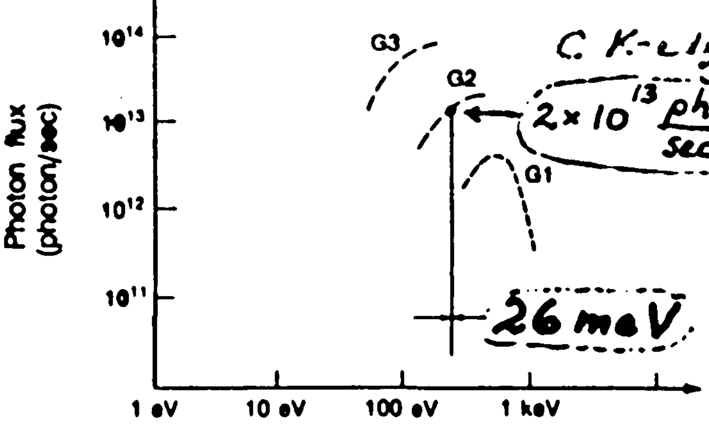

BRILLIANCE
(a)
UNDULATORS
ALS
NSLS
XI SCAN
SSRL
54 Pole
NSLS UV
BEND
NSLS
X-RAY
BEND
PHOTONS/SEC – mm² – mrad² – 0.1% BW
10^18
10^17
10^16
10^15
10^14
10^13
10
100
1000
ħω (eV)
FLUX
(b)
ALS (400mA)
1.5 GeV:
UND
WIG
BEND
NSLS (500mA)
2.5 GeV:
WIG
UND
BEND
SSRL
54 Pole
(100mA)
PHOTONS/SEC – .1% BW INTO 10 mrad
10^17
10^16
10^15
10^14
10^13
10^12
10
100
1000
ħω (eV)

UNDULATOR & SPHERICAL GRATING MONOCHROMATOR



CAN ACCEPT 10mrad (BENDING MAGNET) WITHOUT LOSS IN ENERGY RESOLUTION

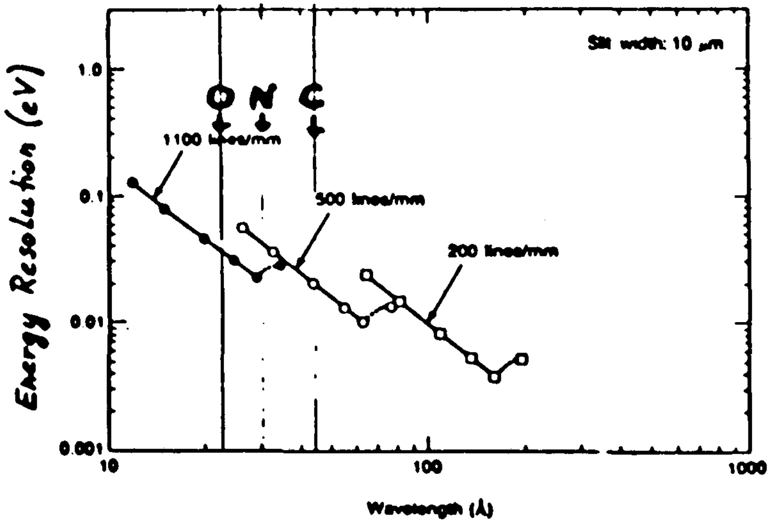
Flux with 10 µm slits



SX-700, BESSY

Presently: 2×10^{10} photons/[illegible], $\Delta E \sim 800$ meV

Optimum Resolution



CHEMICAL STATE IDENTIFICATION

- Question of Resolution
- Not separated from sensitivity however

RESOLUTION

ISSUE

- SOURCE DOMINATED — MONOCHROMATOR PERFORMANCE
- NATURAL LINE-WIDTH DOMINATED — WHICH ELEMENT ? WHICH CORE-LEVEL ?
- SAMPLE DOMINATED — "SOLID STATE EFFECTS" !
- ANALYSER DOMINATED — WHAT'S AVAILABLE ?

- IF SOURCE DOMINATED, NO DOUBT THAT ALS PROPOSED BEAMLINE / MONOCHROMATOR ARRANGEMENTS DO GREAT. – ie combine Flux with resolution
- MOST NATURAL LINE-WIDTHS WILL NOT BE A PROBLEM
- UNFORTUNATELY LAB EXPERIENCE SEEMS TO SHOW THAT IN MANY PRACTICAL CASES WIDTHS ARE SAMPLE DOMINATED

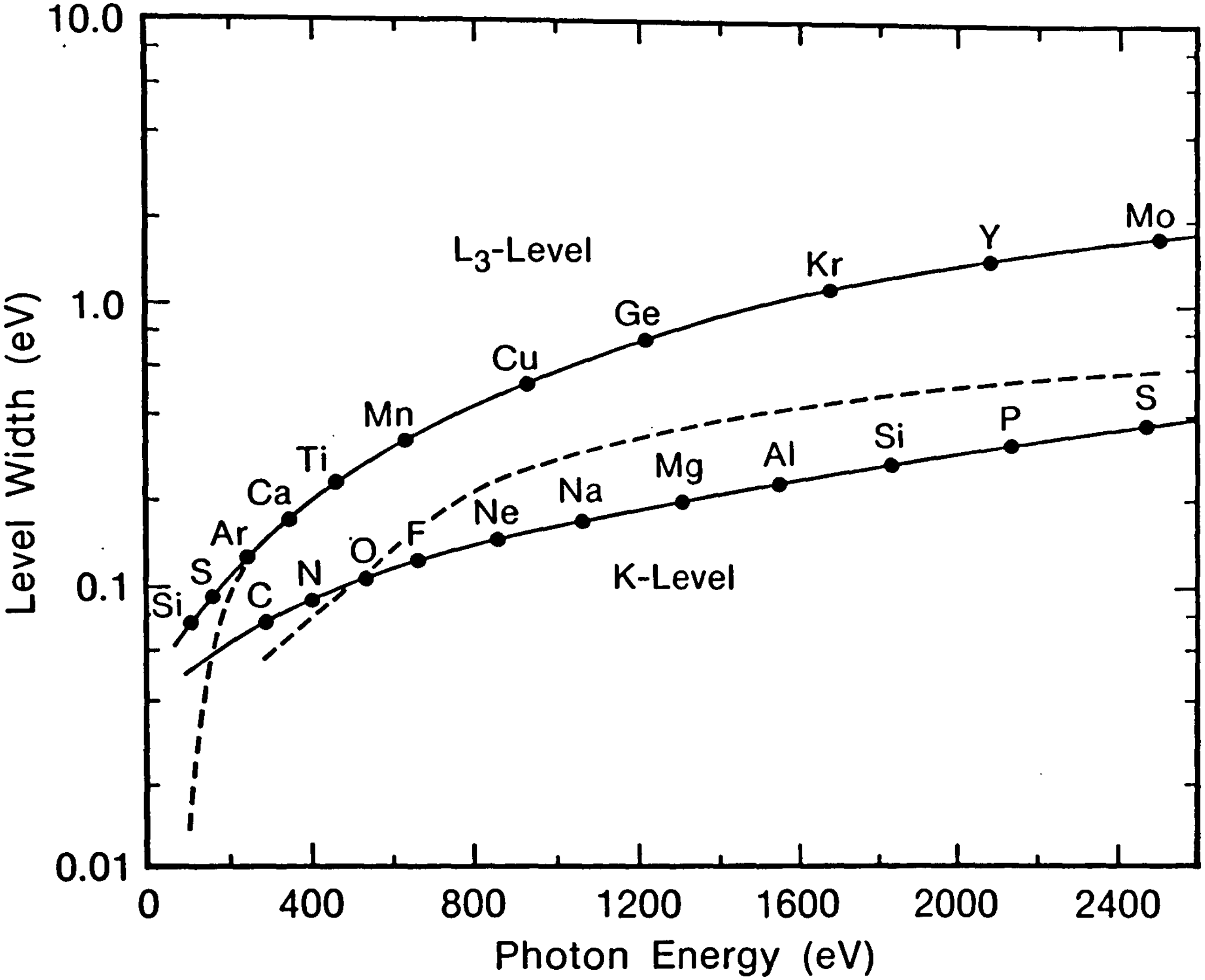
eg C (1s)

— Not Al (2p), Not Si (2p) ?

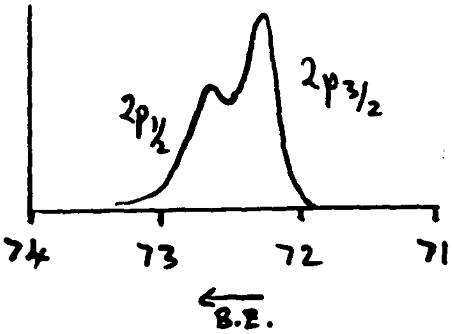
ie WHEN DOES THE EXTRA RESOLUTION DO YOU ANY GOOD ?

WIDTH

Natural Width of Core Levels



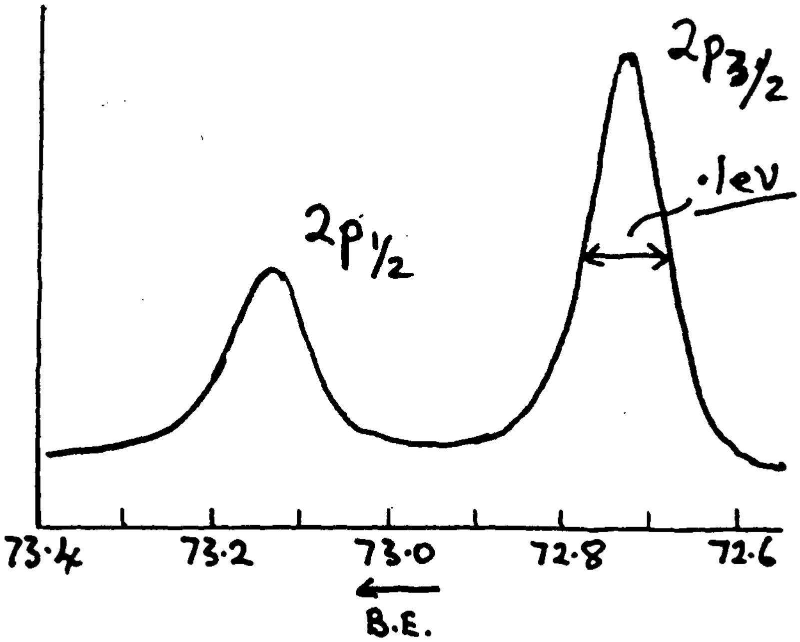
Al (100)



Bagus, Pachioni, Parmigiani
Phys Rev B 43, 5172, 1991

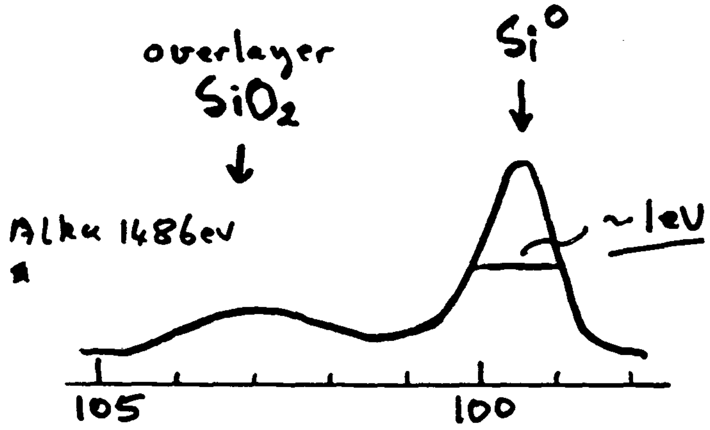
- Perkin-Elmer 5500
- Monochromaticed AlKα (1486eV)

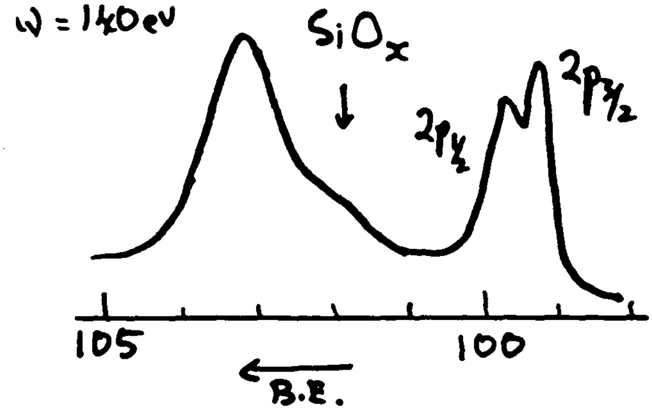
Al (111)



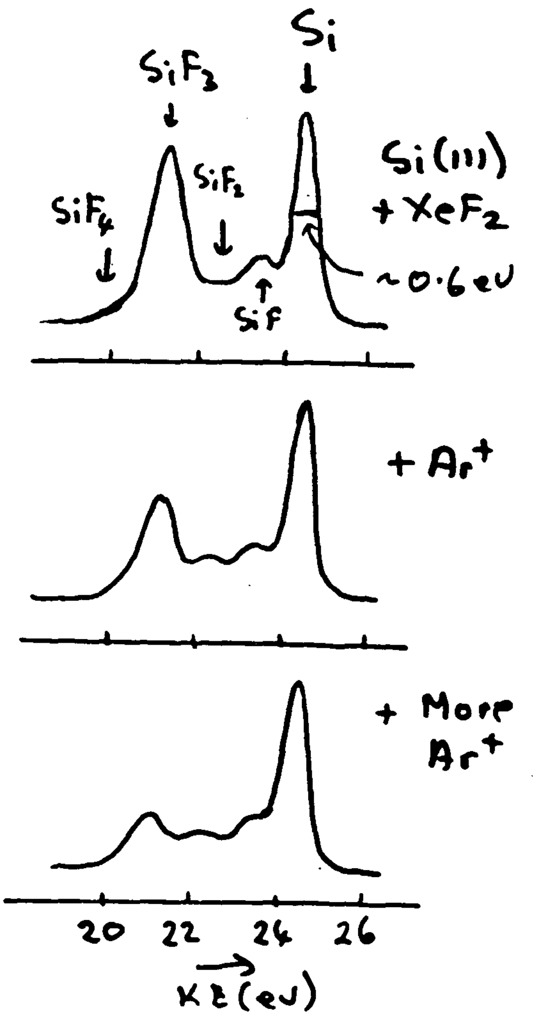
Nyholm, et al, Phys Rev B ----

- MAX-I at Lund
- SX-700 plane grating monochrom
- SCIENTA ANALYSER
- Total Instrumental Resolution ~ 50 meV.
- hν = 110 eV





Brundle, unpublished.



→ Yarmoff & McFeely, SS (198

- NSLS
- $2p_{1/2}$ removed by data proces
- hν = 130 eV

NOW GETTING INTERPLAY OF

RESOLUTION + SURFACE SENSITIVITY } → CHEMICAL STATE IDENTIFICATION FOR MONOLAYER QUANTITIES AT SURFACES

DISTRIBUTION

- LATERAL
- DEPTH
- DEPTH DISTRIBUTION (PROFILING)

DEPTH & DEPTH DISTRIBUTION

① – IF $h\nu$ IS VARIABLE OVER A WIDE-ENOUGH RANGE (PRACTICAL!), ALS (OR ANY SYNCHROTRON) HAS A TREMENDOUS ADVANTAGE OVER FIXED (1486eV) LAB SOURCES BECAUSE λ CAN BE VARIED BY FACTOR OF 5–10.

→ Increased Surface sensitivity
→ Decreased " " ?
→ Non-destructive depth profiling

Q. Can usable intensities be obtained to 3KeV ?

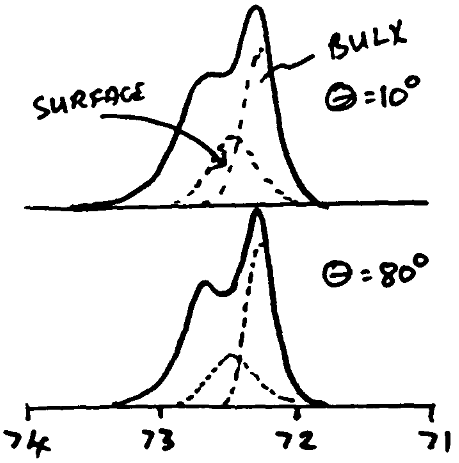
② – EVEN IF ① NOT PRACTICAL, INCREASED SURFACE SENSITIVITY OF LOW $h\nu$ FOR LOW-LYING CORE-LEVELS (eg Ga, As, Al, Si, C) IS STILL A GREAT ADVANTAGE, PROVIDED AN Al$k\alpha$ FIXED SOURCE IS AVAILABLE TOO

Q ROLE OF VARIABLE Θ FOR CHANGING SURFACE SENSITIVITY ?

HOW FAST WAS THIS TAKEN ?

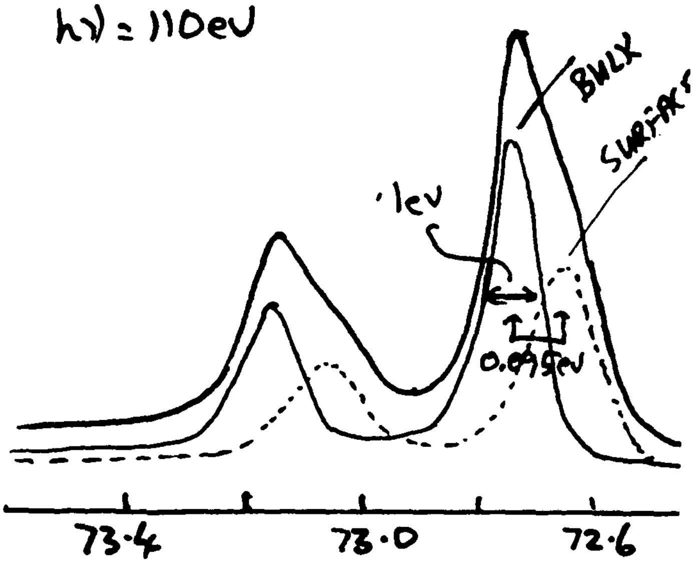
AL (100)

$h\nu = 1486eV$



Al (100)

$h\nu = 110eV$



CONCLUSION :-

- WITH 50meV INSTRUMENT RESOLUTION, PLUS SURFACE SENSITIVITY OF $h\nu = 110\,eV$, SHIFTS OF ~ 0·1eV FOR MONOLAYER AMOUNTS ARE DISTINGUISHABLE FROM THE BULK
- WITH GOOD COMMERCIAL INSTRUMENT, WITH GOOD MONOCHROMATOR PLUS Θ VARIATION THEY ARE NOT.

(NEED ~ 0·3eV TO HAVE A CHANCE)

LATERAL RESOLUTION

COMMERCIAL INSTRUMENTS:

- Majority in use have no real spatial resolution
- Many have 150 µm <u>nominal</u>
- Some have 75 µm
- A few have 5-10 µm
  - special imaging system — no reasonable spectroscopy
- 30 µm compromise will be available
- SCIENTA ?
- Magnetic Projection Microscope → sub-micron

① WHAT FLUX AT WHAT RESOLUTION?

② COST

ALS SCHLACHTER "1000 Å → microns"

TONNER ?

ADE ?

WHY WOULD YOU NOT DO THIS WITH

(a) electrons? DAMAGE!
Less information

(b) Particles? — eg PIXE
— 1 µm micro-beam "available"

- DEEP
- DAMAGE
- No "WELL-ESTABLISHED COMMUNITY"

REAL WORLD EXAMPLES

TWO "CRISIS MODE" EXAMPLES
BUT BOTH LASTED A LONG TIME (TILL SOLVED!)

1) DISK LUBRICATION — IBM San Jose

- Huge general field for many years
- Surface Science Labs made its living off this for several years.

2) CIRCUIT BOARD MANUFACTURING — IBM ENDICOTT

- OLD WORK. SHOWS WHERE COMMERCIAL INSTRUMENTS WERE 10 YEARS AGO, BUT ALSO WHERE CIRCUIT BOARDS WERE 10 YEARS AGO

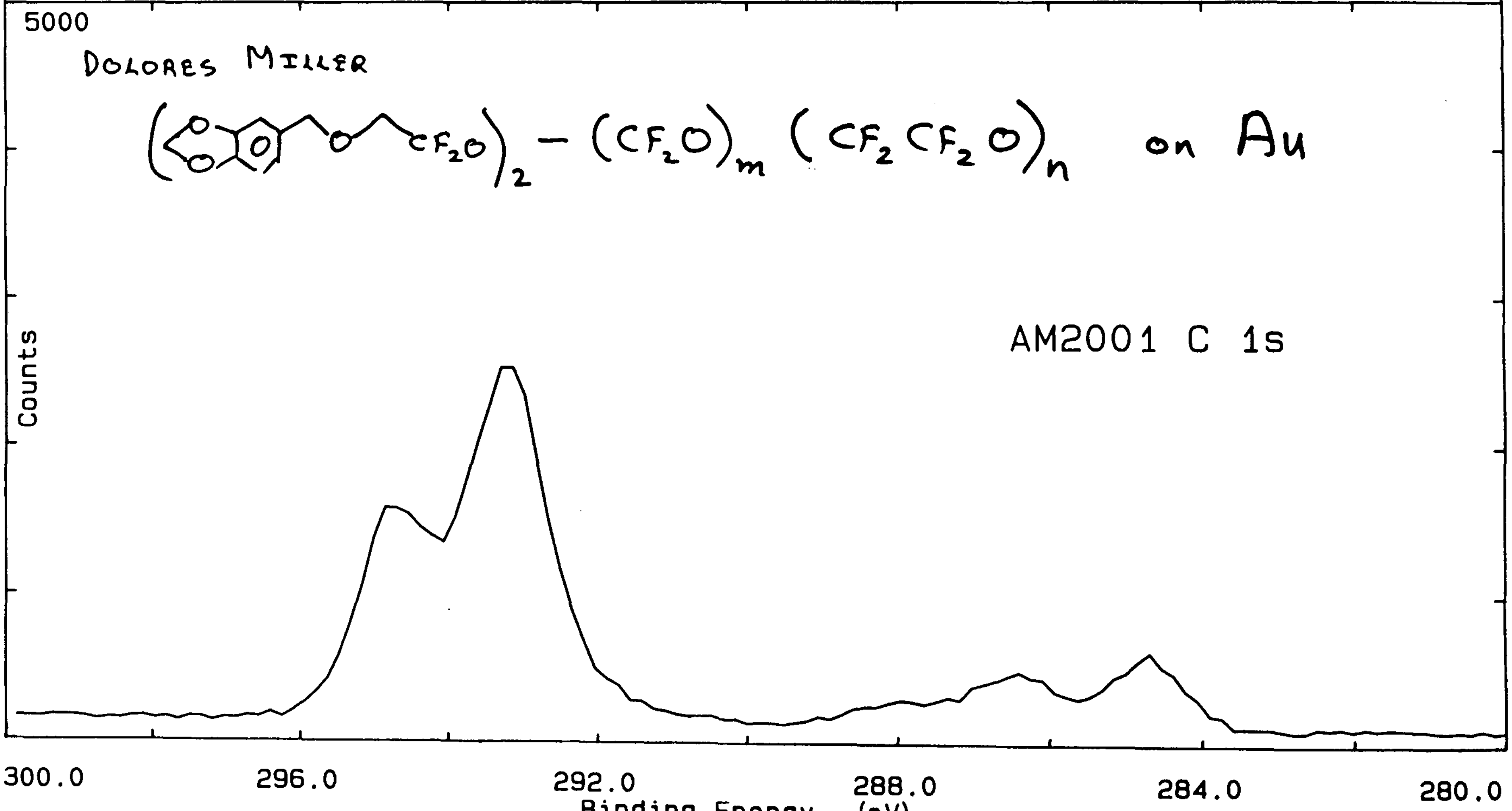
3) A BRIEF LIST OF OTHER EXAMPLES

File: M03734 Region 3	Date: 5/18/1988 Disc: DCM024	Spot: 600 u # of Scans: 5	Flood Gun: 0.0 eV Resolution: 2	Aperture: None

Description: AM2001 lube as received

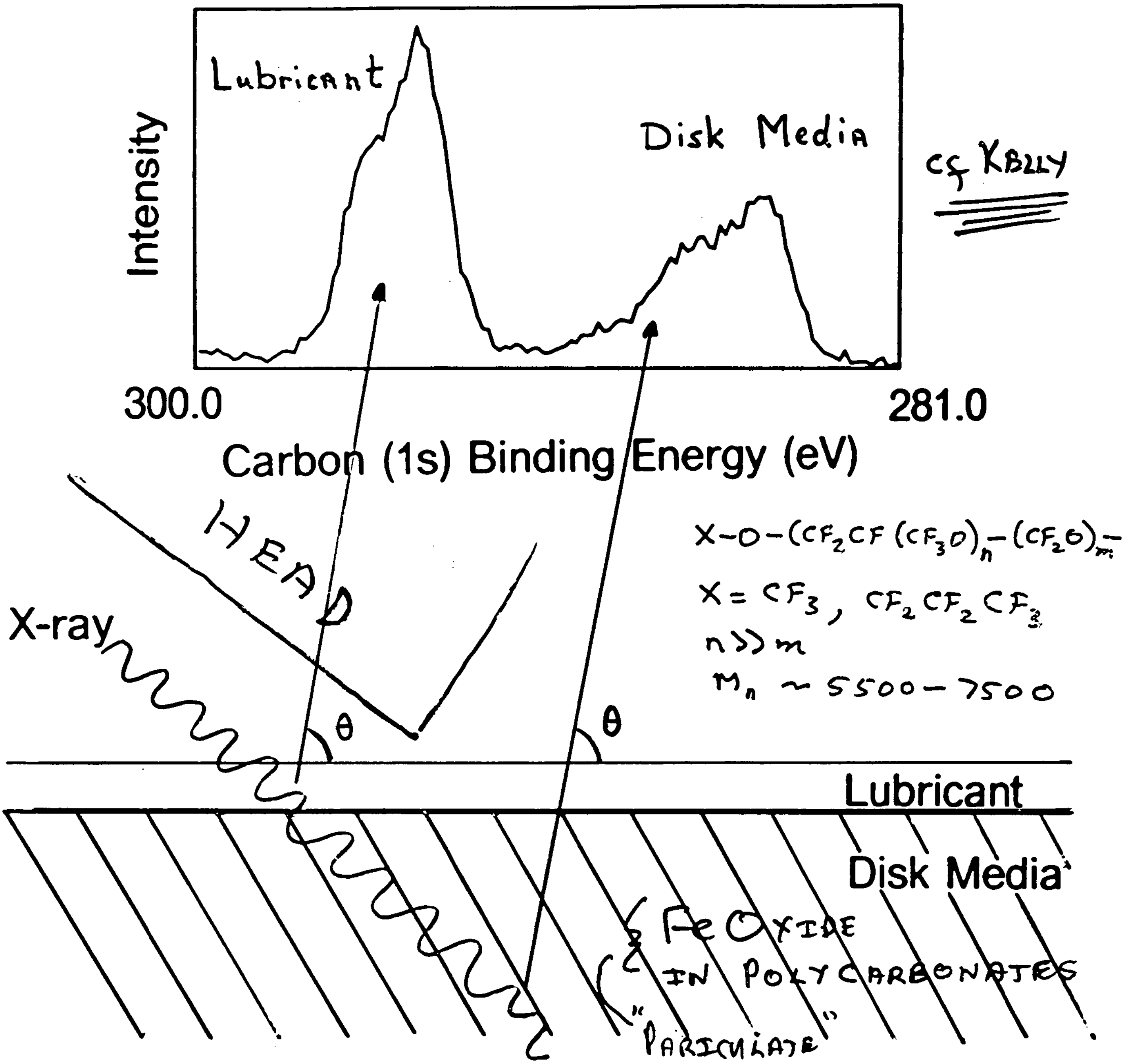
Operator: dcm

DOLORES MILLER



IBM Almaden Research Center

XPS Measurement of Surface Lubricant



cf KELLY

$X-O-(CF_2CF(CF_3O)_n-(CF_2O)_m-X$

$X = CF_3$, $CF_2CF_2CF_3$

$n \gg m$

$M_n \sim 5500-7500$

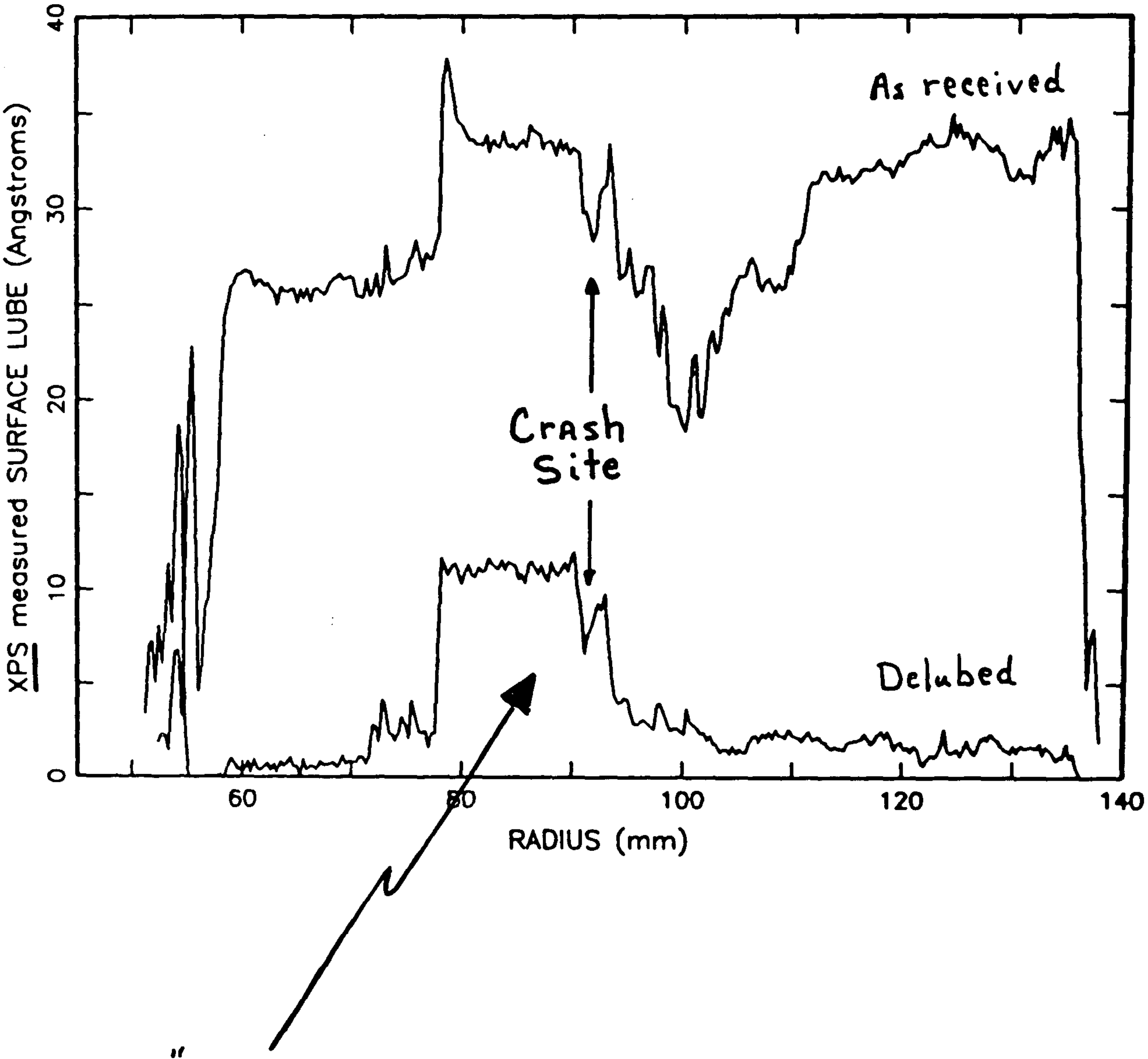
$$thickness = \lambda \sin\theta \quad \ln(aR + 1)$$

$$R = \frac{C(1s)lubricant}{C(1s)disk\ media}$$

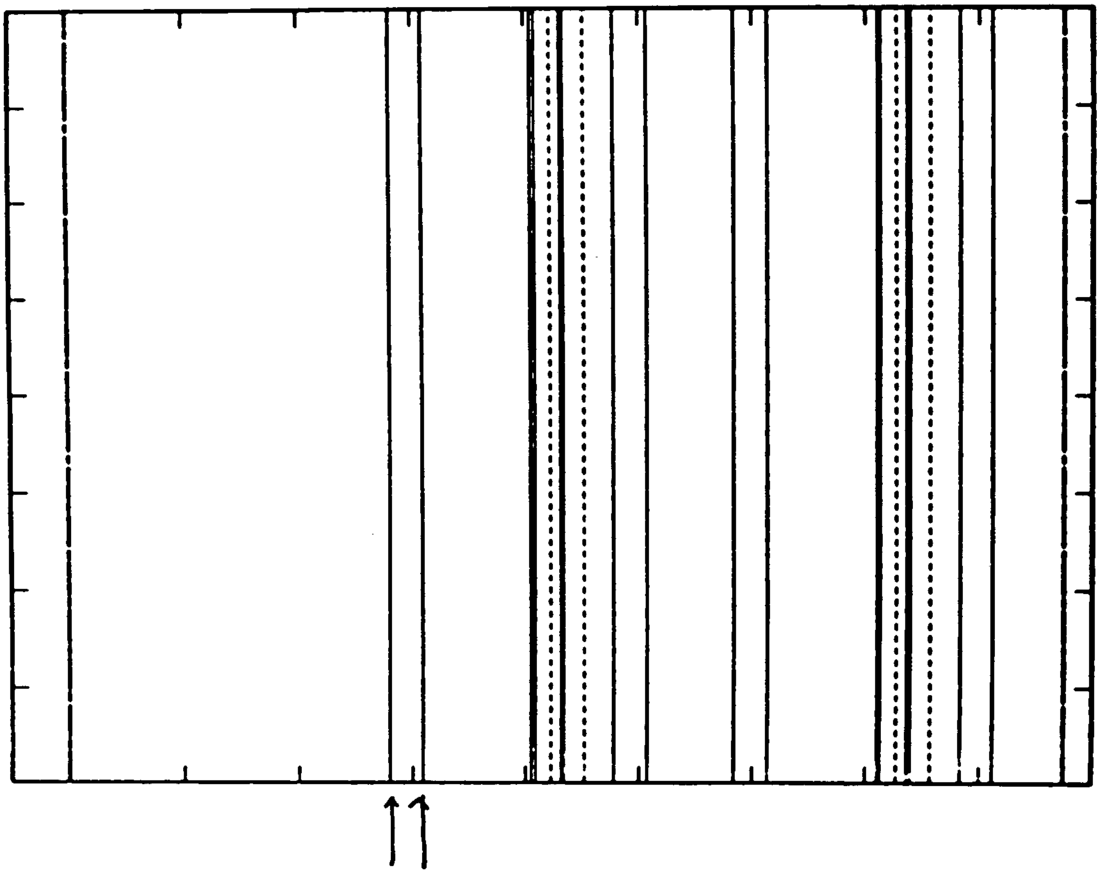
SURFACE SCIENCE
SMALL SPOT ESCA (300µm used)

SURFACE LUBE THICKNESS vs. RADIUS

0763160 – Disk 7B, HDA 1444



"Altered" lubricant

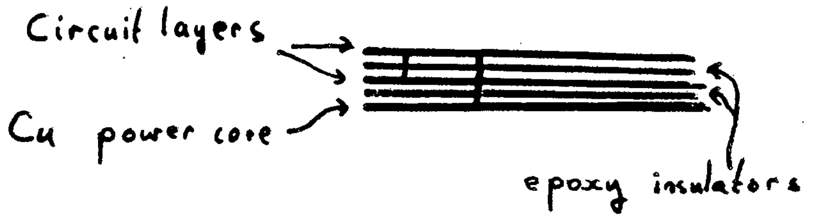


SLIDER RAILS
SLIDER RAIL WIDTH IS 400 μm

- ANALYSIS EXTREMELY SLOW (10 HOURS), EVEN AT DEGRADED SPATIAL RESOLUTION
- SURFACE SENSITIVITY TOO LOW
- SPECTRAL RESOLUTION TOO LOW TO SPECTROSCOPICALLY DISTINGUISH "ALTERED" LUBE

PACKAGING TECHNOLOGY

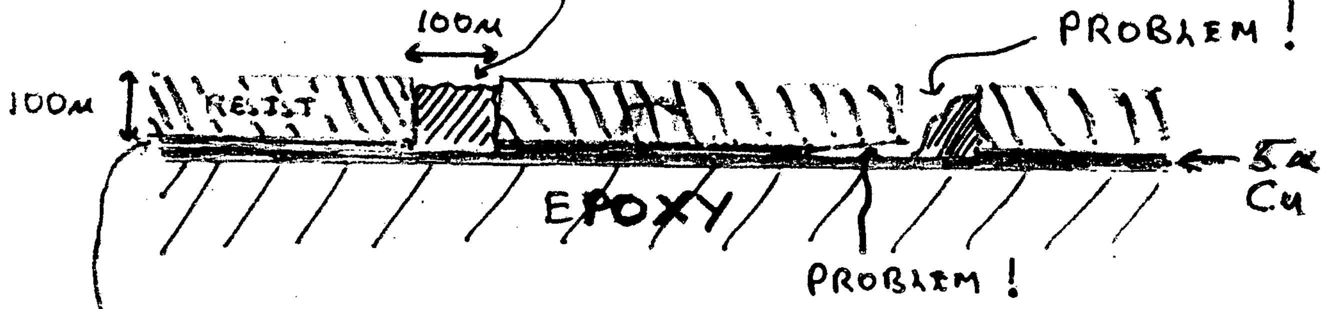
LARGE MULTILAYER CIRCUIT BOARDS (CLARKBOARD)
(4 PER 3081 MACHINE)

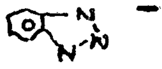


- 2ft × 2ft
- ½ Km wiring each circuit layer in 100μ lines

- made by ~ 200 step process involving wet chemistry, lithography, plating, laser & mechanical drilling, laminating, soldering .....

Electroless plated Cu
(NaOH, HCOOH, Cu^{2+}, EDTA
70°C, 24hrs)

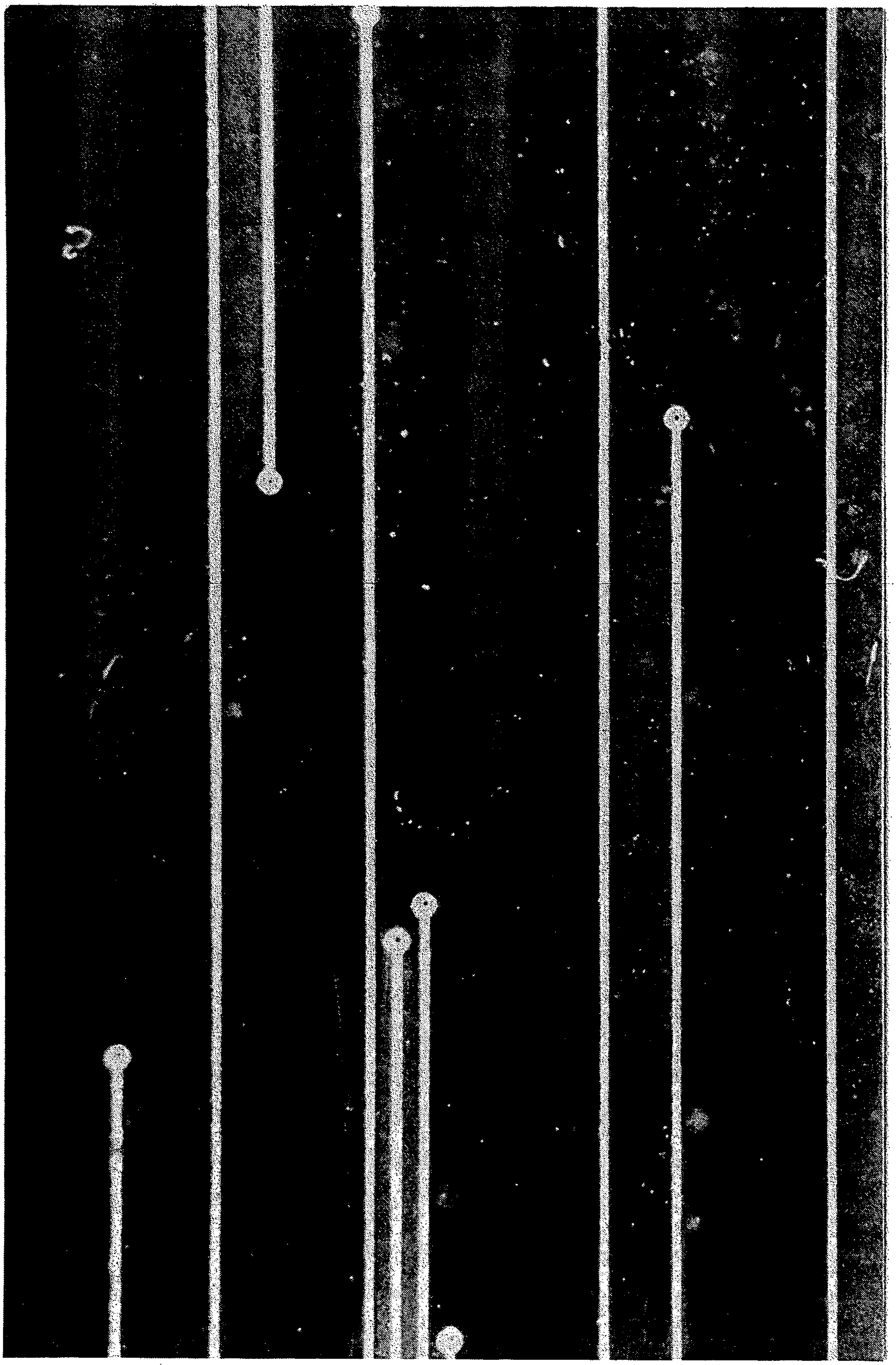


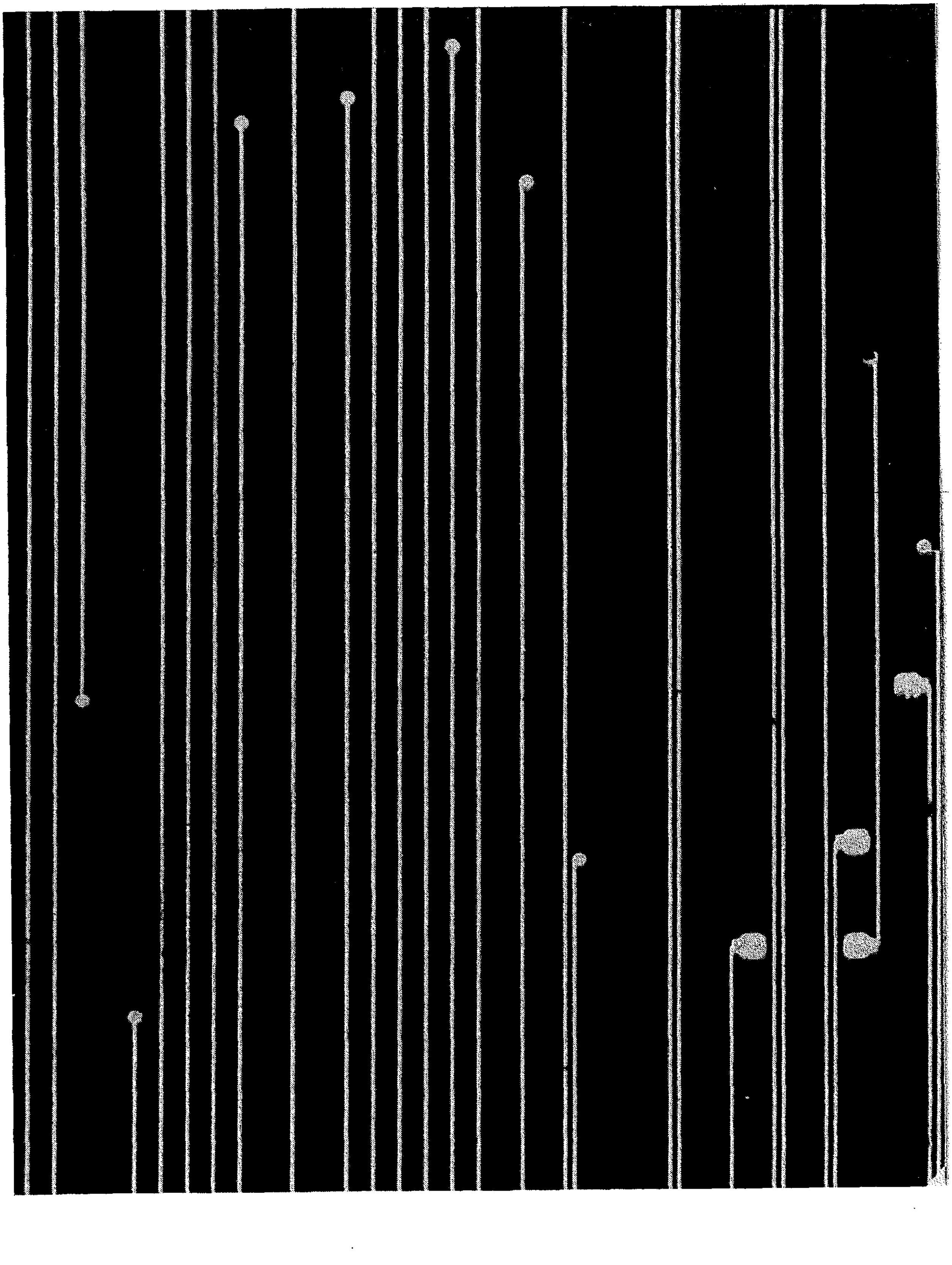
BTA TREATED →


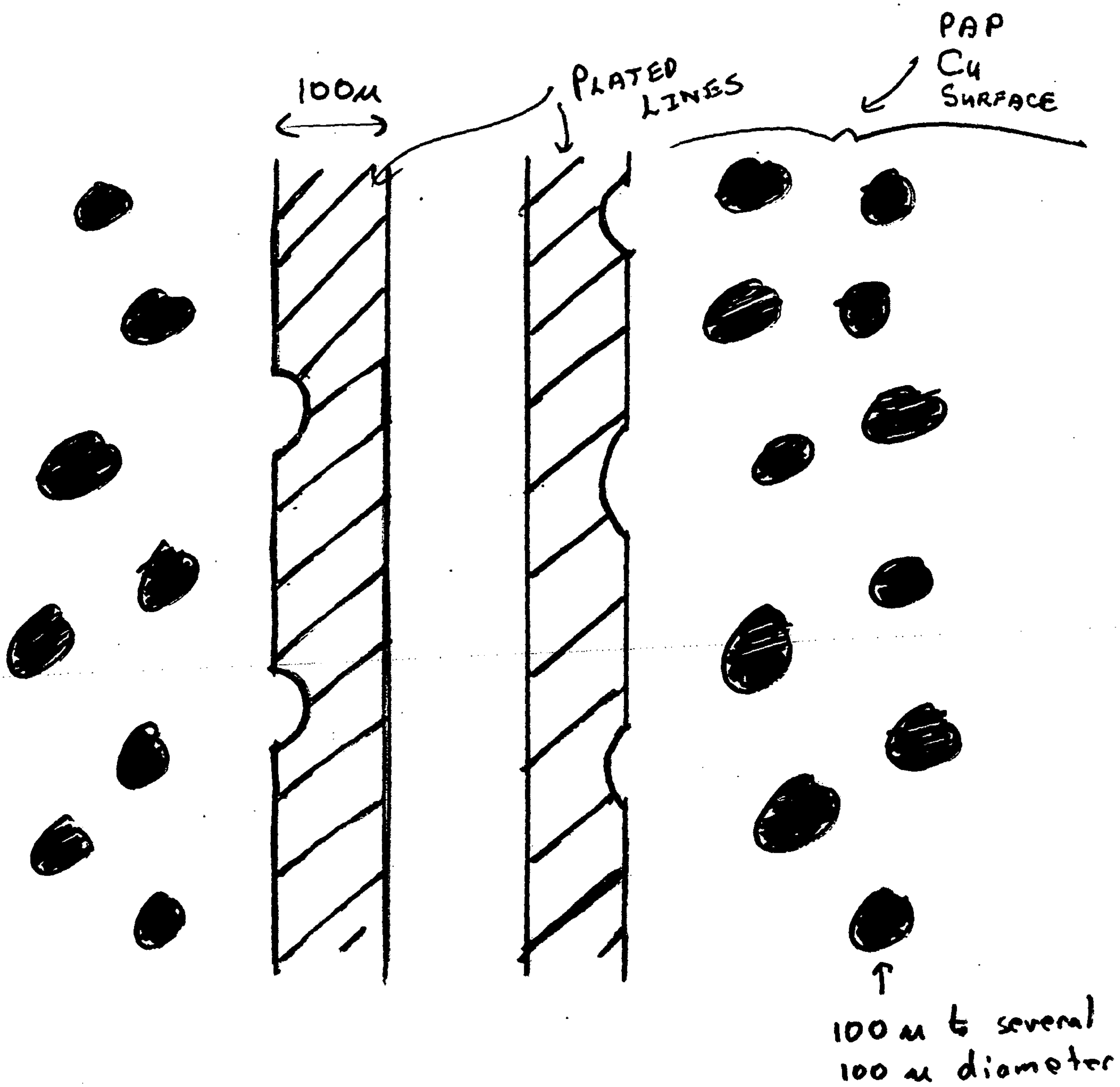
$- Cu^+$

→ ~ 20 Å THICK (Auger, XPS, RBS)
→ Thickness optimised for performance as a CORROSION INHIBITOR (not Adhesion Promoter)
→ Degradation under environmental & processing conditions studied

NO TIME HERE TO DISCUSS THIS
"STANDARD" SURFACE SCIENCE





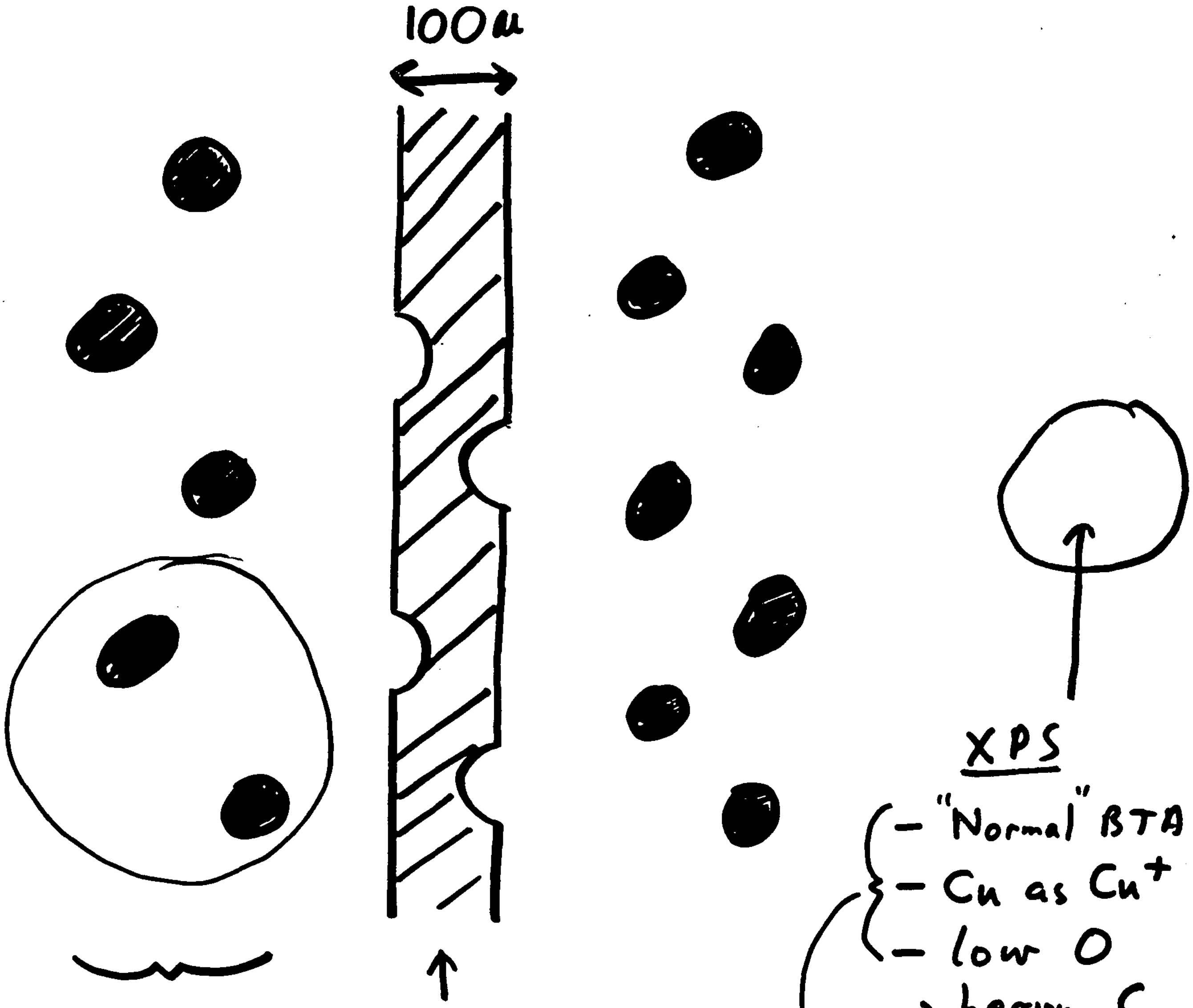


PATTERN DEPENDENCE

— CLOSE LINES V WIDE-LINES

USE
- XPS FOR CHEMICAL STATE ID IN WIDE AREAS ← NO "SMALL-SPOT" XPS
  NO "ESCASCOPE"
- SAM FOR DEPTH PROFILING IN SMALL AREAS (eg a black spot)

XPS — LARGE AREA (



XPS

- No BTA (No N (1s))
- Cu as Cu^{2+}
- heavy O
- light C ← Poor resist adhesion
- Na+ present ← TELLS YOU PLATING BATH HAS BEEN THERE!

XPS

- "Normal" BTA
- Cu as Cu^{+}
- low O

From Resist → heavy C

- No Na^{+}

→ COMPARABLE TO LAB Cu/BTA SIMULATIONS

GENERIC AREAS OF IMPORTANCE WHERE LAB. CAPABILITIES DON'T CUT IT

- ORGANIC CONTAMINANT PARTICLES
- ADHESION / DELAMINATION PROBLEMS
- RAIL EDGE DEBRIS — FEW μ → 100's μ
- POLE TIP CORROSION
  sub to few μm

- COMMERCIAL XPS DO NOT HAVE ADEQUATE SPATIAL RESOLUTION ROUTINELY

- e-beams at these spot sizes are largely useless → DAMAGE

PRACTICAL ISSUES

(1) IS A DEDICATED BEAMLINE NEEDED

(2) ASSUMING "YES", WHAT SHOULD IT LOOK LIKE AND WHAT SHOULD BE AT THE END OF IT?

— All the capabilities you would find in a lab. set-up

- sample manipulation flexability (large area motion, variable angle)
- full automation
- good data analysis
- AN EXPERT
- other instruments eg SEM
  STM
  Optical

(3) HOW WOULD ADMINISTRATION WORK

BOTTOM LINE

— ADDED VALUE COMPARED TO "HOME LAB" CAPABILITIES

— SPEED OF ANALYSIS (PER SPECTRUM)

— COST

— SPEED OF TURNAROUND

Applications of Long-Wavelength X-Ray Fluorescence Spectrometry and X-Ray Powder Diffractometry

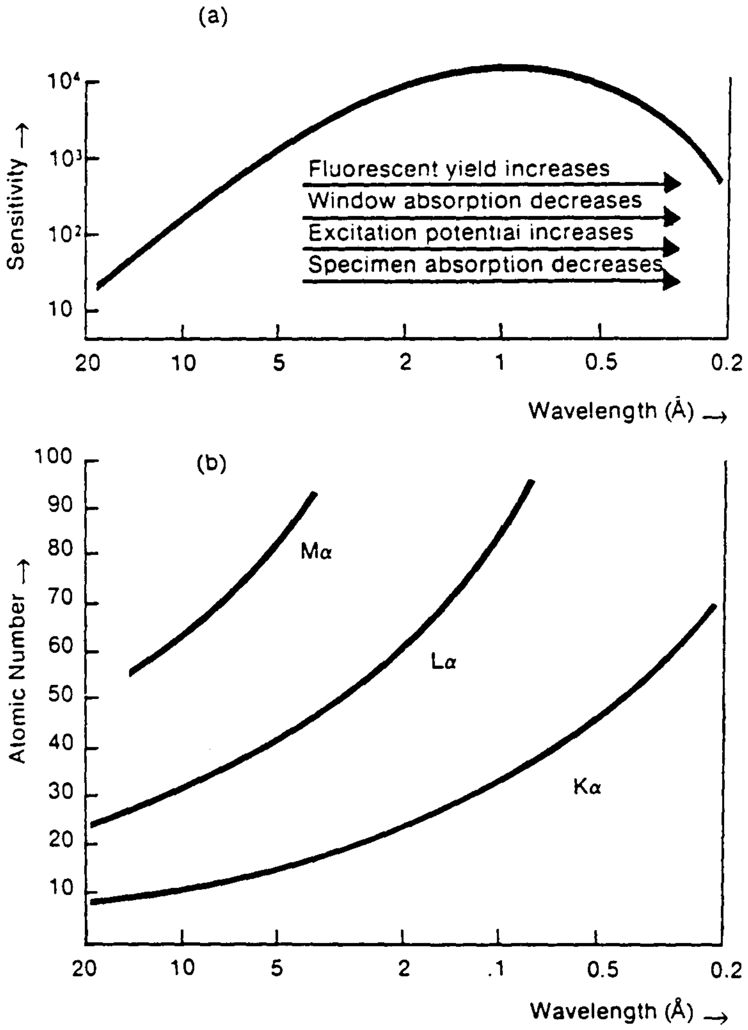
R. Jenkins

International Center for Diffraction Data
Swarthmore, Pennsylvania

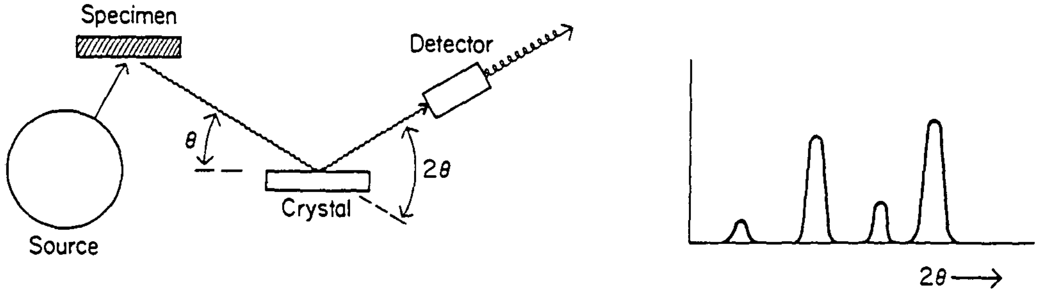
Counting rates and detection limits for various elements in plant materials

Element	Atomic number	m(c/s per %)	R_b (c/s)	T_b (secs)	Detection limit (%)
Sodium	11	16.5	17	200	0.053
Magnesium	12	36	10	100	0.026
Aluminum	13	480	3	100	0.0011
Phosphorus	15	520	6	20	0.0031
Potassium	19	5400	50	4	0.0020
Calcium	20	35,000	100	4	0.0004
Titanium	22	57,000	90	10	0.0002
Manganese	25	20,000	90	20	0.0002
Iron	26	43,000	90	20	0.0001
Nickel	28	138,000	800	10	0.0002
Copper	29	60,000	900	10	0.0005
Zinc	30	100,000	900	10	0.0003

Wavelength Range and Sensitivity of the Wavelength Dispersive Spectrometer



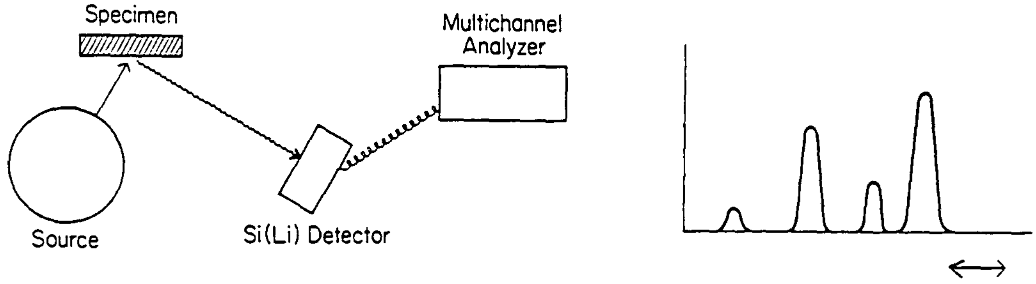
The Wavelength Dispersive Spectrometer and the Energy Dispersive Spectrometer



a) Single crystal of fixed 2d acts as a spectrum analyzer.

b) Scanning 2θ range allows the complete spectrum to be acquired.

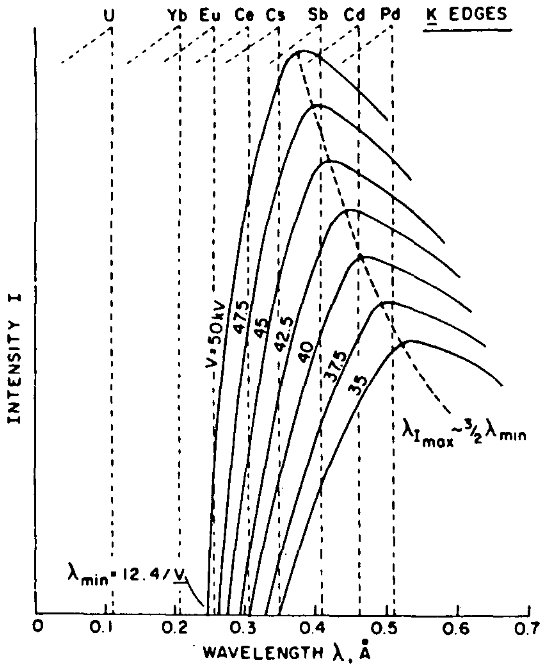
c) Selection of single wavelength is achieved by selection of equivalent 2θ value.



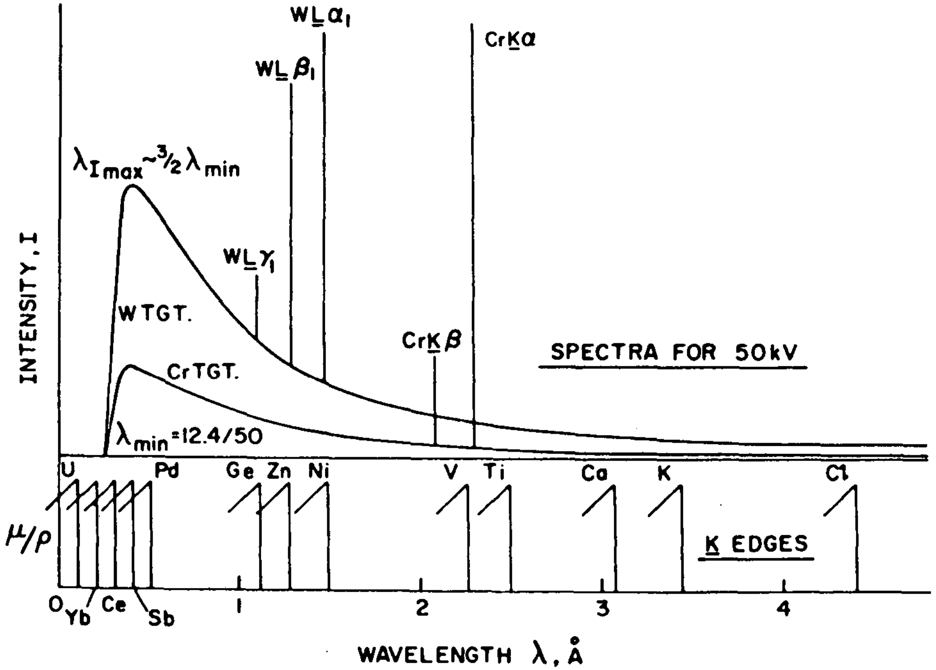
a) Proportional Si(Li) detector gives a distribution of voltage pulses proportional to the spectrum of X-ray photons.

b) A multichannel analyzer is used to isolate the voltage pulses into discrete intervals. Consecutive output of the MCA intervals allows complete spectrum to be displayed.

c) Selection of a single energy interval is obtained by selection of appropriate voltage window (i.e., range of channels) on the MCA.

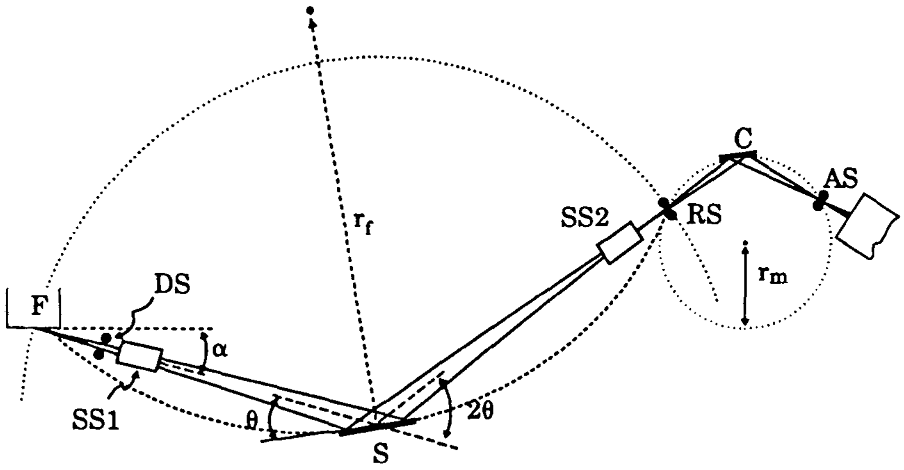


(19) Excitation by the continuum.



(20) Excitation by x-ray tube target lines.

Bragg-Brentano Parafocusing Geometry

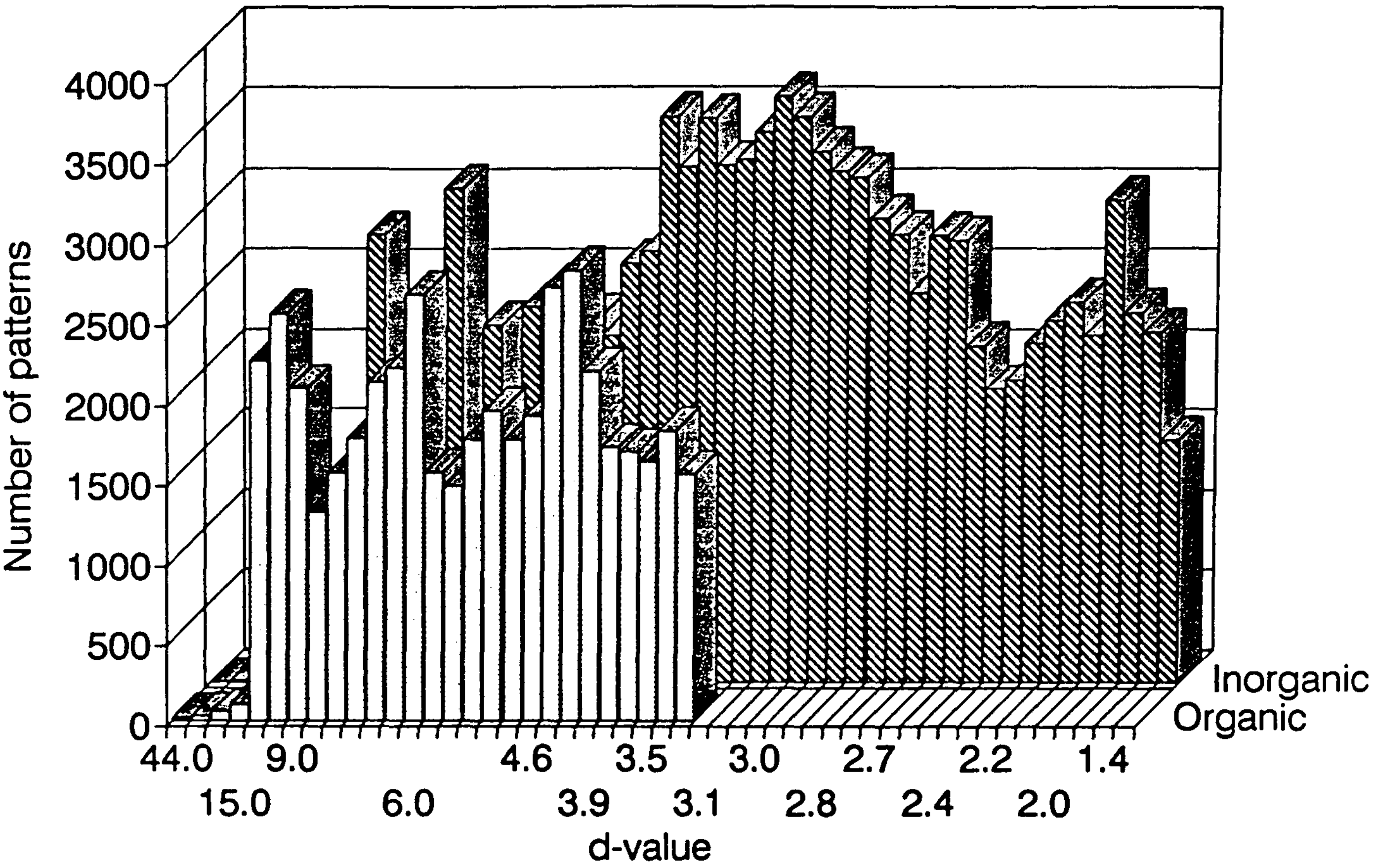


Goniometer Circle Radius

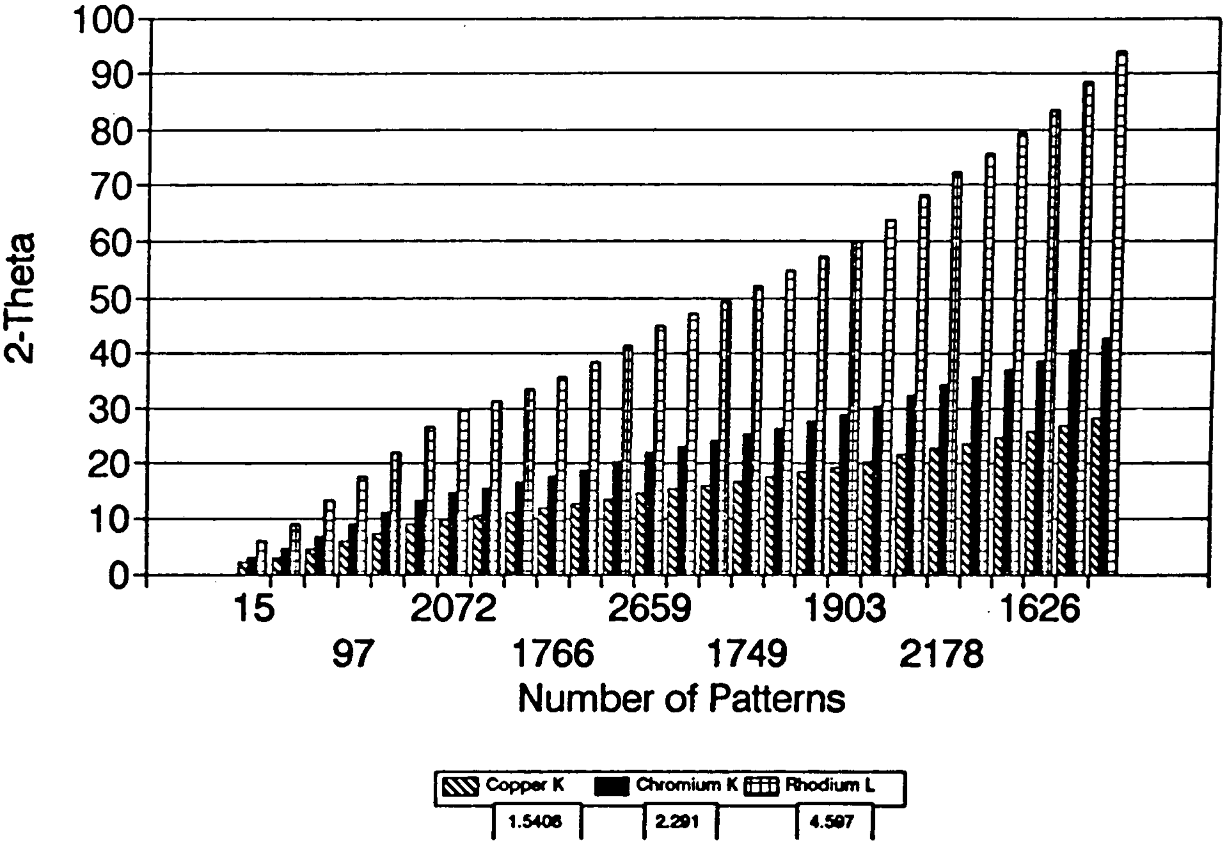
R = F → S = S → RS

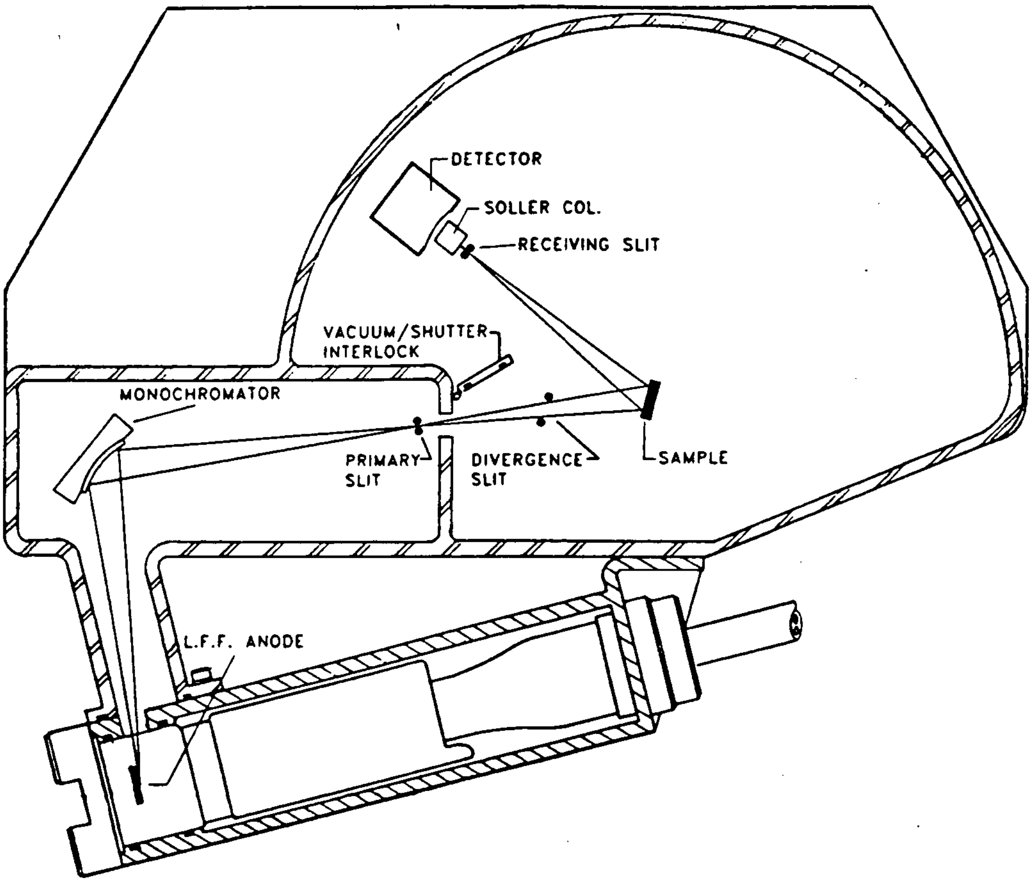
Distribution of d-Spacings

Inorganic & Organic Files



Distribution of Organic Patterns
as a function of wavelength





Prototype Long Wavelength Diffractometer.

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