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PROCEEDINGS OF THE WORKSHOP ON APPLICATIONS OF SYNCHROTRON RADIATION TO TRACE IMPURITY ANALYSIS FOR ADVANCED SILICON PROCESSING

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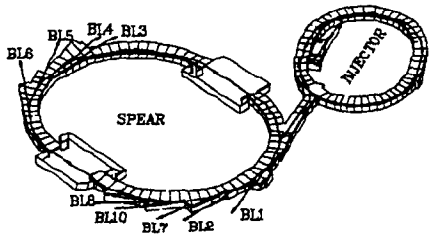

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Acknowledgment

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I. Summary

S. Laderman, P. Pianetta

Summary

Wafer surface trace impurity analysis is essential for the development of competitive silicon circuit technologies. Current best methods for chemically identifying and quantifying wafer surface and near surface impurities include grazing incidence x-ray fluorescence techniques utilizing rotating anode sources. To date, these methods fall short of what's needed for future process generations. A small community of scientists and engineers from Fisons Instruments, Hewlett Packard, Intel, the Stanford Synchrotron Radiation Laboratory (SSRL) and Toshiba have recently pursued benchmark experiments at SSRL in order to assess the possibility that synchrotron sources would provide the means to usefully extend such trace impurity analysis methods. The results of the Hewlett Packard/Toshiba experiments imply that with second generation synchrotron sources such as SSRL plus existing monochromator, detector and sample handling technologies, grazing incidence x-ray fluorescence methods can be extended sufficiently to meet important needs of the leading edge silicon circuit industry through nearly all of the 1990's.

In view of these promising preliminary results, a workshop was held to (1) identify individuals and groups potentially interested in the use of synchrotron radiation based methods for trace impurity analysis in support of advanced silicon processing technologies and, (2) document needs and concerns relevant to establishing strategy and tactics for further development. These workshop goals were met. At the end of the workshop, representatives from Advanced Micro Devices, Hewlett Packard, IBM, Intel, Motorola and Toshiba clearly stated an intention to utilize synchrotron radiation based methods if the technical potential described in the workshop report is realized and if each company's operational needs and concerns are met.

The logic leading to this high level of interest and the nature of the needs and concerns can be described by reviewing the central points made by several of the workshop speakers and by some of the attendees during the discussion session. These points are summarized below.

In the opening presentation, M. Liehr of IBM addressed the "Microcontamination Needs in Silicon Technology." This review of the level of contamination control necessary to succeed in the silicon circuit business covered financial incentives, strategies for developing manufacturable processes, and specific contamination concerns. A principal conclusion was that for leading edge dynamic random access memory (DRAM) process technologies expected to be in manufacturing by the end of 1994, metal impurity contamination levels will need to be on the order of 1×10^9 atoms/cm^2 or less. Processes released to leading edge manufacturing sites around 1998 will need

to be contamination free at the level of 1 x 10^8 atoms/cm^2. (For comparison, there are about 10^{15} atoms/cm^2 of silicon on the wafer surface.) Of course, the silicon process development community seeks analytical capabilities with these detection limits years before a manufacturing release and such techniques, if available, would likely be used after these dates as well. (To better understand the overall industry perspective, it is helpful to know that traditionally, DRAM manufacturing releases of a given silicon process technology complexity and feature size have preceded the releases of analogous leading edge static random access memory (SRAM) circuits, microprocessor circuits and application specific integrated circuits (ASICS). Thus, the development phases of process technologies for these latter classes of circuits can be expected to continue past the DRAM dates cited above.)

In addition to detection limit requirements, Dr. Liehr made clear that being sensitive to as wide an elemental range as possible is very desirable. Some twenty elemental contaminants having atomic numbers in the range from boron to polonium have been found to lead to serious difficulties at IBM. Dr. Liehr remarked that if IBM had the ability to quantify others very sensitively, they might well be on the list too. Finally, Dr. Liehr reminded the audience that the ability to spatially resolve chemical contamination patterns is extraordinarily valuable in the pursuit of designing and controlling manufacturable silicon circuit technologies.

In the second presentation, A. Shimazaki of Toshiba addressed the current "Analytical Methods for Wafer Surface Contamination." Today's most sensitive method for simultaneously identifying and accurately quantifying surface contaminants on silicon wafers is Toshiba's wafer-surface-analysis (WSA) method, invented and developed by Shimazaki-san. This method is a destructive wet chemical method in which impurities are collected from the entire wafer surface. At Toshiba, it is today capable of detecting about 10^8 atoms/cm^2 in many cases. Shimazaki-san reported that further advances in the WSA method will be very difficult. She went on to compare WSA to the much less complicated procedures based on commercially available total reflection x-ray fluorescence (TRXRF) equipment. Although the detection limit for rotating anode based TRXRF is now at best 2 x 10^9 atoms/cm^2, TRXRF offers the advantages of being nondestructive, relatively high speed and capable of depth resolution. We can also include wafer mapping capability and equal sensitivity to all chemical states of any particular element as additional significant advantages. For these reasons, TRXRF is used in trace impurity analysis today at every state-of-the-art semiconductor manufacturer, including Toshiba.

A natural way to look to improve TRXRF methods is to examine the benefits of changing from a rotating anode source to a synchrotron radiation source. This was the motivation for

Hewlett Packard's and Toshiba's joint benchmark experiments described by S. Laderman in his report "TRXRF Using Synchrotron Sources." The intent of these first benchmark experiments, which were performed this past spring and summer, was to compare detection limits, elemental range and depth resolution between rotating anode based TRXRF equipment and an existing SSRL wiggler beam line and standard experimental station. (The experiments were carried out on Beam Line VI, using focusing optics and a Si(111) double crystal monochromator.)

To accomplish this, standard samples were carefully prepared at Toshiba. The samples were uniformly contaminated six-inch silicon wafers having calibrated quantities of iron, nickel and zinc. The contamination levels were checked redundantly with WSA and with a calibrated rotating anode based TRXRF apparatus. The contamination uniformity, essentially guaranteed on physical grounds according to the contamination procedure, was confirmed with TRXRF wafer mapping. Samples used to probe the detection limits were made with 1×10^{11} atoms/cm^2 contamination levels in order to be close enough to the expected limits to provide an accurate estimate while being high enough to limit the risk that the data would be compromised by changes in the sample due to time dependent processes or handling. In addition, clean wafers and samples having higher levels of contamination were studied. A specially designed wafer chuck was made by Toshiba for these experiments and a stainless steel chamber designed and built by SSRL was used along with a solid state detector provided by Fisons Instruments. Steps taken to insure that no additional contamination was introduced in handling and loading the wafers at SSRL included cleaning the hutch, use of clean plastic tarps, use of plastic tweezers, use of cleanroom garments, and minimizing the time the wafers were exposed to air. The success of these procedures were proven by comparing (1) the spectra obtained from the 1×10^{11} atoms/cm^2 and the clean samples using rotating anode based TRXRF equipment at Toshiba just after the samples were prepared to (2) the spectra obtained from the same samples at SSRL. However, it is important to note that the sample handling procedures, while adequate for the benchmark experiments, were too cumbersome, too slow and too unreliable to be appropriate for standard use.

In this way, the capabilities of existing SSRL experimental stations could be directly compared to highly engineered and optimized rotating anode based equipment. Dr. Laderman reported that for this set of experiments, the detection limits for iron and for nickel using the synchrotron were the same as those obtained with the rotating anode. The total counts per second in the detectors were also comparable, and well below the detector saturation limits. However, the detailed count rates were not the same. In particular, due to the polarization of the synchrotron x-ray beam, the background signal due to scatter of the incident synchrotron beam was about an order of magnitude less than that of the rotating anode beam, relative to the fluorescence signals.

This, along with the broad band nature of the synchrotron source, provides a very important opportunity for improvement at the synchrotron. Dr. Laderman described a simple scheme using filters and multilayer optics which might lead to more than an order of magnitude improvement in the detection limit for the synchrotron case. If, in addition, an array of solid state detectors is used in place of the single detector employed so far, additional gains could be made. Other improvements are likely to follow from more carefully optimizing the beam divergence and the detector acceptance angle. As the earlier reports made clear, even one order of magnitude improvement over the rotating anode based equipment would be of great significance for the semiconductor industry.

Dr. Laderman further described the promising outlook for depth resolution improvements. The data described above were obtained in a configuration where the grazing angle divergence was about five times less than that offered by the rotating anode based equipment. This makes routine depth profiling more certain. Thus, for example, the ability to distinguish the four cases of (1) impurities at the surface, (2) impurities distributed throughout a gate oxide, (3) impurities at the interface between the gate oxide and the substrate and, (4) impurities distributed into the substrate, is enhanced at the synchrotron. The ability to distinguish between contamination layers and particles on the surface is similarly enhanced. Analysis will soon be complete to quantify how great an improvement is obtained at this collimation level. It can be said now that the synchrotron will provide a way to attain higher detection limits without sacrificing, and indeed with some improvement in depth profiling capability.

An additional improvement now available at the synchrotron arises simply from the tunability of the source. The elemental range is easily extended. An explicit example shown by Dr. Laderman is the case of zinc. The rotating anode equipment optimized for detecting stainless steel constituents uses a tungsten L-beta line as the source. The scatter from this source overlaps sufficiently with the zinc K-alpha fluorescence to significantly obscure the zinc signal. Dr. Laderman showed spectra where the incident x-ray energy was chosen to be several hundred electron volts above the tungsten L-beta energy, making the detection limit for zinc at the synchrotron the same as that for iron and nickel and thus much better than in the case of the rotating anode equipment. At Beam Line VI, even with focusing, the incident beam is easily tunable to 20 keV. This is high enough to excite K-edge or L-edge fluorescence from every naturally occurring element in the periodic table. This makes possible, in a simple way, high detection limits for elements which cannot even be excited to fluoresce with any appreciable intensity using a rotating anode equipment.

A synchrotron source offers another potentially very significant advantage. Due to the relatively high level of silicon K-alpha fluorescence, rotating anode based TRXRF equipment is much less sensitive to elements with atomic numbers below that of silicon as compared to the elements above silicon and less than zinc. Tunable soft-x-ray synchrotron sources could be used to excite the K-edges of the lighter elements without exciting any silicon K-alpha fluorescence. Careful benchmark experiments to determine the detection limits for elements such as sodium and aluminum are now being designed.

At the start of the afternoon session of the workshop, M. Scott reviewed in some detail the processes in silicon fabrication requiring surface contamination control. Generally, these include surface preparation, surface reactions, film deposition, patterning and ion implantation. TRXRF methods are especially compatible with the silicon industry's need for quantitative, element specific wafer surface analysis because x-ray fluorescence is element specific and quantitative, unpatterned silicon wafers are very flat and thus well suited to total reflection x-ray methods, automated sample handling is straightforward, analysis is nondestructive, and both spatial mapping and depth resolution are possible. This is why rotating anode based TRXRF measurements are now commonly used in the silicon industry to support materials selections, equipment development and qualification, process development and qualification, yield enhancement and quality monitoring and cleanroom facilities control.

In view of the technical advantages of synchrotron radiation based TRXRF, Dr. Scott went on to describe some practical requirements a synchrotron based facility must meet to be usable by the semiconductor industry. These include: (1) reliable, timely, easy access as made possible by low initiation costs, low overhead for continued interaction, flexible scheduling, and high equipment and facility availability; (2) interest at SSRL in "Advanced Manufacturing Science"; (3) protection of proprietary interests; and, (4) technical staff support. Dr. Scott continued by pointing out that an appropriate experimental station would have: (1) clean sample preparation capability and measurement environment; (2) detection limits tracked with standards; (3) user transparent data collection and experiment automation; (4) six- and eight-inch wafer compatibility (in the discussion, it was suggested that this list include four-inch wafer compatibility as well in order to maintain compatibility with Stanford's Center for Integrated Systems); (5) detectors and beam characteristics capable of a wide elemental range; (6) future capability for in-situ process chambers using corrosive gases; and, (7) straightforward alignment.

During the discussion session, Dr. Scott's list of requirements were reviewed and unanimously endorsed by the semiconductor industry representatives. Detailed discussion of

administrative and organizational issues led to the conclusion that SSRL's strong record of user support, long-standing dedication of its staff scientists to facility enhancements, and proven support of fast turnaround and other special purpose experimental stations suggests that SSRL could, if it had the means and the interest, support a TRXRF facility which would meet industry needs. From the standpoint of technical capability, there was strong interest in high sensitivity to elements with atomic numbers below silicon and elements with atomic numbers above silicon; strong interest in depth profiling and wafer mapping; and, strong interest in trying to acquire chemical state or chemical bonding information. Nevertheless, if only the first of these interests were satisfied, that is, if a facility existed at SSRL with significantly improved detection limits and the ability to measure more elements, both as compared to rotating anode based TRXRF equipment, and if that facility were, apart from geographic separation, essentially as easy to use, as reliable as, and as cost effective as in-house equipment, this would be sufficient to draw industry scientists and engineers to SSRL as users. If it were here today, they would be using it now.

As a result of this workshop, three action items were identified. First, the formal workshop report is to be completed and distributed. Second, experiments designed to (a) accurately benchmark the detection limit for 3d transition elements using multilayer optics and, (b) accurately benchmark the detection limits for those elements plus sodium and aluminum using soft x-rays, are to be performed this winter and spring. Third, SSRL is to draft a detailed facility plan and distribute it to semiconductor industry representatives for comment. The minimum distribution list for the plan would be the industry representatives who attended the workshop. It was felt that with these items accomplished, final design goals could be established precisely and, funding permitting, a synchrotron radiation based TRXRF facility truly useful to the semiconductor industry could be made operational at SSRL.

II. Participants

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III A. Introduction and Welcome, including workshop preamable and program

P. Pianetta

Workshop on Applications of Synchrotron Radiation to Trace Impurity Analysis for Advanced Silicon Processing

Determine usefulness to industry

Determine SSRL's role

Identify details

Workshop on Applications of Synchrotron Radiation to Trace Impurity Analysis for Advanced Silicon Processing

SSRL/Stanford University
October 21, 1992

Chairmen: S. Laderman, P. Pianetta

Trace impurity analysis is essential for the development of competitive silicon circuit technologies. Current best methods for chemically identifying and quantifying surface and near surface impurities use grazing incidence x-ray fluorescence techniques and rotating anode x-ray sources or chemical preconcentration of impurities and liquid analysis. To date, these methods fall short of what's needed for future process generations. Recent synchrotron radiation based benchmark experiments performed at SSRL have demonstrated that the high flux, high collimation and tunability of the synchrotron source lead to improvements in both the nondestructive analyses employing grazing incidence methods and in the preconcentration analyses employing a liquid analysis scheme based on ultrathin membranes and x-ray fluorescence detection.

Synchrotron radiation based techniques may become the best means of extending current capabilities. This workshop's goals will be to (1) document needs and concerns relevant to establishing strategy and tactics for furthur investigations and, (2) identify individuals and groups potentially interested in the use of synchrotron radiation based methods for trace impurity analysis in support of advanced silicon processing technologies. Invited talks reviewing industry needs, existing synchrotron radiation benchmark data, projected additional advantages of synchrotron radiation methods, and options for pursuing further work will be presented and discussed

The preliminary program is on the back of this sheet.

WORKSHOP ON APPLICATIONS OF SYNCHROTRON RADIATION TO TRACE IMPURITY ANALYSIS FOR ADVANCED SILICON PROCESSING

Building 137, Stanford Linear Accelerator Center
Stanford University
October 21, 1992

8:00AM **Registration and Continental Breakfast** - SLAC AUDITORIUM

8:30AM Introduction and Welcome
P. Pianetta
SSRL and Department of Electrical Engineering
Stanford University

8:45AM "Microcontamination Needs in Silicon Technology"
M. Liehr
T. J. Watson Research Laboratories
IBM

9:45AM "Analytical Methods for Wafer Surface Contamination"
A. Shimazaki
Integrated Circuits Advanced Process Engineering Department
Toshiba Corporation

10:30AM **Coffee Break**

10:45AM "Trace Impurity Analysis of Liquid Drops Using Synchrotron Radiation"
D. Wherry
EDXRF Products
Fisons Instruments

11:30AM "TRXRF Using Conventional and Synchrotron X-Ray Sources"
S. Laderman
Integrated Circuits Business Division R&D Center
Hewlett-Packard Company

12:00PM **Lunch** (SLAC Auditorium)

1:00PM "Potential Role of Synchrotron Radiation TRXRF in Si Process R&D"
M. Scott
Integrated Circuits Business Division R&D Center
Hewlett-Packard Company

1:30PM "Potential Developments of Synchrotron Radiation Facilities"
S. Brennan
SSRL
Stanford University

2:00 "Identification of Goals, Needs and Concerns"
M. Garner
Intel Corporation

2:45PM Closing Remarks
P. Pianetta

3:00PM Tour of Facilities

6: 00PM Joint reception with SSRL and SLAC Users Organization and Participants in *Workshop on Scientific Applications of Short Wavelength Coherent Light Sources*

III B. Microcontamination Needs in Silicon Technology

M. Liehr

Microcontamination Needs in Silicon Technolgy

Michael Liehr

IBM Research Division
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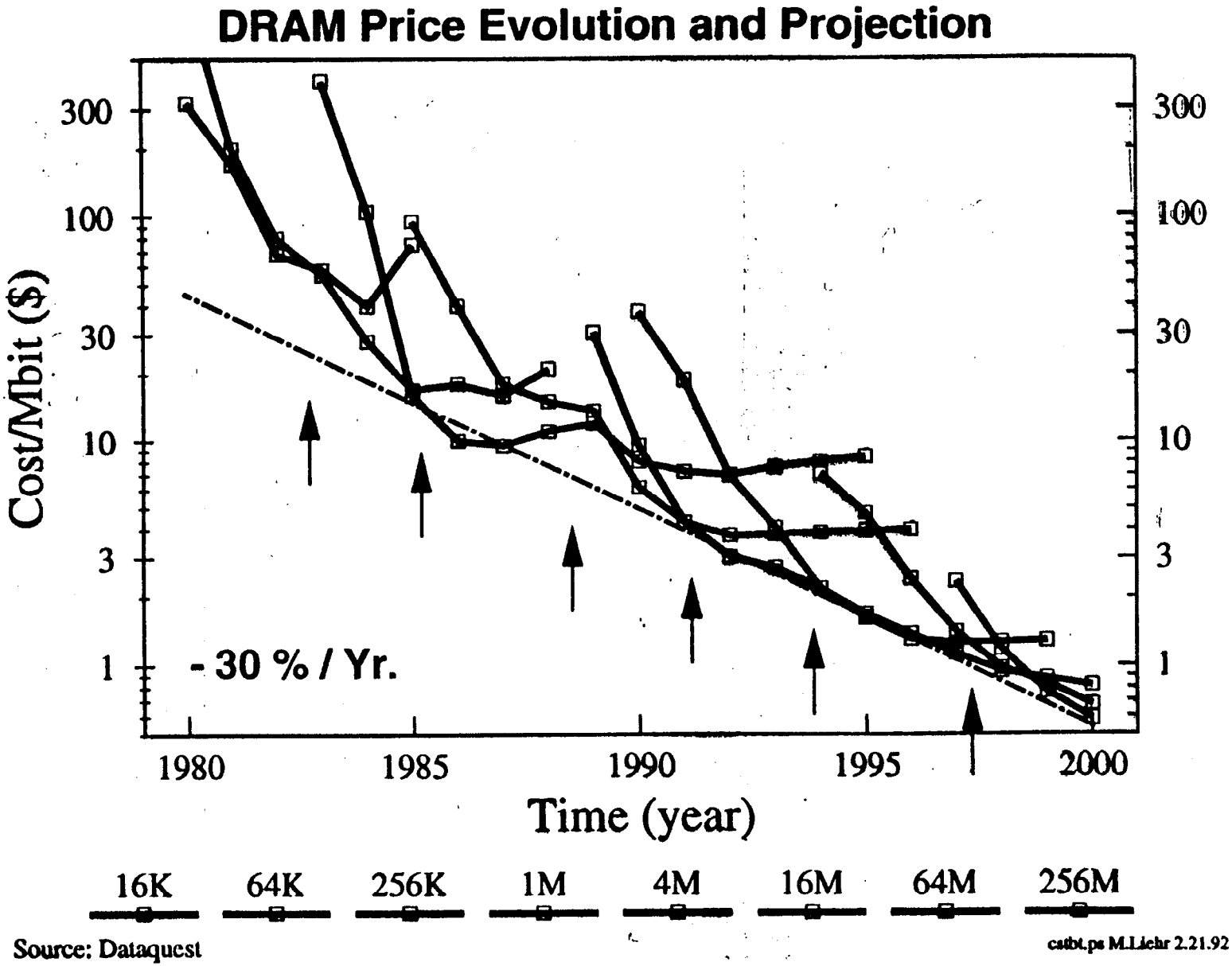
Yorktown Heights, NY, USA

- Device defect control
- Types of contaminants
- Device effects
- Typical contamination levels
- Roadmaps
- Adequate detection techniques
- Contamination removal


DRAM Price Evolution and Projection
Cost/Mbit ($)
300
100
30
10
3
1
- 30 % / Yr.
1980
1985
1990
1995
2000
Time (year)
16K
64K
256K
1M
4M
16M
64M
256M
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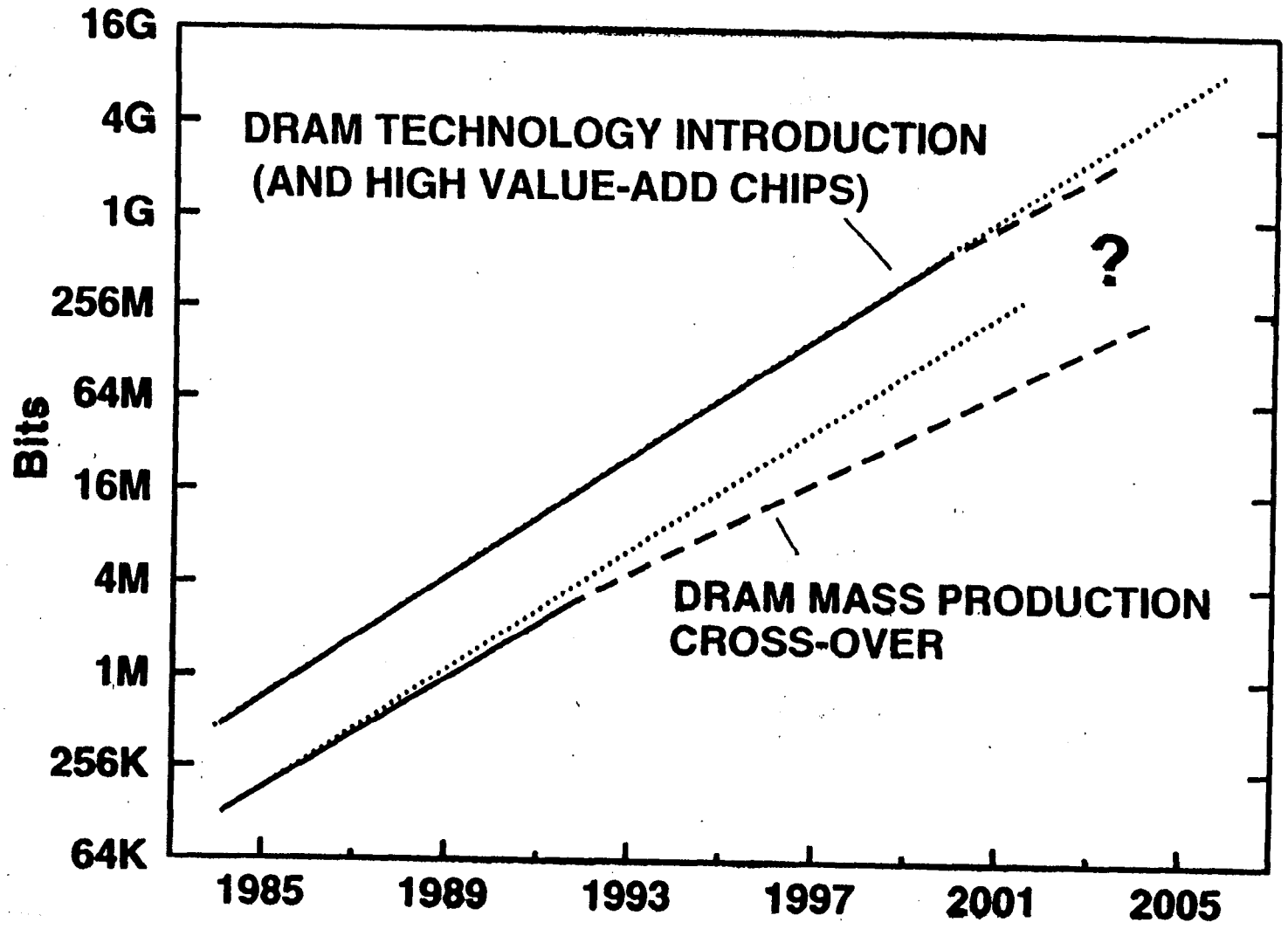
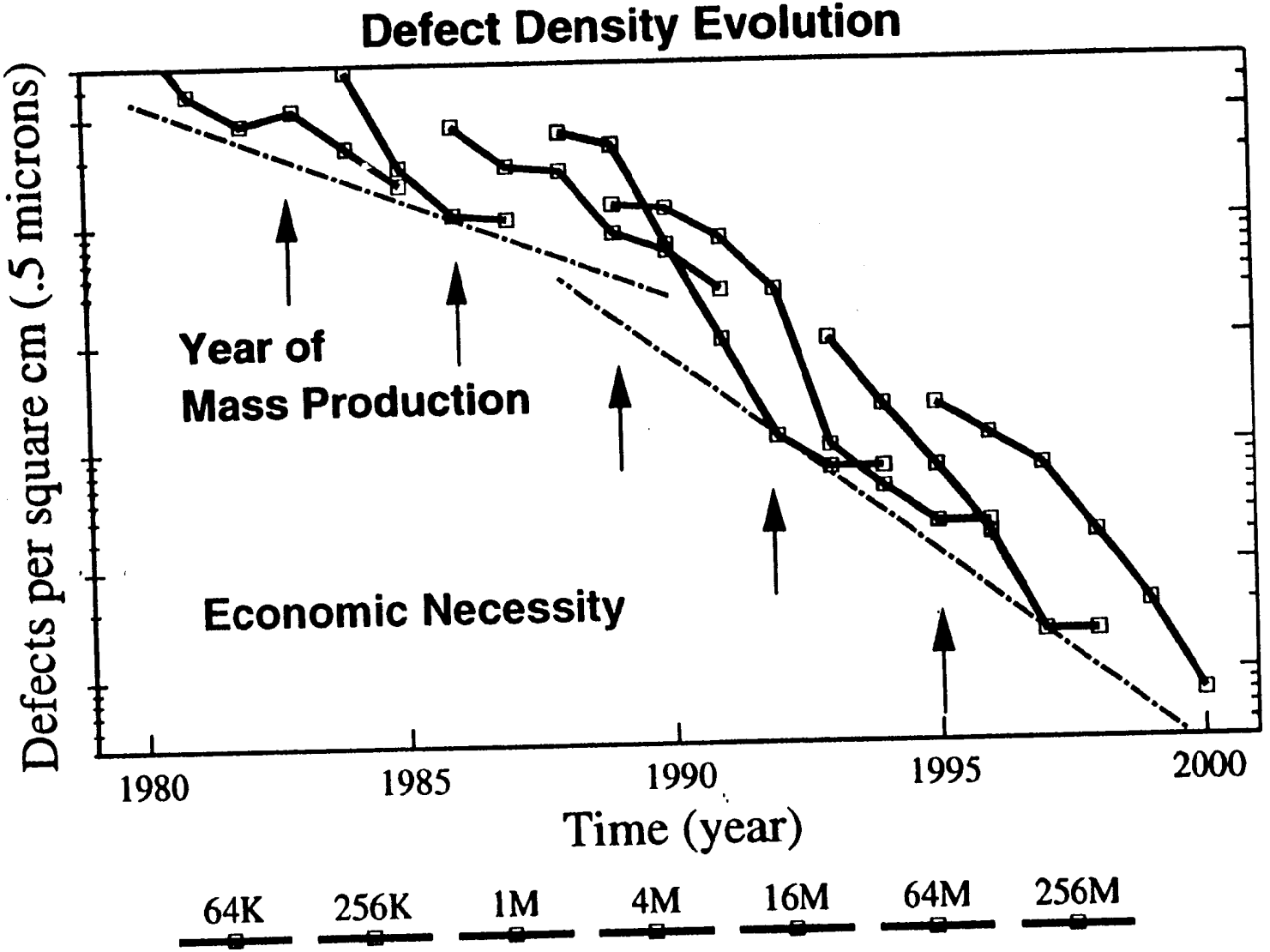
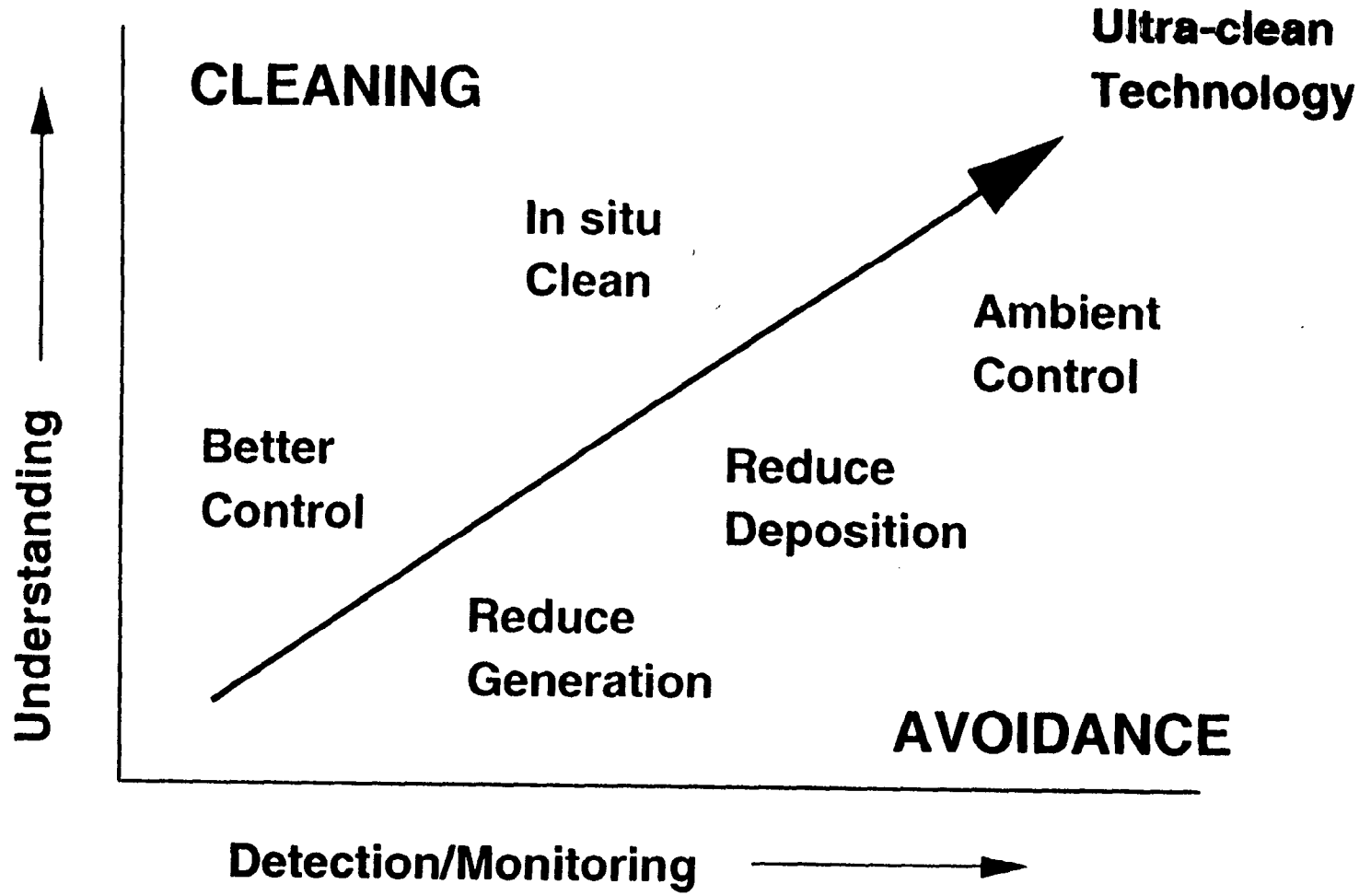
SEMICONDUCTOR TECHNOLOGY TRENDS





Defect levels are sum for critical lithographic levels

defect1.ps M.Liehr 1.20.92



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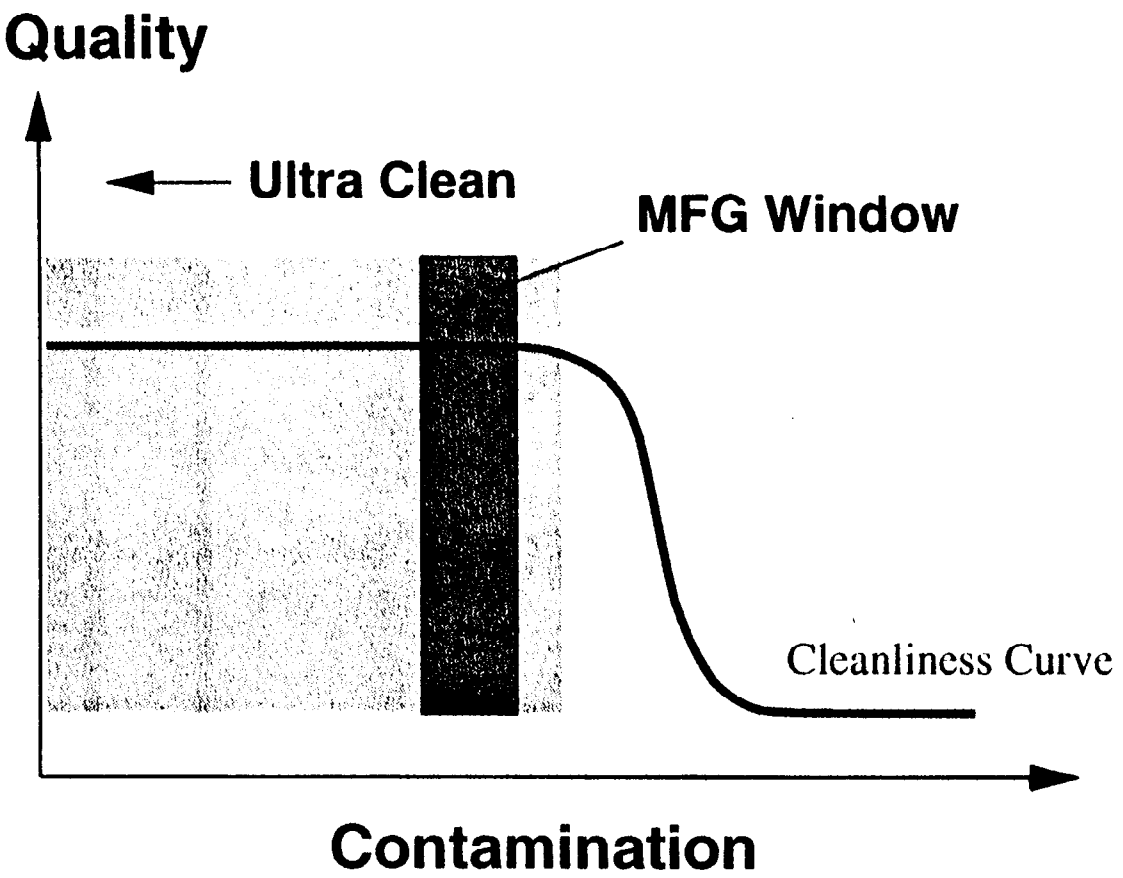
Development for Manufacturability

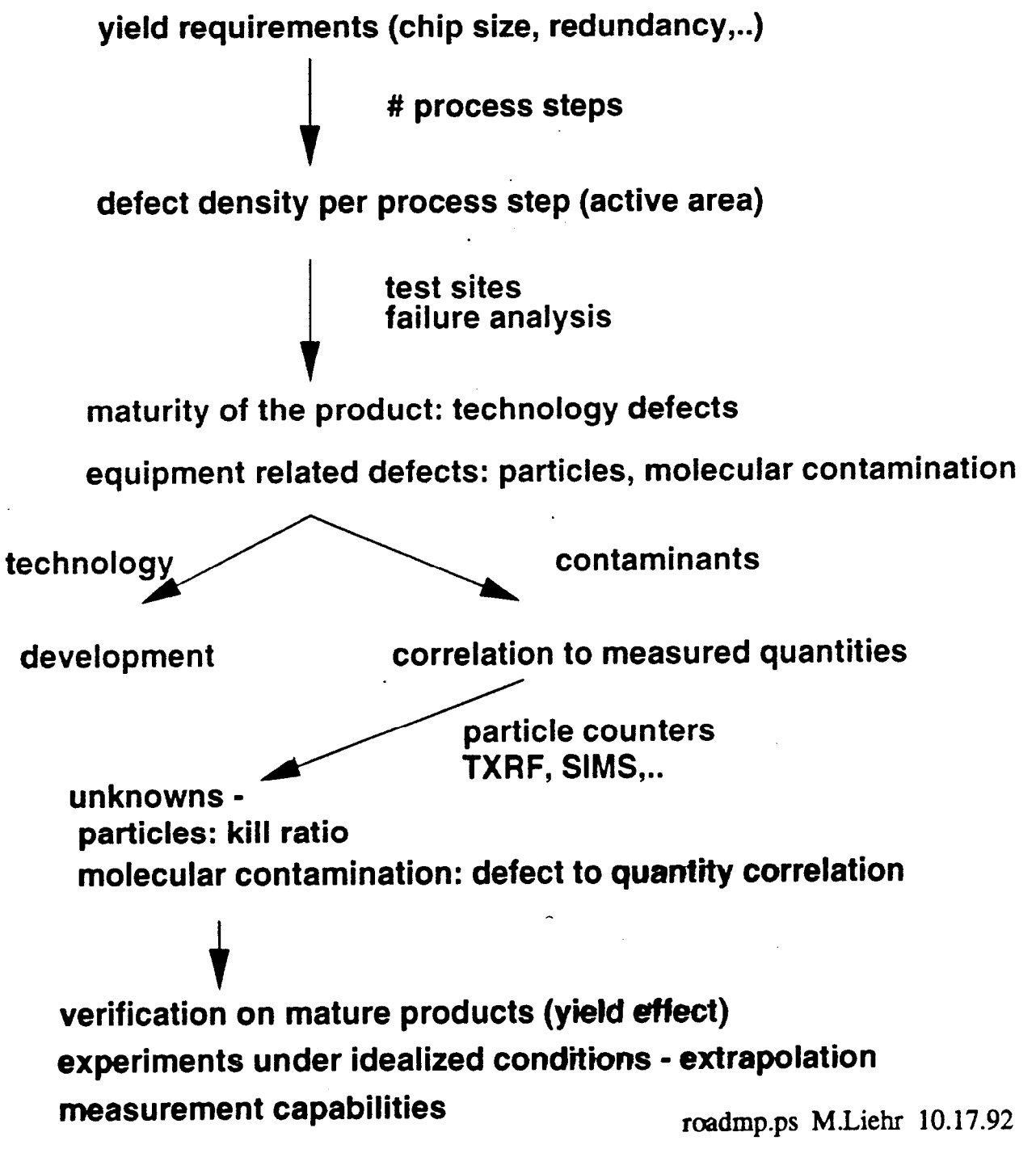


- process
- transfer medium

- reactive impurities
- particles

clean.ps M.Liehr 2.1.91

How Do We Create a Roadmap?



roadmp.ps M.Liehr 10.17.92

Microcontamination Areas in Si Technology

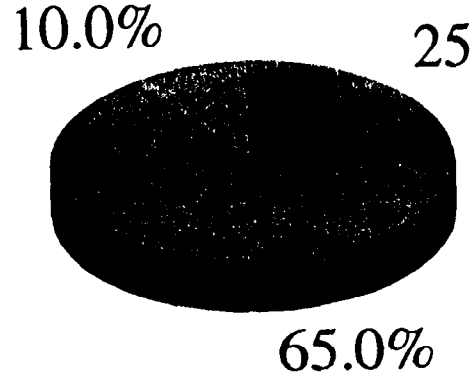
- **Particles**
  - Horizontal and vertical scaling
  - Roadmaps
  - Cleaning techniques
- **Organic and Oxide Contamination**
  - Measurement and identification
  - Device effects
  - Roadmaps
  - Product isolation schemes
- **Metal Contamination**
  - Device effects
    - *Substrate effects*
    - *Oxide effects*
  - Roadmaps
  - Identification
  - Cleaning

IBM

contint.ps M.Liehr 10.13.92

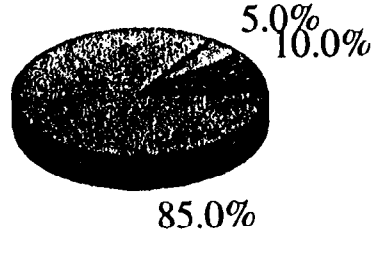
Particulate Defects

1990



20 X
Reduction

1995



- **Chemicals, Air**
- **Wafer handling**
- **Tools, Processes**

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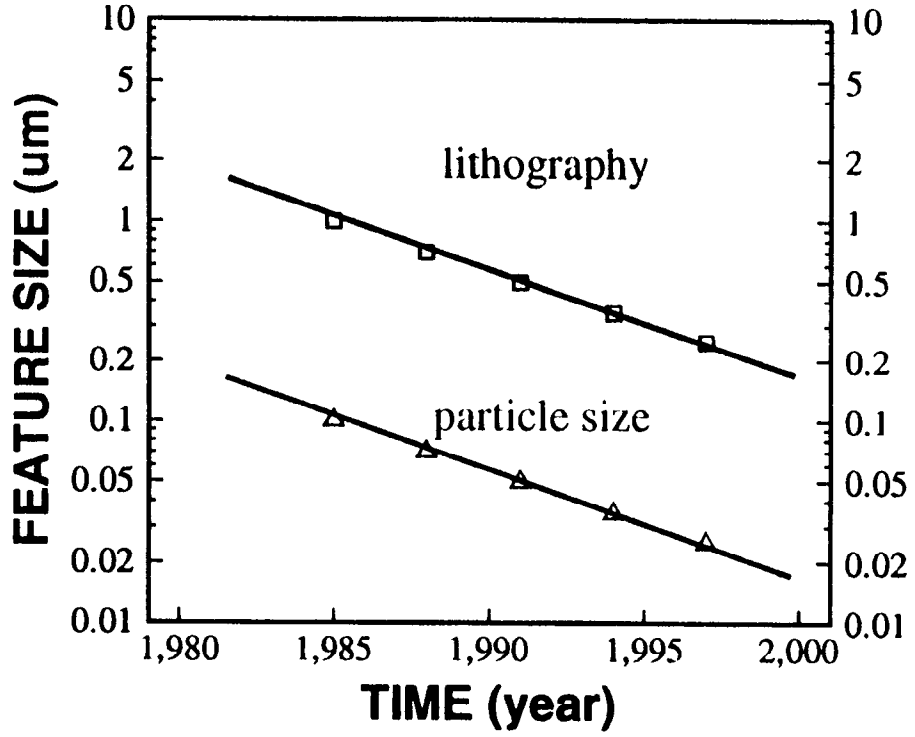
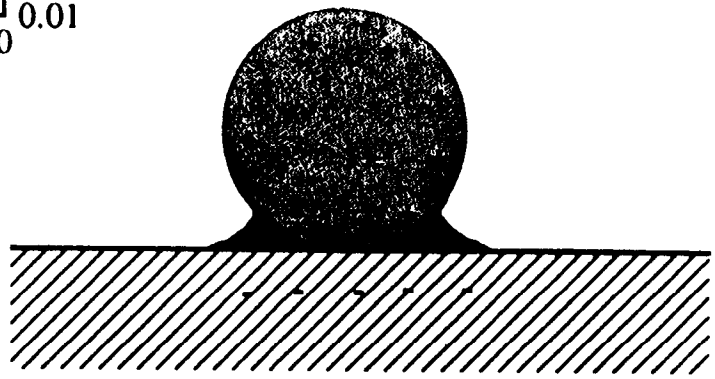
Particle Roadmap

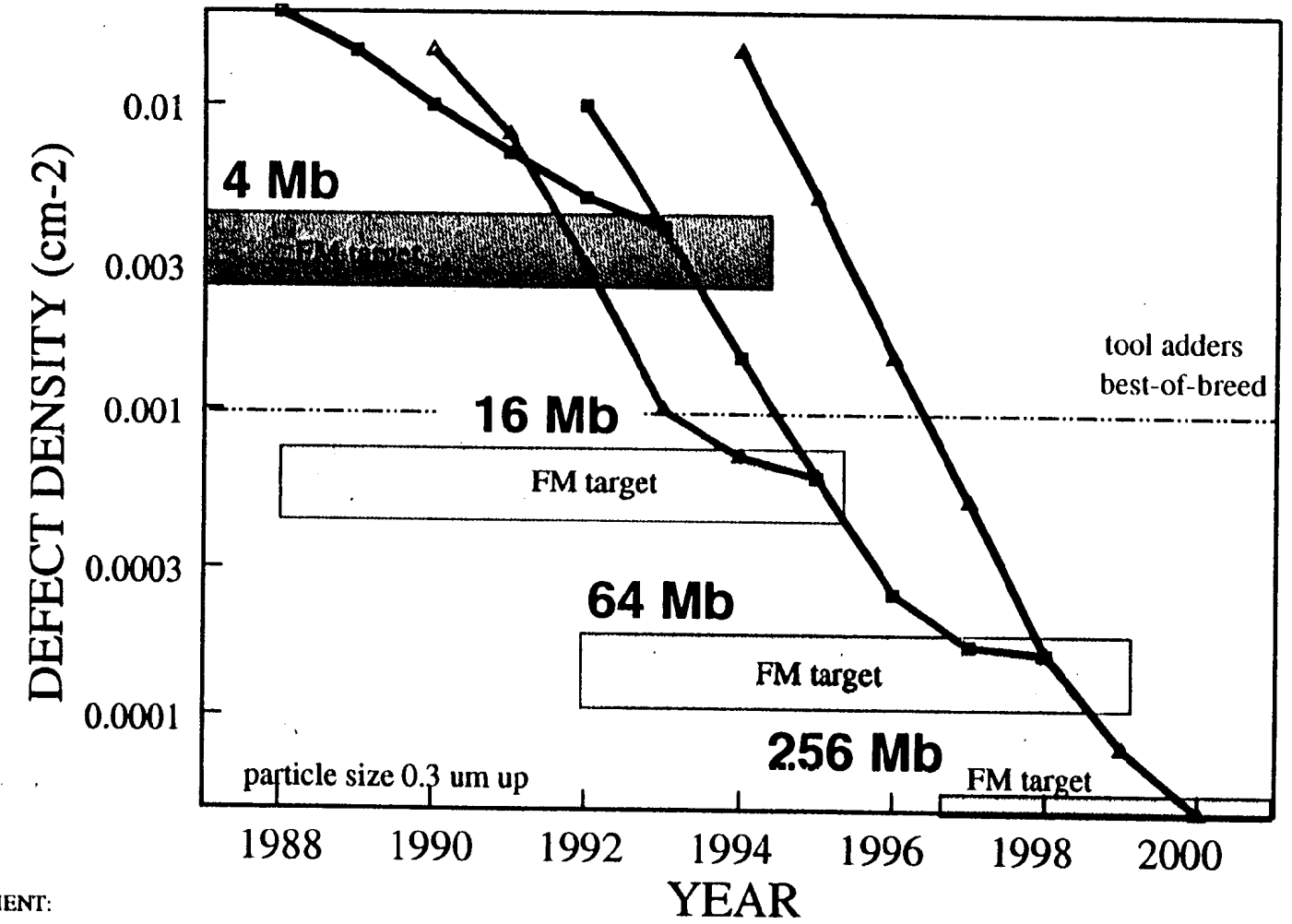


Adhesion forces:

- Surface Charges
- Capillary Effects
- Van der Waals Forces
- Topography
- Chemical Reaction



PARTICLE CONTAMINATION TARGETS
WAFER CLEANING TOOLS



COMMENT:
Vertical scaling assumed

fmtarget2.ps 8.15.92 M.Liehr

Particle Cleaning Techniques

- **Wet cleaning**
  - Megasonics
  - Rinse and quick-dump cleaning
  - Spin cleaning
  - Brush cleaning
- **Vapor cleaning**

Cryogenic Particle Removal

Techniques:

CO2 cryogenic cleaning

Ar cryogenic cleaning

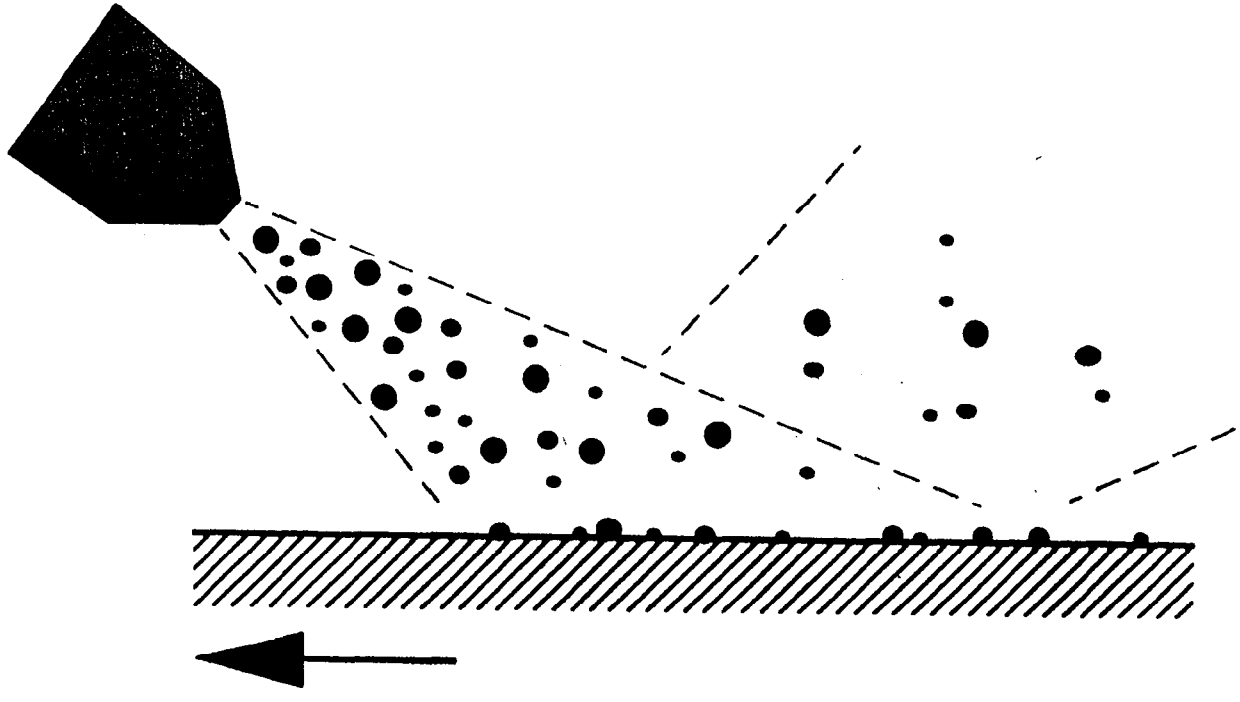
water/ice scrubber

Science Issues:

Adhesion force

Pellet melting

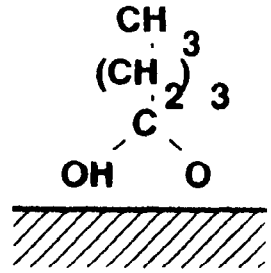
Hydrocarbon removal



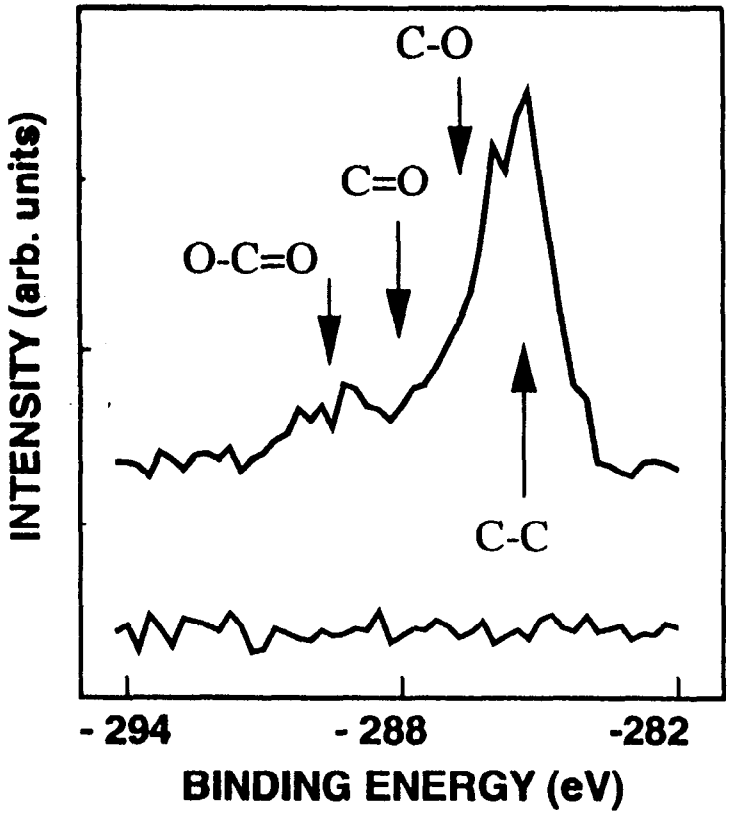
Molecular Contamination Issues

- Identification
- Ambient contributions
- Surface reactions during processing
- Impact on device
- Removal

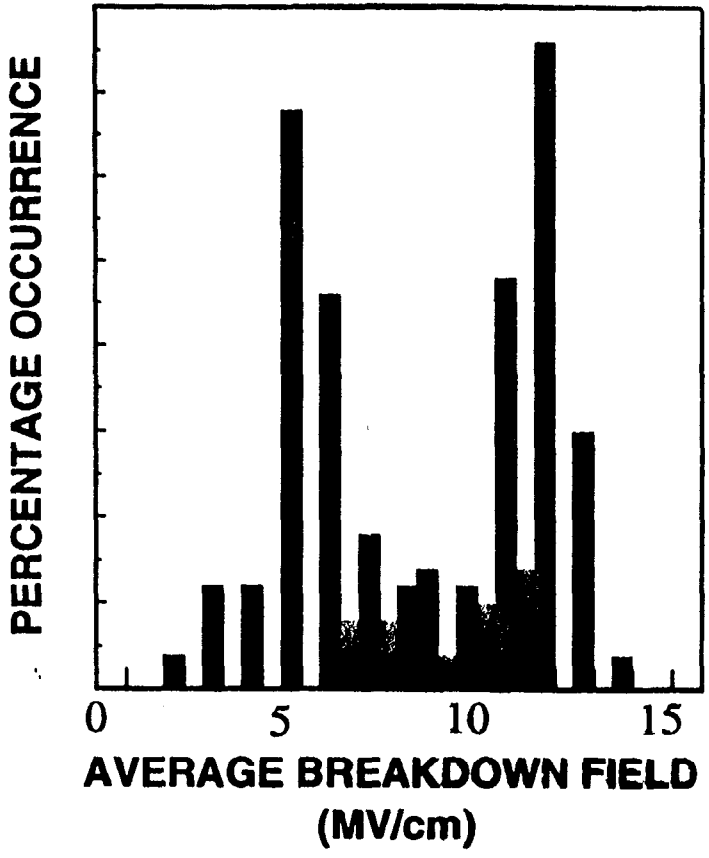
Molecular Contamination



XPS C_{1s} scan



MOS I/V curves

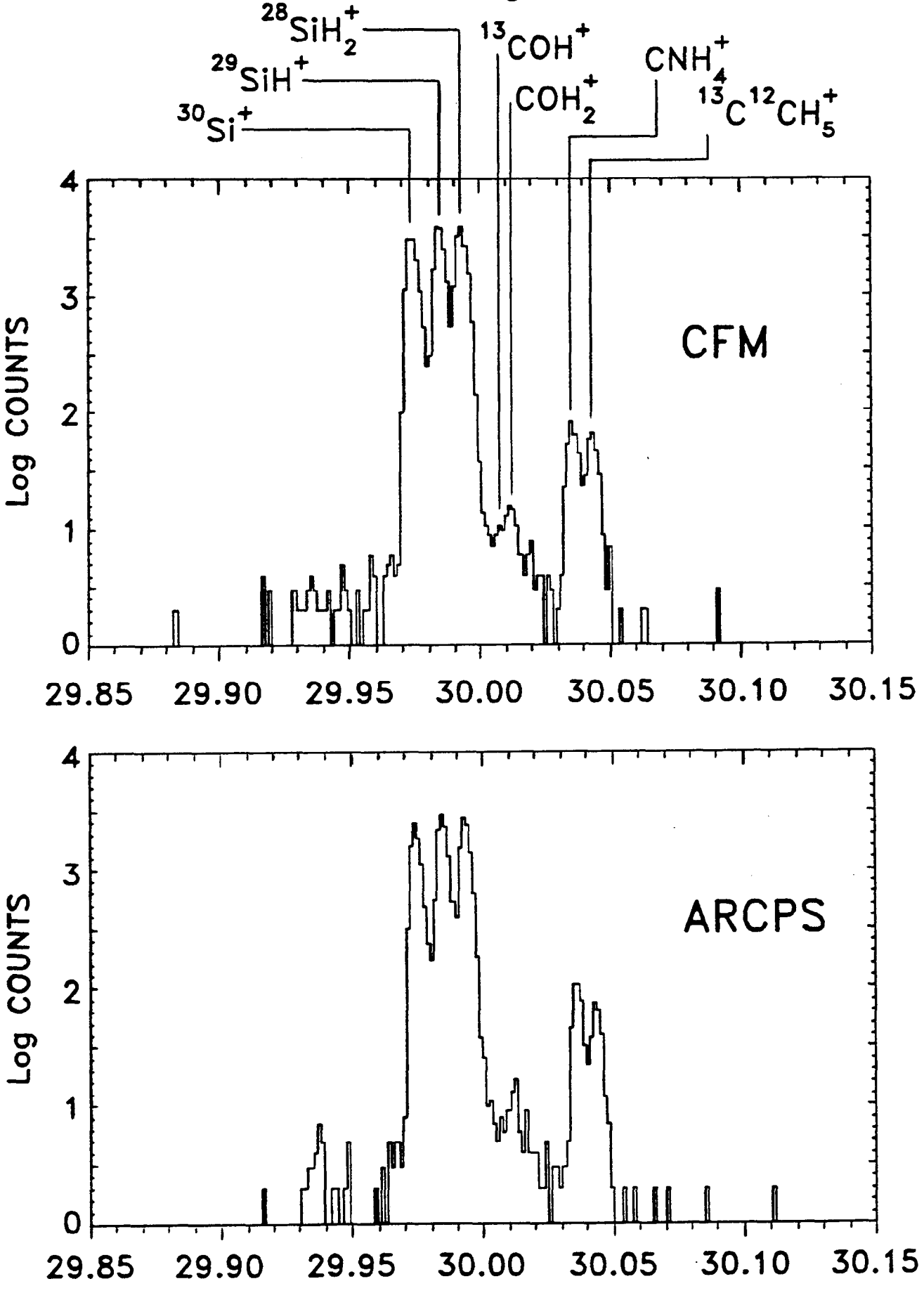


S.R.Kasi and M.Liehr,
Appl. Phys. Lett. 59, 108 (1991)

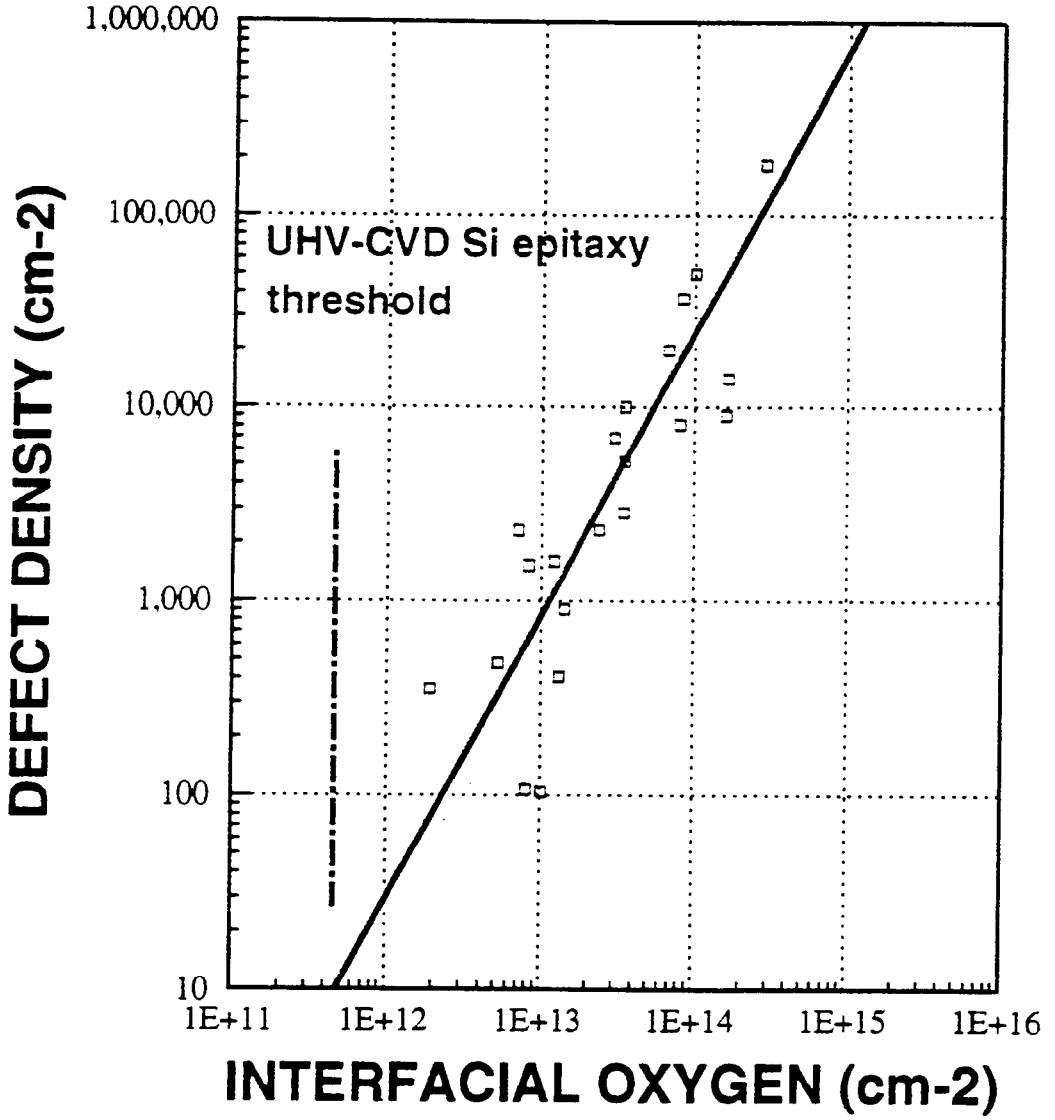
mitval.ps 1.22.92 M.Liehr

■ RCA cleaned ■ RCA/HF/valeric acid

Details of mass 30 region



Defect to Impurity Correlation
Interfacial oxygen to epitaxial film defects

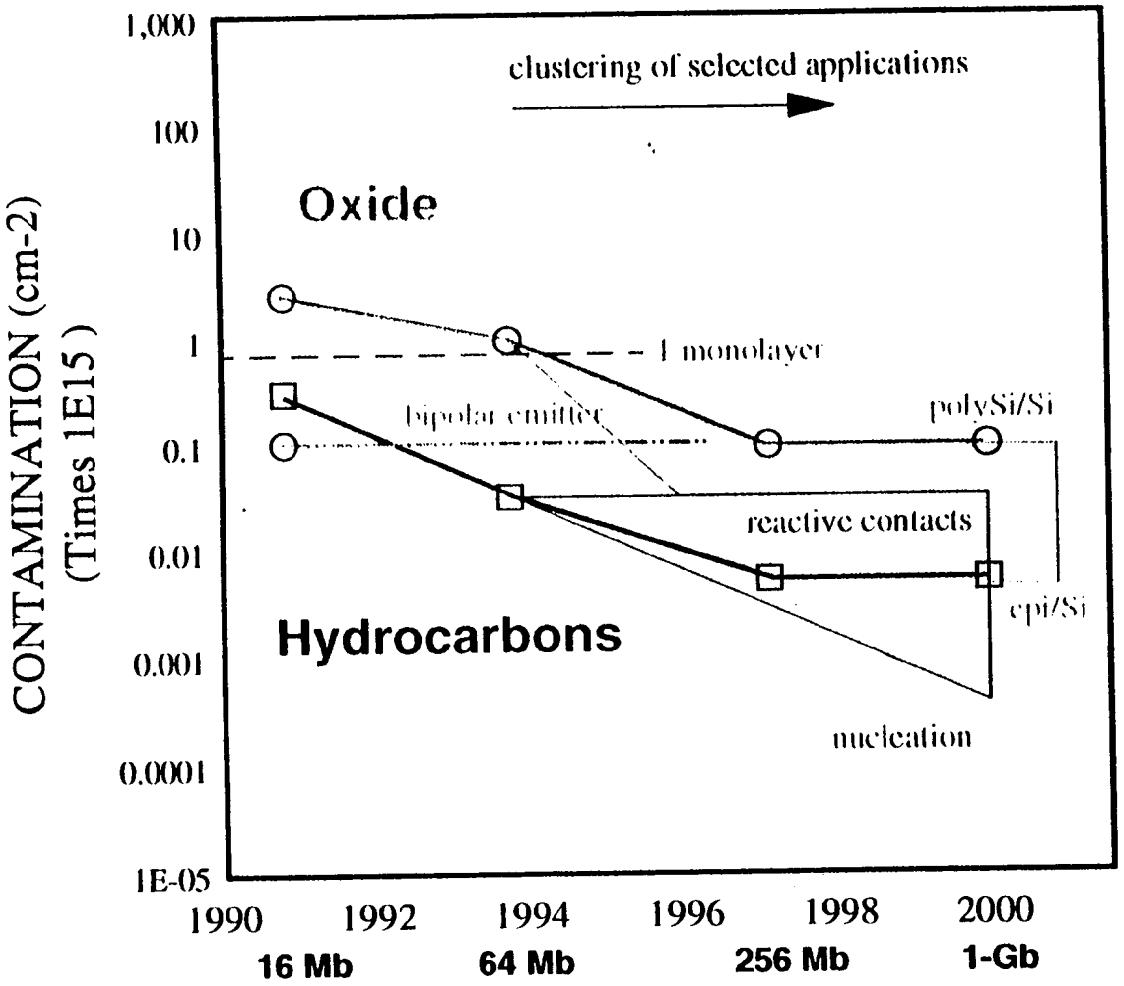


to be published in MRS proceedings vol 259
M.Tejwani and P. Ronsheim

IBM

oxydef.ps M.Liehr 10.16.92

NON-PARTICLE WAFER SURFACE CONTAMINATION ROADMAP



CRITICAL LEVELS ONLY

contam4.ps 10.13.92 M.Liehr

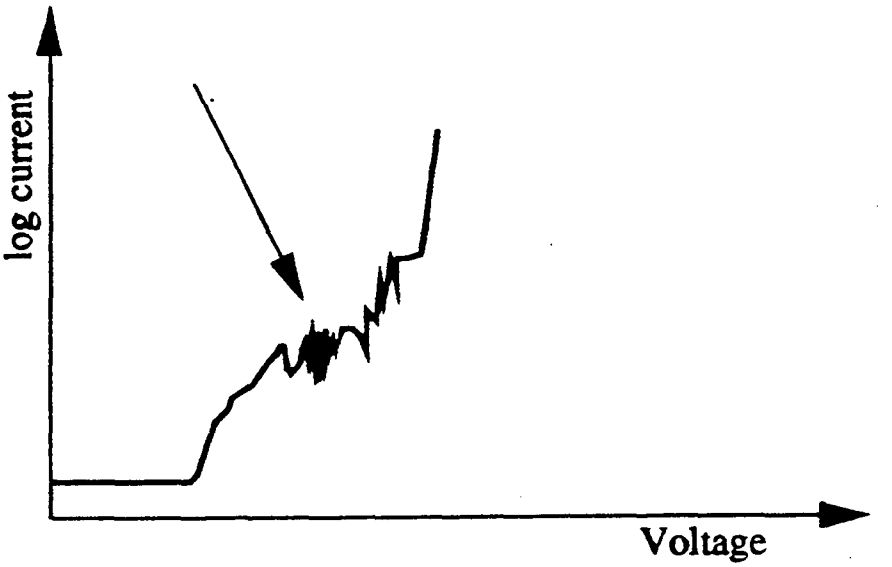
Effect of Metals on Silicon Devices

- Metals introduce trap levels into the silicon forbidden gap
- Metals cause formation of silicon defects
- Metals reduce breakdown strength of SiO2
- Metals change film growth rates
- Alkaline metals change FET thresholds
- Dopant metals cause mainly p-type accumulation

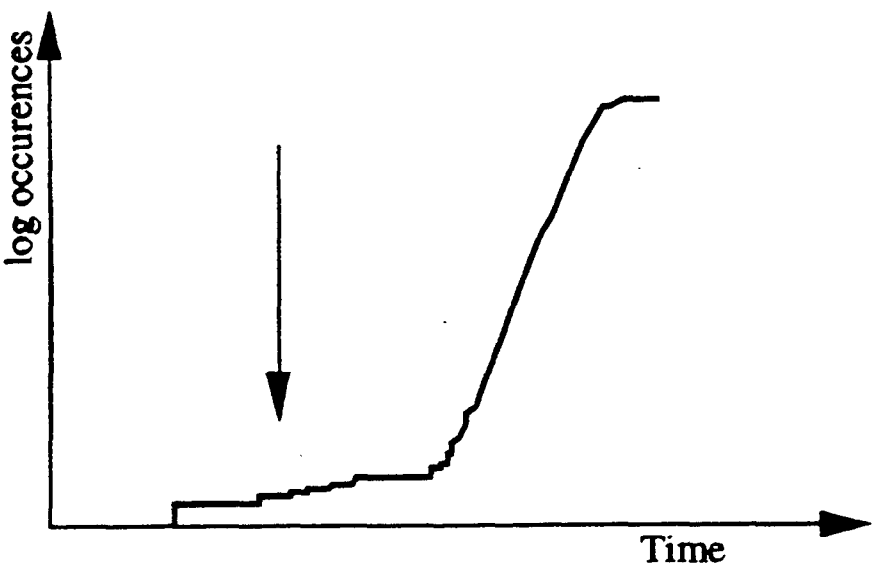
metint.ps M.Liehr 9.15.92

CONSEQUENCES OF METAL CONTAMINATION

NODE
OXIDE
BREAKDOWN



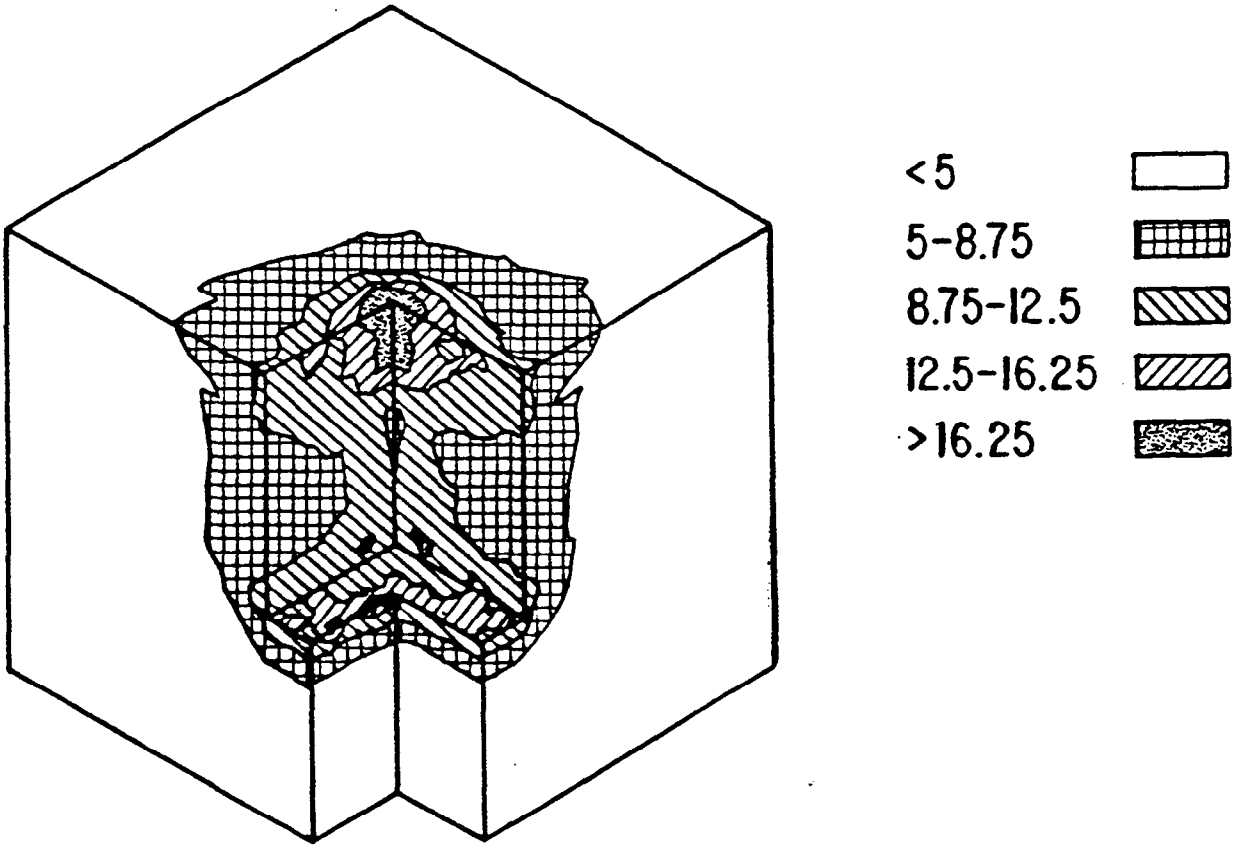
RETENTION
TIME
FAILURE



conseq.ps M.Liehr 9.12.92

Metal Precipitation

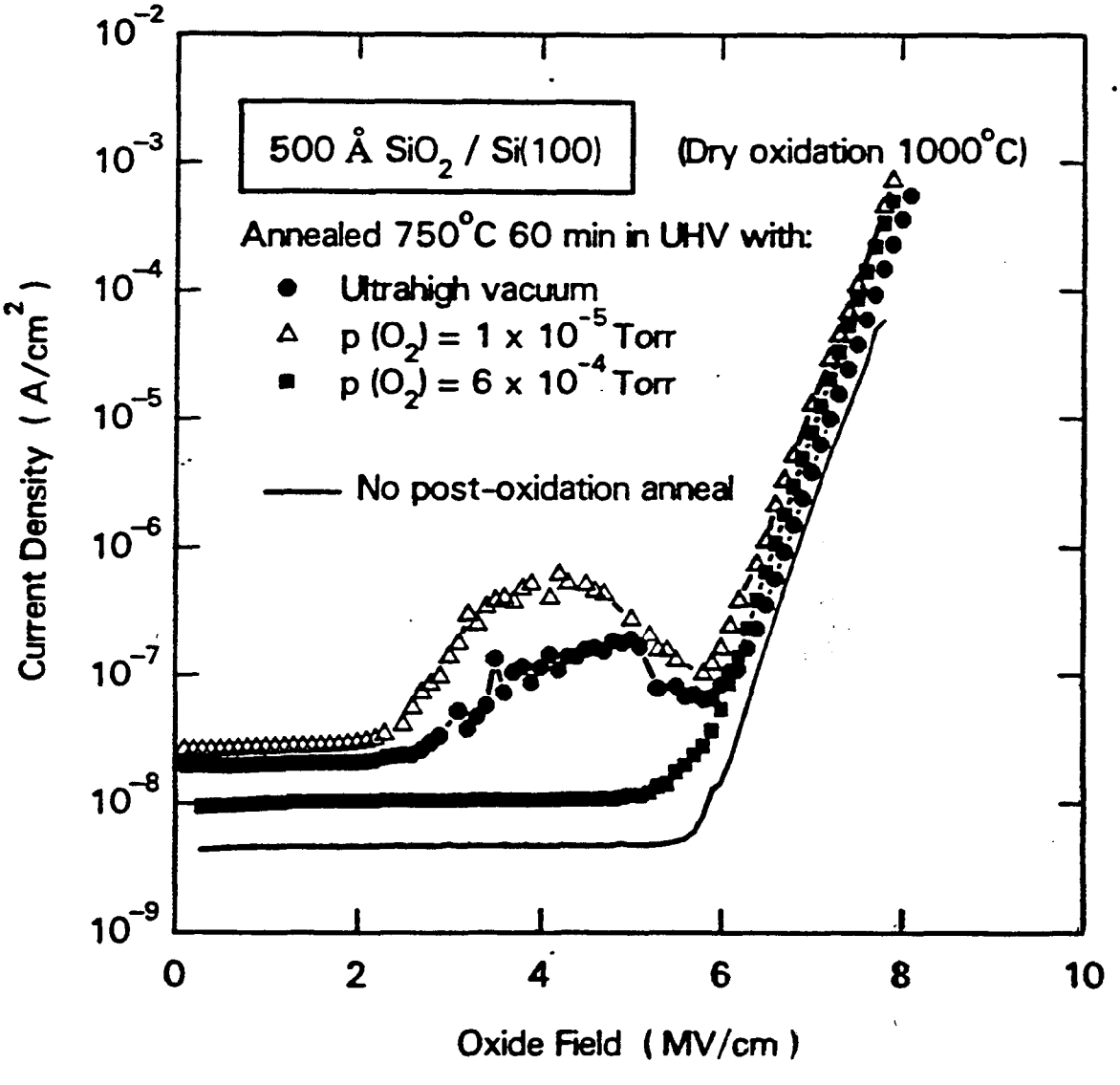
- Volumetric density of silicide vs. silicon determines tendency to precipitate
  $Si_{lattice} + N_M M_{int.} = M_x Si_{y,\,precip} + N_I Si_{int.}$
- Cu, Fe, Ni, Sn, Zn form precipitates
- Precipitation occurs preferrentially at defect locations or in areas of high internal stress
- Stress related slip lines are likely to be decorated by metal precipitates



*) - Von Miese stress in 10^8 dynes/cm^2
S.Stiffler et al., trans. of Electr. devices, to be published

Gate Oxide Leakage and Premature Breakdown

- Oxide decomposition reaction $SiO_2 + Si \rightarrow 2\ SiO$ during post-oxidation, inert ambient anneals
- Reaction equilibrium governed primarily by the SiO vapor pressure



Oxide Decomposition reaction

- ***Oxidation***

$$2Si + O_2 \rightarrow 2SiO$$
$$2SiO + O_2 \rightarrow 2SiO_2$$

- ***Decomposition***

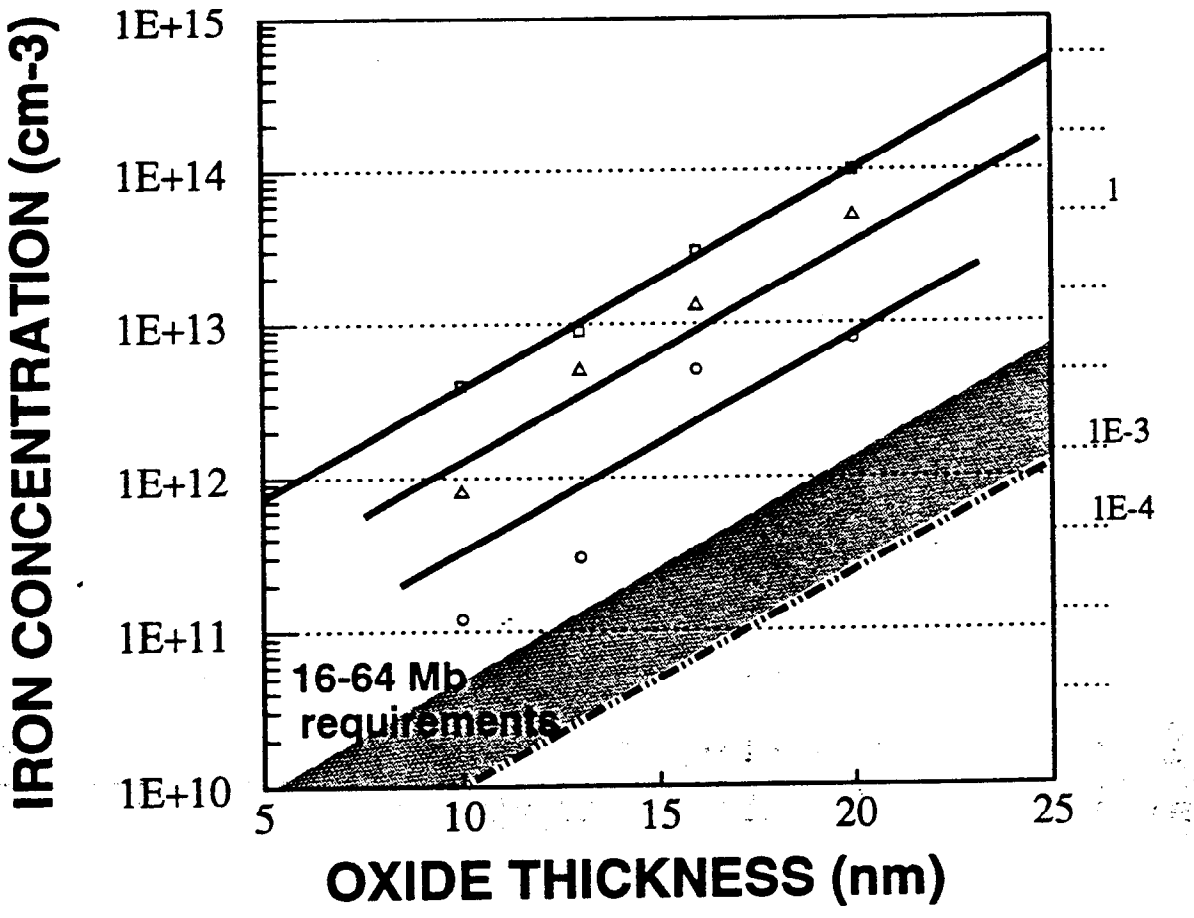
$$SiO_2 + Si \rightarrow 2SiO\uparrow$$

- ***Re-oxidation***

$$2SiO + O_2 \rightarrow 2SiO_2$$

- Reaction catalyzed by metals with high electron density at the Fermi level
  - **Transition metals, near-noble metals, noble metals**
  - Oxide decomposition through void formation (requires oxide defect)
  - No chemical reaction with SiO_2
  - Electrical defect are early stage
  - Impact oxide growth rate as well
- Silicate formation leads also to oxide decomposition
  - **Alkaline, earth-alkaline and early transition metals**
  - Homongeneous decomposition
  - Charged defects in the oxide (mobile ions)
  - Impact oxide growth rate as well

Effect of Iron Contamination on Gate Oxide



Oxide defect density

100 cm-2

10 cm-2

1 cm-2

W.Henley, L.Jastrzebski, and N.Haddad
MRS proceedings, to be published

feox.ps M.Liehr 10.16.92

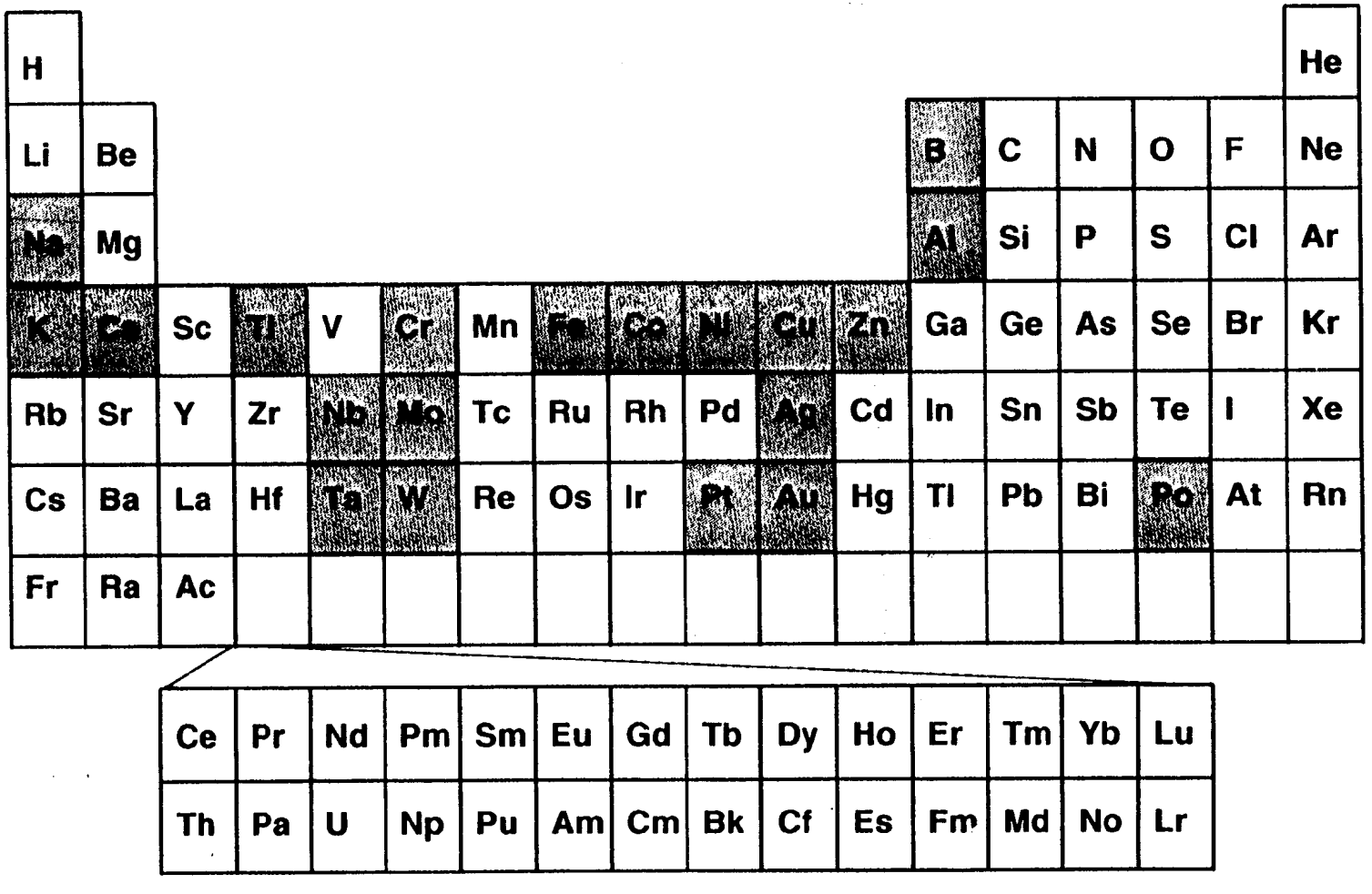
Metal Contamination Effect on Silicondioxide

(Device use)

- **Metals that do not react with SiO2**
  - Penetration through oxide defects
  - Interface roughening - Fowler Nordheim tunneling
  - SiO-like defect injection after anneal
  - Oxide decomposition on exposed areas
  - Oxide growth rate changes
    - * *Diffusion barriers, contact materials*
- **Metals that react with SiO2**
  - Silicate formation - oxide thinning
  - Mobile ion formation
    - * *Adhesion layers, metallization*

metsum.ps M.Liehr 10.13.92

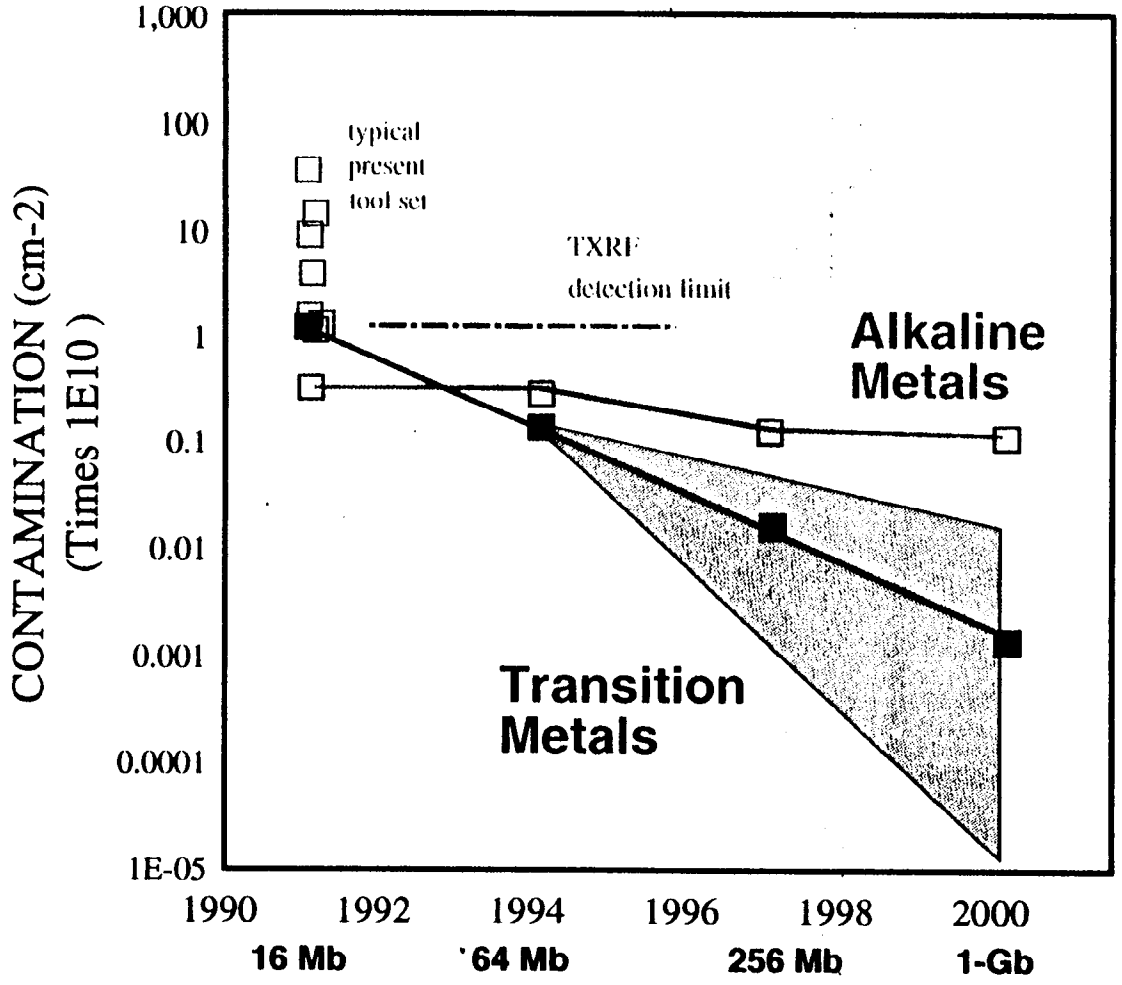
PERIODIC TABLE OF THE ELEMENTS



experienced negative device impact

period.ps M.Lichr 9.16.92

METAL WAFER SURFACE CONTAMINATION ROADMAP



CRITICAL LEVELS ONLY

contam3.ps 10.13.92 M.Liehr

Typical Metal Contamination Levels and Sources

- **Noble metals**
  - ***Cu, Pt***
  - Origin: RIE, incoming wafers, cleans, contact metallization
  - Levels up to $10^{13} cm^{-2}$
- **Transition metals**
  - ***Cr, Fe, Ni, Mo, W, Ti***
  - Origin: RIE, stainless steel, implanters, metallization, paint
  - Levels up to $10^{13} cm^{-2}$
  - Levels up to $10^{14} cm^{-2}$ on patterns
- **Dopants**
  - ***Al, B***
  - Origin: RIE, cleans, metallization, windows
  - Levels up to $10^{13} cm^{-2}$
- **Alkaline metals**
  - ***Na, K, Ca***
  - Origin: humans, bacteria, streets, air, plastics
  - Levels up to $10^{14} cm^{-2}$

Metal Contamination Detection

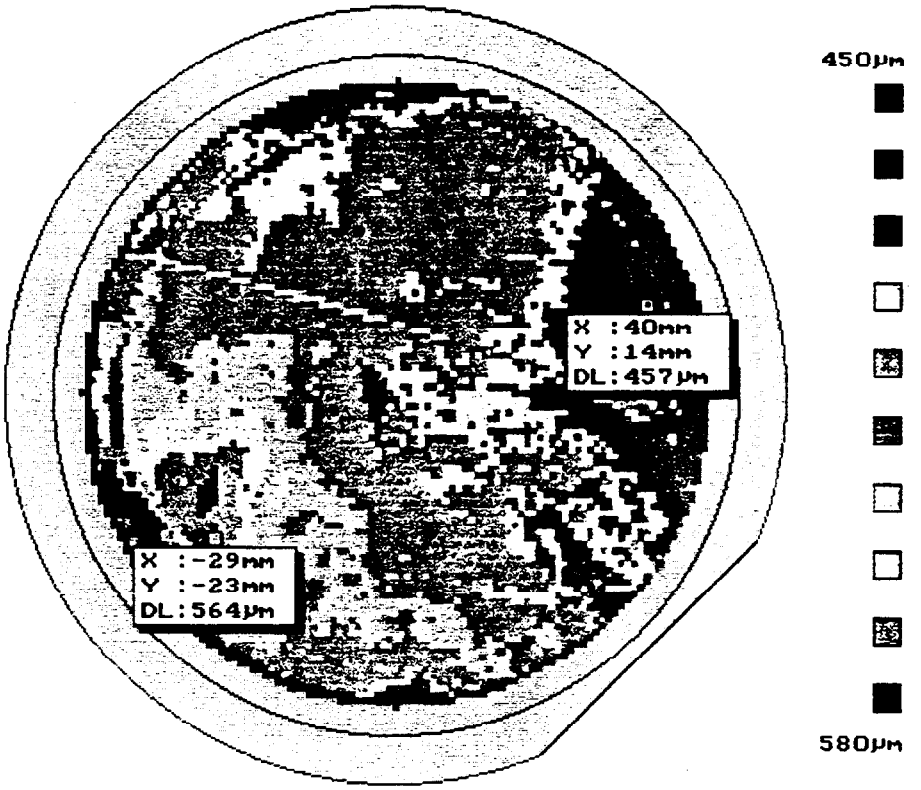
- **Critical levels**
  - as low as $10^{10} cm^{-2}$
- **Detection techniques**
  - Heavy ion backscattering spectrometry
  - Deep Level Transient Spectroscopy
  - Surface Photo Voltage
  - Elymat
  - Haze Test
  - Vapor Phase Decomposition Techniques
  - Total Reflection X-Ray Fluorescence
  - Time-of-Flight SIMS
  - Inductively Coupled Plasma - Mass Spectrometry
  - *All useful techniques are slow and expensive*
- **In-situ sensors**

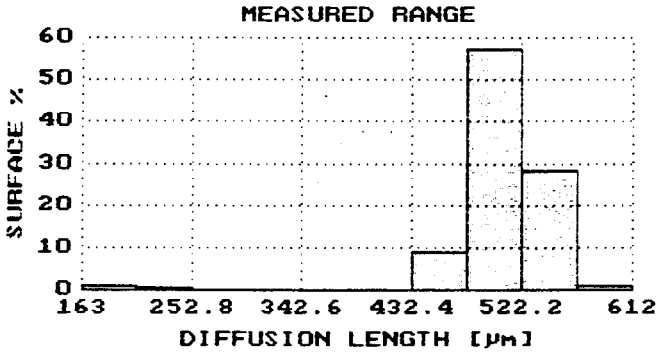
ELYMAT DIFFUSION LENGTH MEASUREMENT Version 2.53

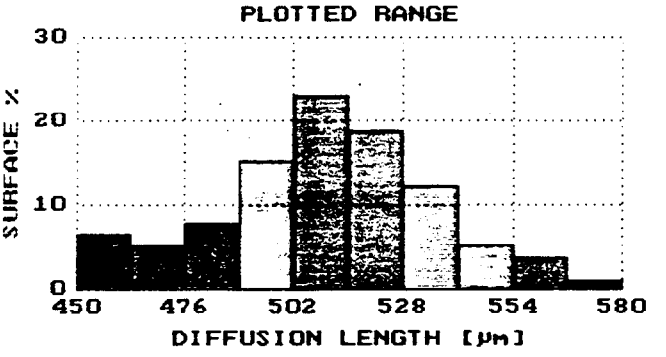
Comment : "good" starting wafer
Date : 07/11/91
Operator : ZEINDL
Sample : MOT CLEANMON
Filename : MOTCMB1

MaxPhCurr: 1700 µA
Thickness: 675 µm
Diameter : 5 Inch
Type : P
Laser W.l: HeNe 633 nm
Bias : 6 Volt
Raster : 1 mm/point
Contact : BPC
Source 1 : Cont. 2
Source 2 : Cont. 2

Data from scan	
Diffusion Length	
Average	: 501µm
Minimum	: 163µm
Maximum	: 611µm
Deviation	: 65.3µm







Metal Contamination Removal

- Metal removal is most effective using wet chemistry
  - Removal efficiency is function of solution chemistry
  - Possible contamination from insufficient chemicals purity
- Vapor phase removal
- Modeling
  - Tool scale models
  - Microfeature scale models

Wet Cleaning

- **RCA clean** - standard process since ≃ 1965

HF oxide strip		
SC-1: $NH_4OH/H_2O_2/H_2O$	1/1/5	50-80°C
SC-2: $HCl/H_2O_2/H_2O$	1/1/5	50-80°C

- ***Oxide removal (HF)***
  - Sensitive to hydrocarbon contamination
  - Prone to plate metal on exposed Si surface (eg, Cu)
  - Removes stable metal oxides imbedded in SiO_2 matrix
- ***Hydrocarbon removal (SC-1)***
  - Oxidizes hydrocarbons
  - Prone to metal hydroxide contamination
  - Etches Si thereby removing particles
  - Large chemical consumption drives cost
- ***Metal removal (SC-2)***
  - Utilizes metal chloride solubility
  - Sequence of SC-2 last required
  - Large chemical consumption drives cost

Surface Metal Contamination

Issues:

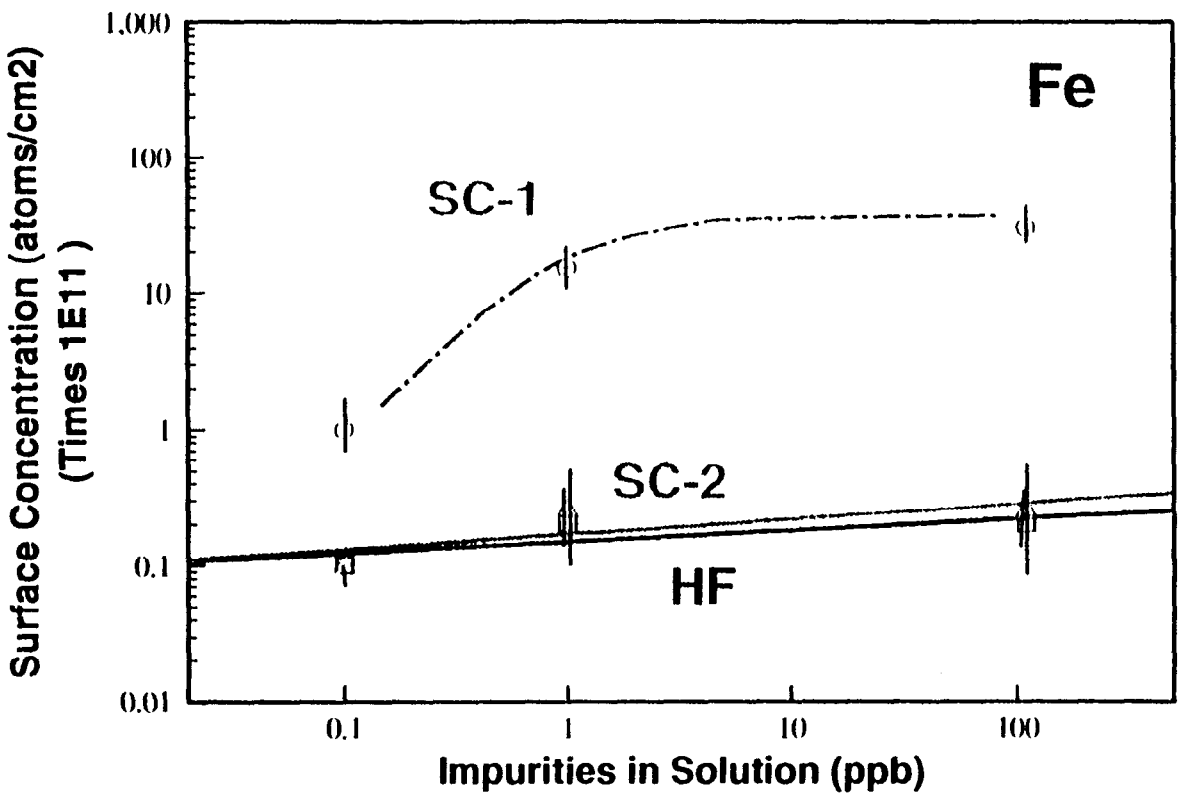
Surface roughness

Plating

Particle removal

Solution limit

Bath life



H.Hiratsuka, Toshiba

M.Liehr, 3.18.92, hiratsuk.ps

Summary

- **Particle contamination is still the key problem**
  - Particle kind and removal
- **Organic contamination characterization is complex**
  - Detection techniques
  - Defect effects
  - Product isolation
- **Metal contamination probes our detection limits**
  - Large variety of device failures
  - Contamination levels as low as $10^9 cm^{-2}$ or lower are critical
  - Detection techniques exist, but do not reveal structural, spatially resolved, or detailed chemical information
  - The mechanistic understanding of micro-chemistry is often lacking

III C. Analytical Methods for Wafer Surface Contamination

A. Shimazaki

ANALYTICAL METHODS FOR WAFER SURFACE CONTAMINATION

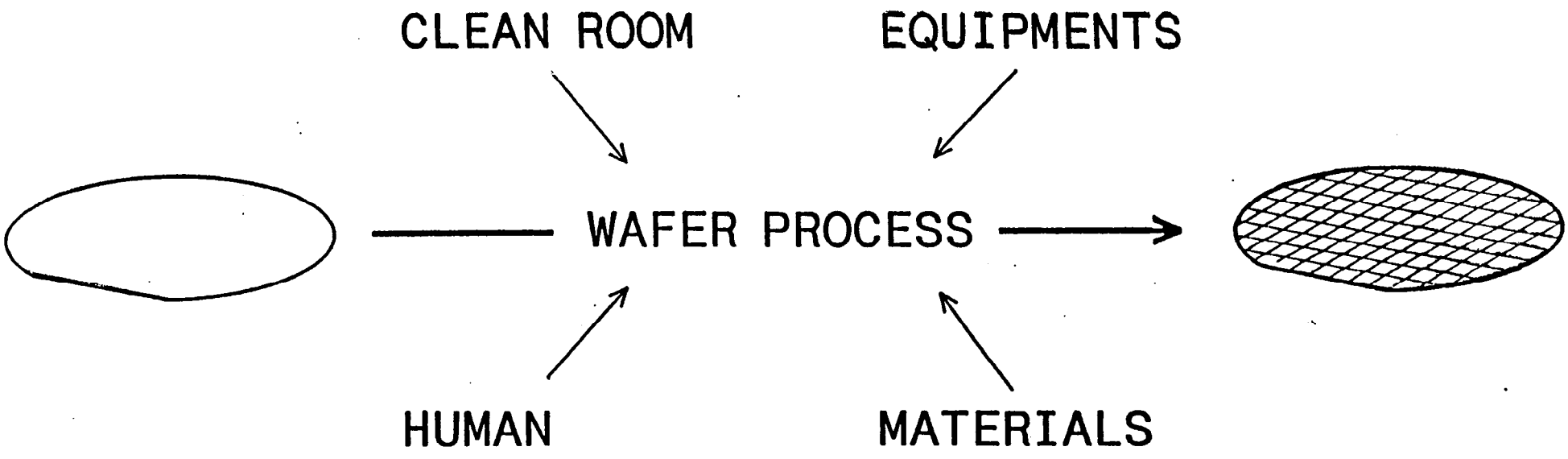
Ayako Shimazaki

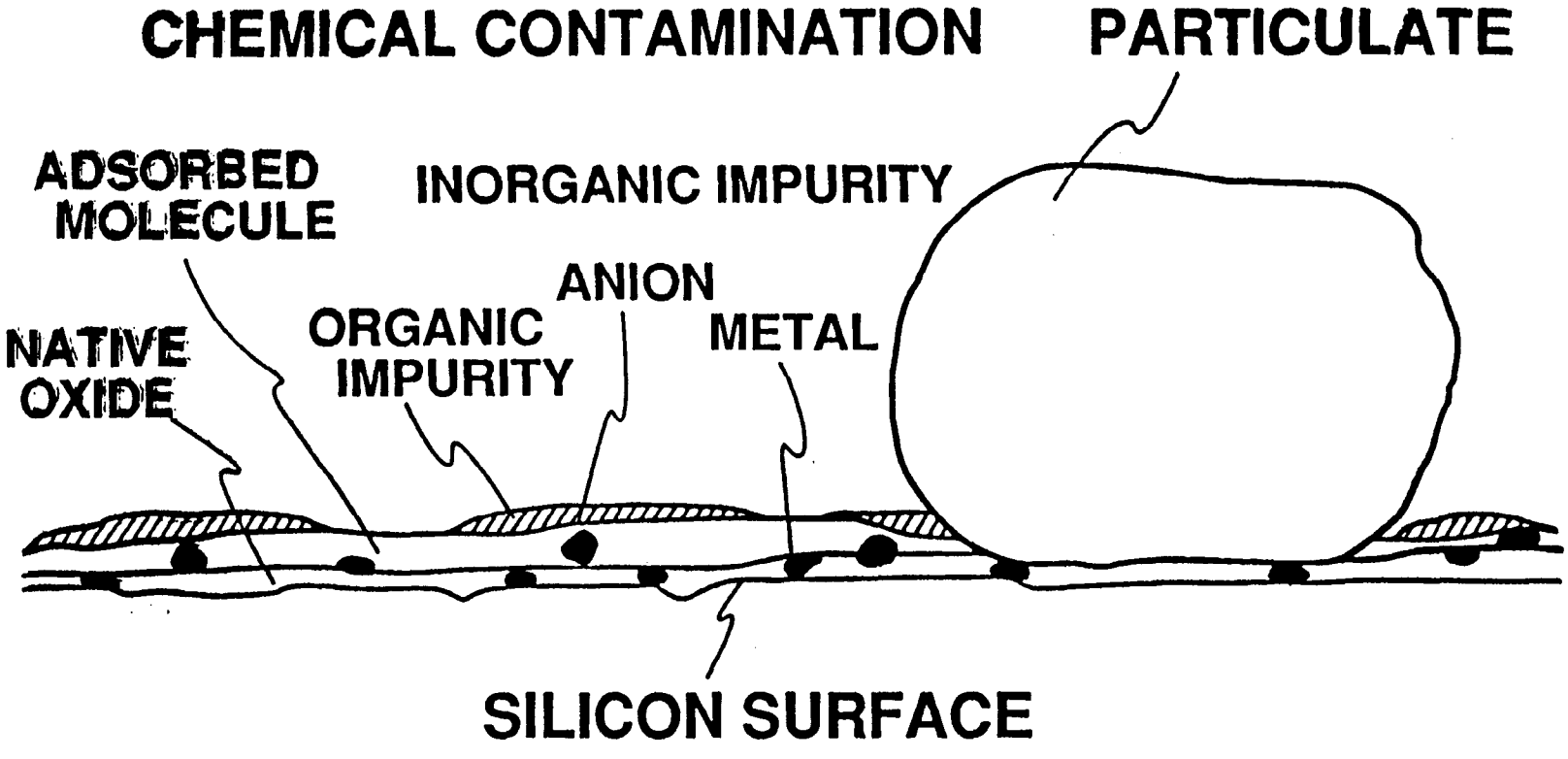
Integrated Circuit Advanced Process Engineering Dep.

Toshiba Corporation

TOSHIBA

CONTAMINATION CONTROL




CHEMICAL CONTAMINATION
PARTICULATE
ADSORBED MOLECULE
INORGANIC IMPURITY
ANION
NATIVE OXIDE
ORGANIC IMPURITY
METAL
SILICON SURFACE

ANALYTICAL METHODS

CONTAMINANTS		METHODS
METALS	on Si surface in SiO_2 , Si_3N_4 in other thin films, Si bulk on surface/near surface	WSA VPD } + GFAAS or ICP-MS TLA TRXRF
ANIONS	on surface	DIW EXTRACTION + IC TRXRF (S, Cl)
ORGANIC COMPOUNDS	on surface	DIW EXTRACTION + TOC THERMAL DESORPTION + GC-MS

WSA:Wafer Surface Analysis
VPD:Vapor Phase Decomposition method
TLA:Thin Layer Analysis
GFAAS:Graphite Furnace Atomic Absorption Spectrometry
ICP-MS:Inductively Coupled Plasma - Mass Spectrometry

TRXRF:Total Reflection X-ray Fluorescence Analysis
IC:Ion Chromatography
TOC:Total Organic Carbon
GC-MS:Gas Chromatography - Mass Spectrometry

OUTLINE:

Introduction
Chemical Analysis (WSA)
TRXRF
Summary

TOSHIBA

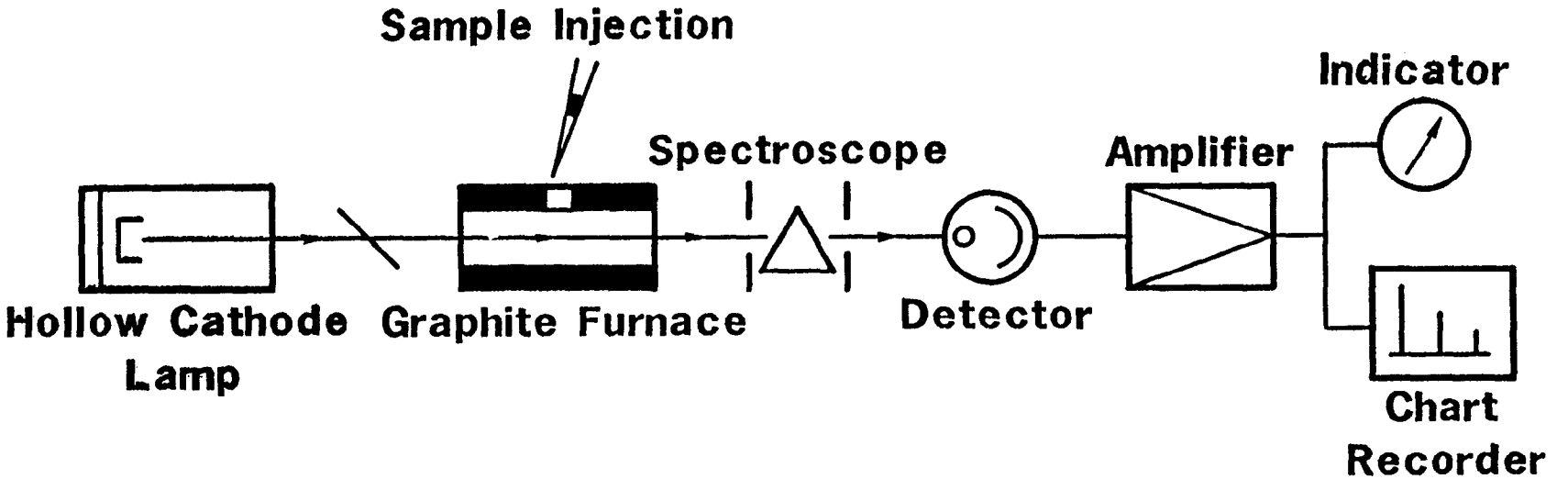
CHEMICAL ANALYSIS

1) sample preparation

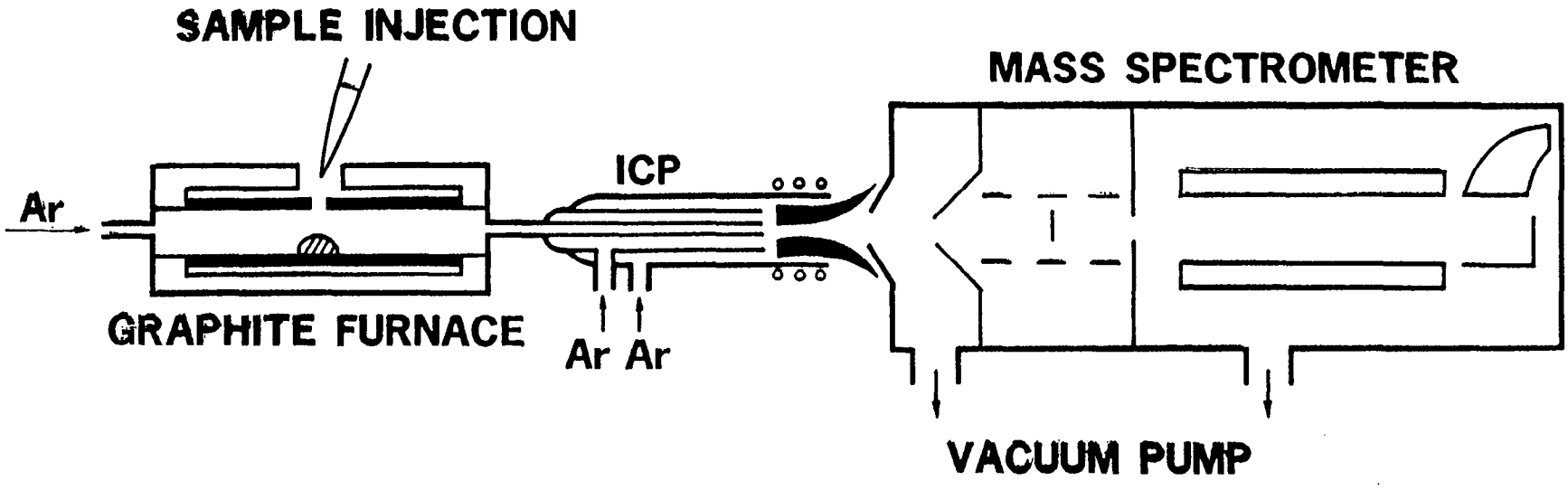
2) measurement

SIGNIFICANT POINTS IN SAMPLE PREPARATION PROCEDURES

1) High Recovery
2) High Concentration
3) Low Background (Contamination Free)



Flameless Atomic Absorption Analyzing System



ELECTRO-THERMAL VAPOURIZATION-ICP/MS ANALYZING SYSTEM

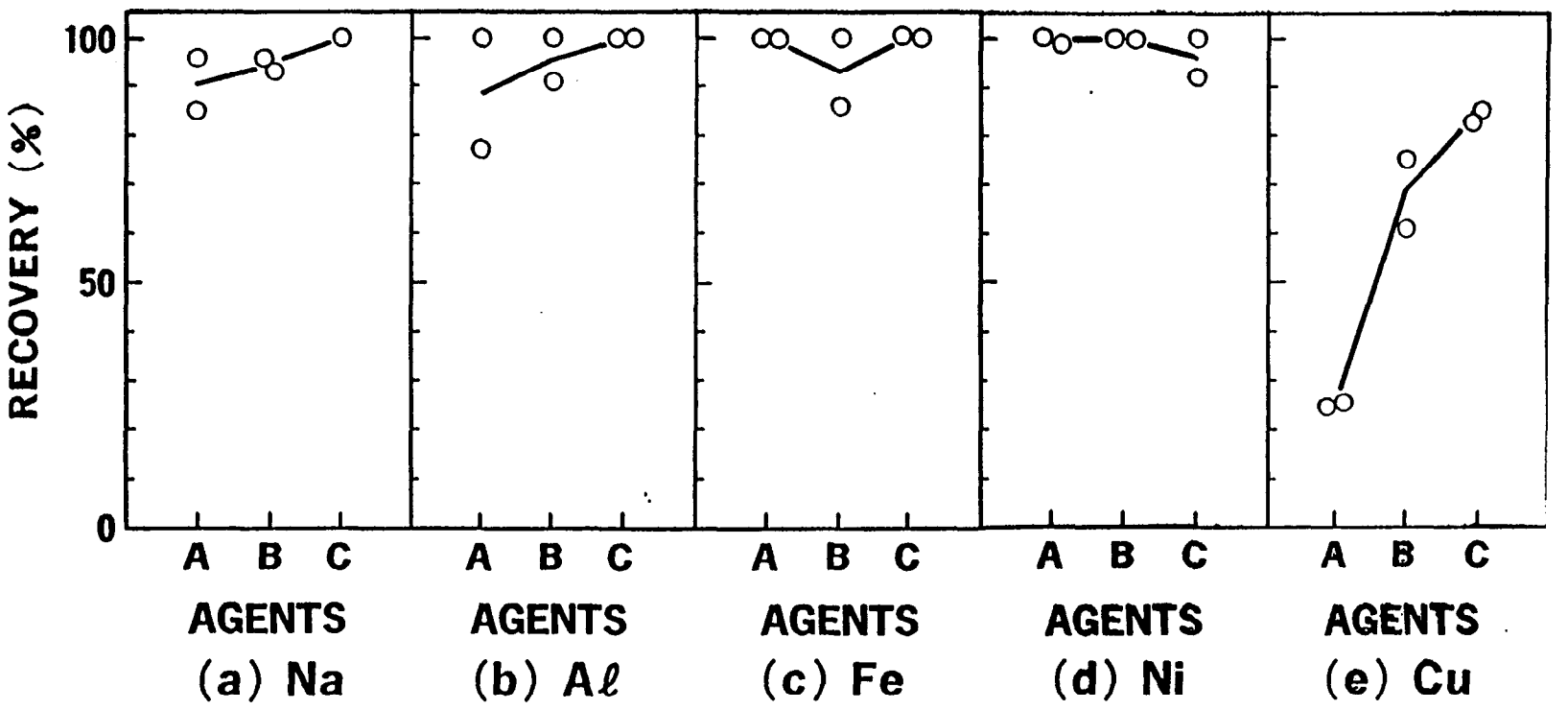
SIGNIFICANT POINTS IN SAMPLE PREPARATION PROCEDURES

1) HIGH RECOVERY

2) HIGH CONCENTRATION

3) LOW BACKGROUND
(CONTAMINATION FREE)

AGENTS	
A	1%HF
B	1%HF+3%H_2O_2
C	0.3%HCℓ +3%H_2O_2


RECOVERY (%)
100
50
0
A B C
AGENTS
(a) Na
(b) Aℓ
(c) Fe
(d) Ni
(e) Cu

DETECTION LIMITS OF WSA, VPD ANALYSIS

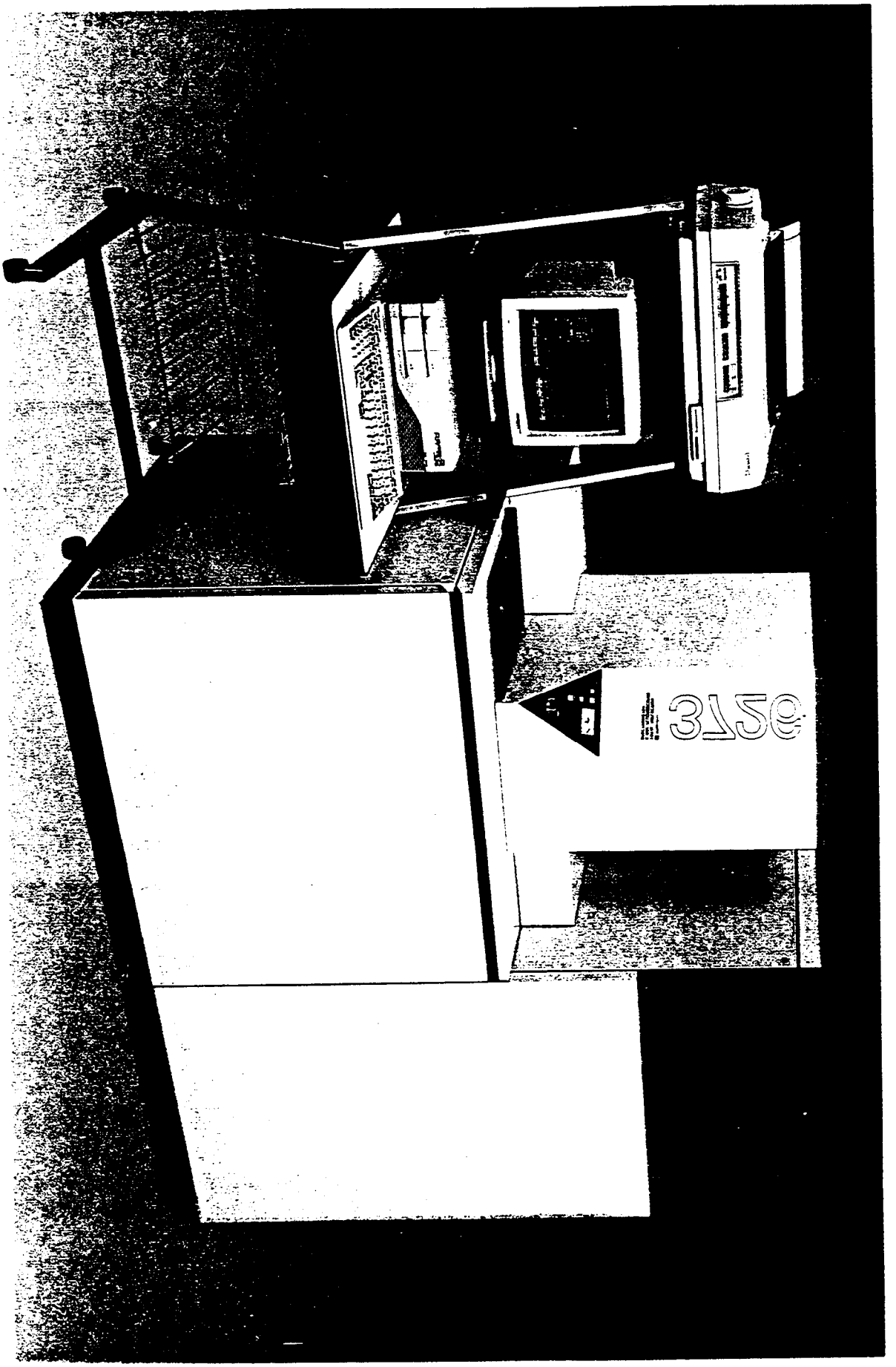
[$\times 10^{10}$ atoms/cm^2]

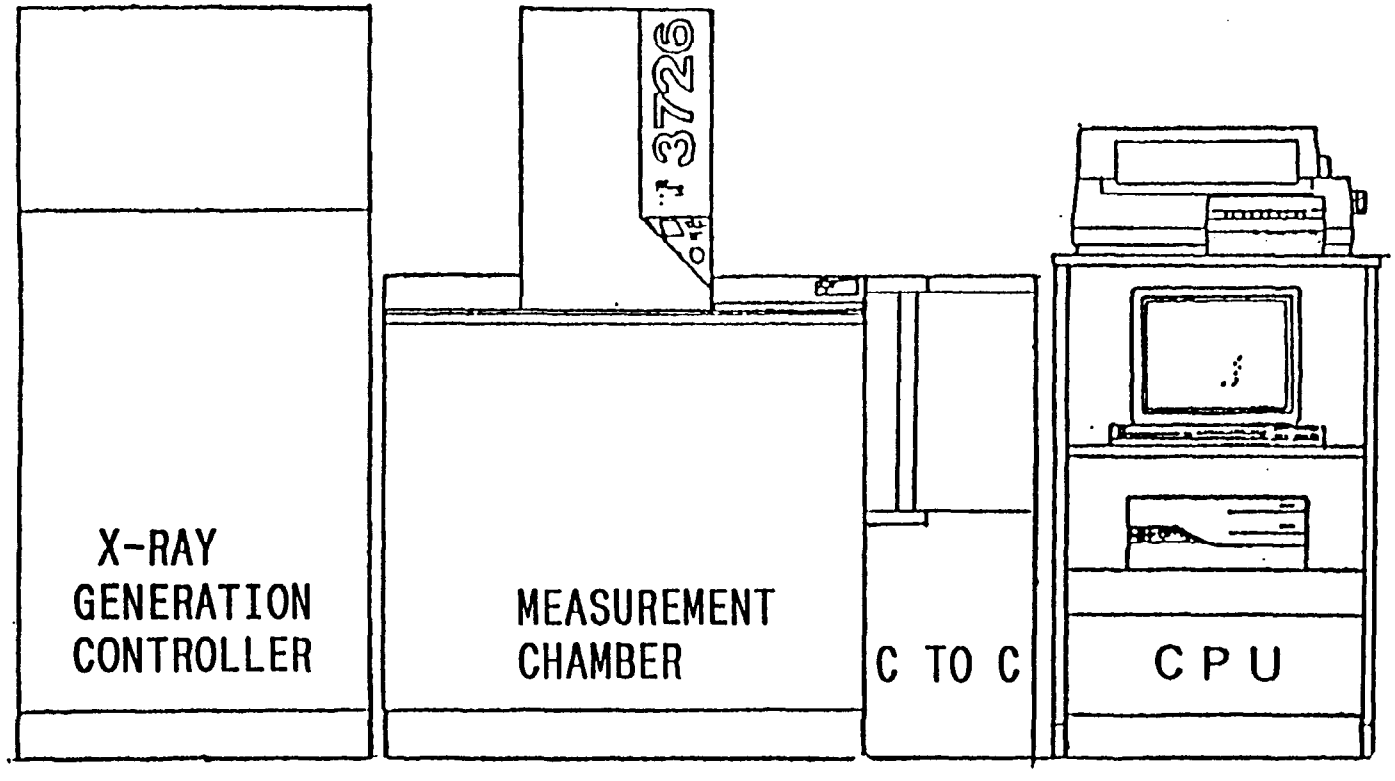
MEASUREMENT METHODS	Na	Al	Fe	Cu	Cr	Ni
GFAAS	0.2	1	0.3	0.3	0.3	2
ETV ICP-MS	0.03	0.03	0.006	0.03	0.01	0.03

PHYSICAL ANALYSIS METHODS (SIMS, XPS, AES,···)

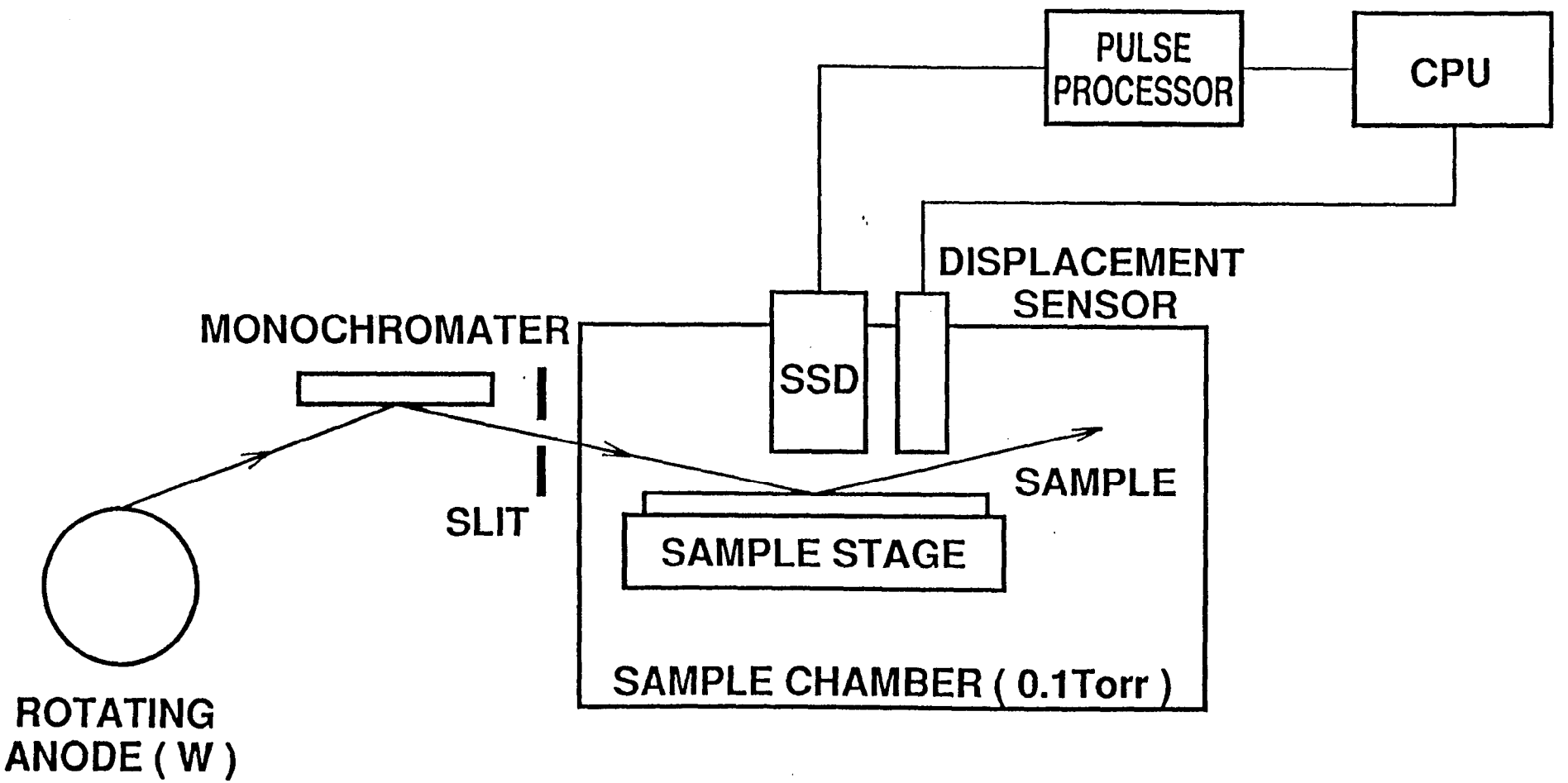
- o small areas
- o physical states

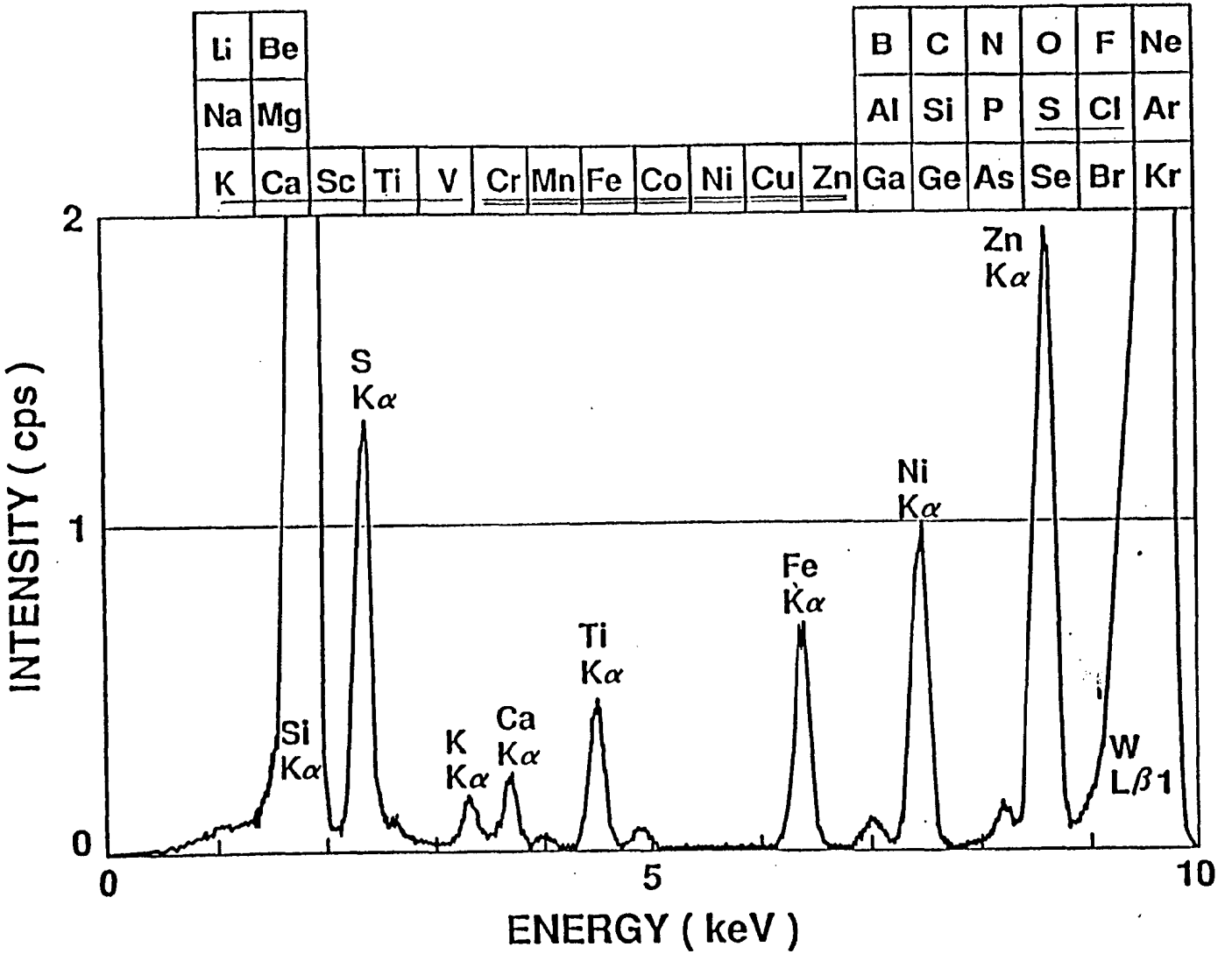
- ● low sensitivity
- ● poor quantitativity
- ● large apparatus


3150



Rigaku SYSTEM 3726


PULSE PROCESSOR
CPU
DISPLACEMENT SENSOR
MONOCHROMATER
SSD
SAMPLE
SLIT
SAMPLE STAGE
SAMPLE CHAMBER (0.1Torr)
ROTATING ANODE (W)

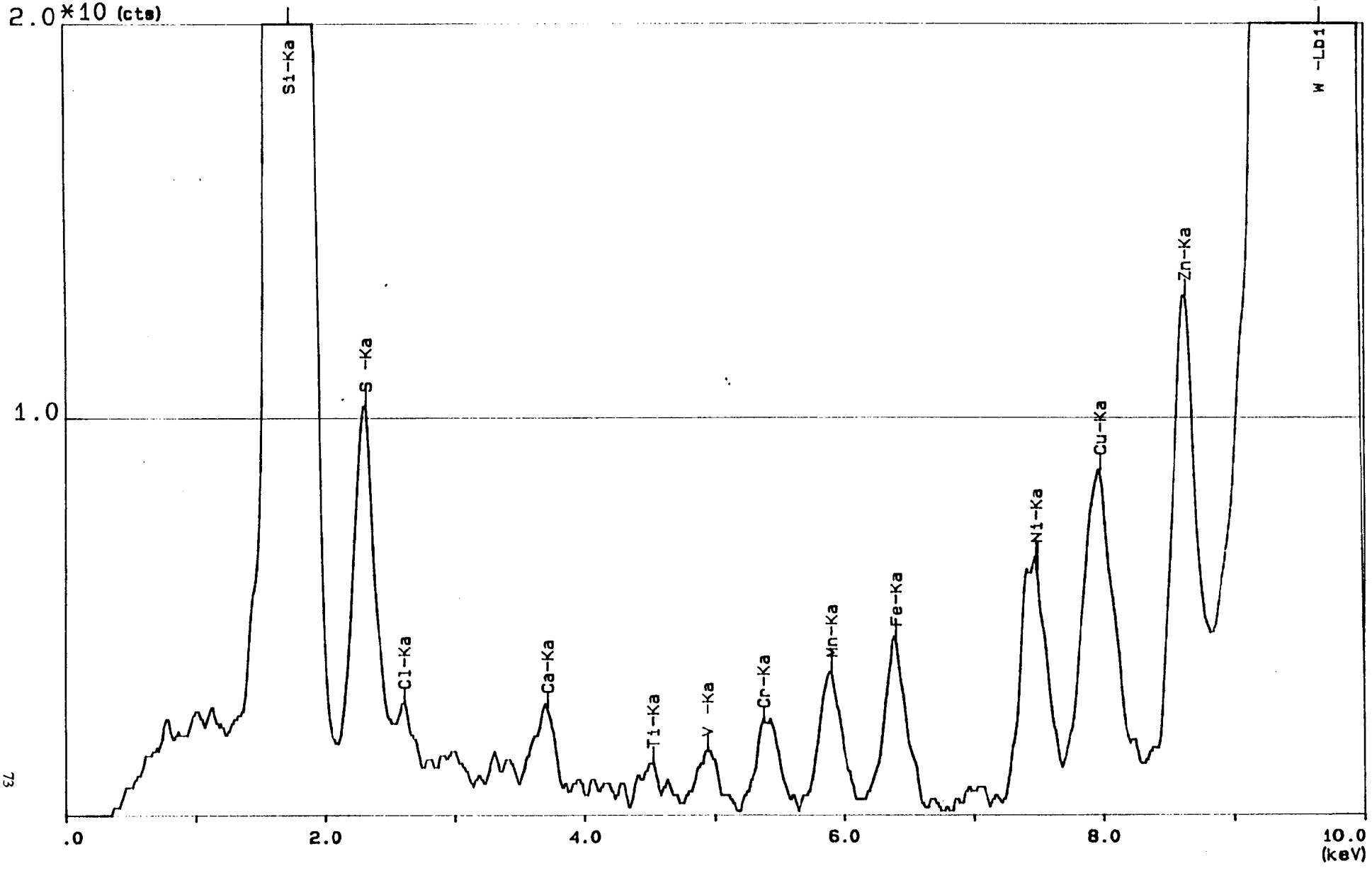

Li Be
Na Mg
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
B C N O F Ne
Al Si P S Cl Ar
Ga Ge As Se Br Kr
INTENSITY (cps)
2
1
0
0
5
10
ENERGY (keV)
Si Kα
S Kα
K Kα
Ca Kα
Ti Kα
Fe Kα
Ni Kα
Zn Kα
W Lβ1

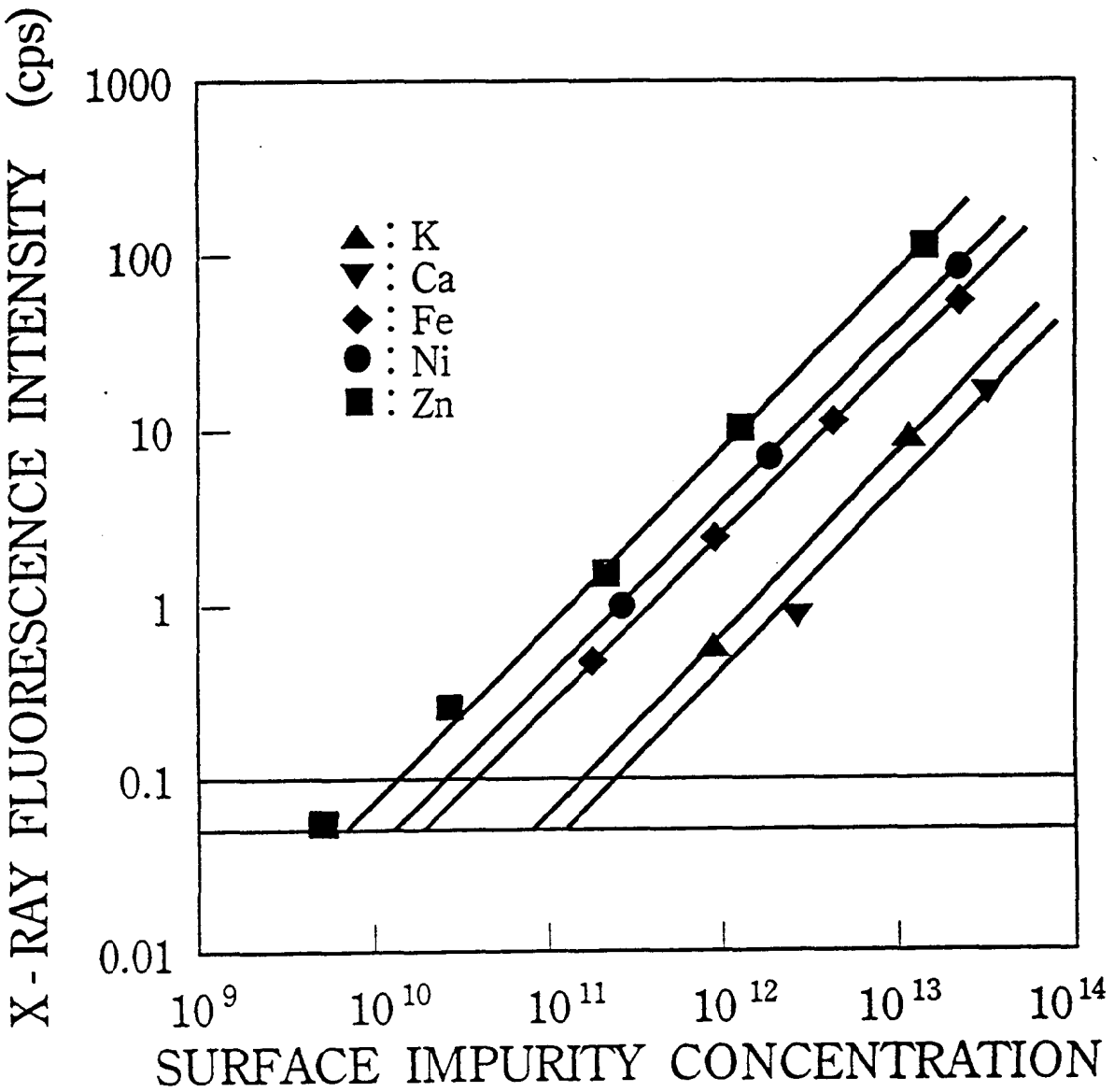
DROP SAMPLE (2.5E11 ATOMS/CM2)

FILE : DR25E11

DATE 91/ 7/18
TIME 14:59: 2

PSET	500 S	CURSOR	30.0kV 400mA
LIVE	500 S	7.49 keV	(X) -20.0 mm
REAL	658 S	62 cts	(Y) .0 mm
DEAD	24.0 %		PHI .120 deg





CALIBRATION CURVES

IMPROVEMENT OF DETECTION LIMITS

($\times 10^{10}$ atoms/cm^2)

	K	Ca	Fe	Ni	Zn
ROI	10	10	2	2	1
Simplex	1	3	0.5	0.2	0.3

ANALYTICAL METHODS

METHODS	SENSITIVITY	ADVANTAGES	DISADVANTAGES
WSA, VPD	10^{8} atoms/cm²	• high sensitivity	• complicated procedure
A-TLA, TLA	10^{10}、10^{12}	• variety of sample • depth profile	• complicated procedure • high background
DIW EXTRACTION +IC +TOC	10^{11} 10^{13}	• simple • conventional	• large volume of sample solution • extraction process
THERMAL DESORPTION +GC-MS	10^{12}	• high qualitativity	• high background • desorption process
TRXRF	10^{9} (Cr~Zn) 10^{11} (S, Cl)	• non-destructive • high speed • contamination morphology (mapping, depth, profile)	• large apparatus • low sensitivity for light elements

TRXRF

O High sensitivity
- improvement of x-ray optics
- improvement of resolution processing of overlapped peaks

O High stability (reproducibility)
- easy alignment of beam path

O High depth resolution
- parallel beam

O Clean system

O Easy operation

O Down sizing .... etc.

III D. Trace Impurity Analysis of Liquid Drops Using Synchrotron Radiation

D. Wherry

X-ray Micro-Fluorescence Analysis

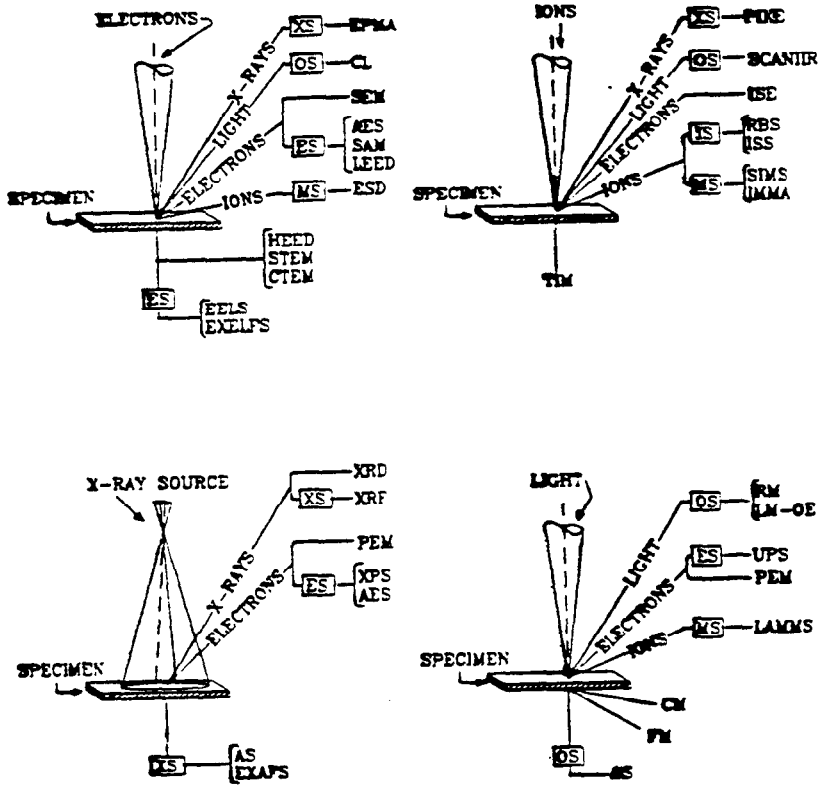
Microprobe Technology for Heterogeneous Materials

Macro-Probe Technology for Trace Element Analysis

October 1992

MICROBEAM ANALYSIS

THE INAUGURAL ISSUE: CELEBRATING THE HISTORY OF MICROBEAM ANALYSIS



The Official Journal of the Microbeam Analysis Society

VCH

EDITOR: Richard W. Linton
Volume 1, Number 1
ISSN 1061-3420
September/October 1992, Pages 1-60

MAS

XRF MICROBEAM ANALYSIS

- XRMF MICROANALYSIS QUALITIES
- SPECTROMETER TECHNOLOGY
- APPLICATIONS TARGETS
- DEVELOPMENT DIRECTIONS
- COMPARISONS WITH EPMA

Why X-ray Micro-Fluorescence?

- **In-Homogeneous Materials Analysis**
  - = Thin Films + Coatings + Most Bulk Materials
- **Truly Non-destructive Analysis**
  - = Preparation + Presentation + Analysis
- **Trace Element and Micro-Mass Analysis**
  - = Sensitivity Gain of 0-->million vs. Bulk EDXRF
- **Chemical Feature Location and Analysis**
  - Chem Image-Locates Elemental/Structural Variation
  - X-Map Correlates and Calculates Phase Compositions

XRMF QUALITIES

- NONDESTRUCTIVE
  - PREPARATION
  - PRESENTATION
  - ANALYSIS
- SENSITIVE
  - VOLUME
  - THICKNESS · Å
  - MASS · pg/10^{12} ATOMS
- SPATIAL RESOLUTION
  - LATERAL 10-100μ
    SOURCE LTD. ONLY
  - DEPTH .1 – 1000μ
    ENERGY, MATRIX, SAMPLE LTD.
- ELEMENT RANGE
  - F –U GENERAL CASE
  - B,C,N,D SPECIAL CASE

HISTORY OF XRMF DEVELOPMENT

CURVED CRYSTAL FOCUSSING

- Adler & Axelrod (1955)
  < 1 mm spot, WDXRF
- Wittry et al (1986)
  35 micron, 8 kV monochromatic

SYNCHROTRON SOURCES

- Underwood et al (1987)
  10 micron, coated mirrors (synthetic multilayers)

FRESNEL LENSES

- Ceglio (1983)
  Coded imaging, electron beam lithography fab.
- Bionta et al (1988)
  9 micron spot, 8 keV microfocus X-ray tube

CAPILLARY TUBES

- Carpenter (1988)
  20 micron spot, internal reflection, broadband
- Yamamoto (1988)
  20 micron, parabolic internal surface

COLLIMATION

- GURKER (1979)
  100 micron spot, X—Theta stage + deconvolution
- Nichols et al (1987)
  30 micron, pinhole aperture

SPECTROMETER TECHNOLOGY

X-RAY SOURCES
- MICROFOCUS
- ROTATING ANODE TUBES
- S.O.R.

OPTICS
- APERTURES - $1/R^2$ EFFICIENCY
- TOTAL REFLECTION MIRROR CAPILLARY

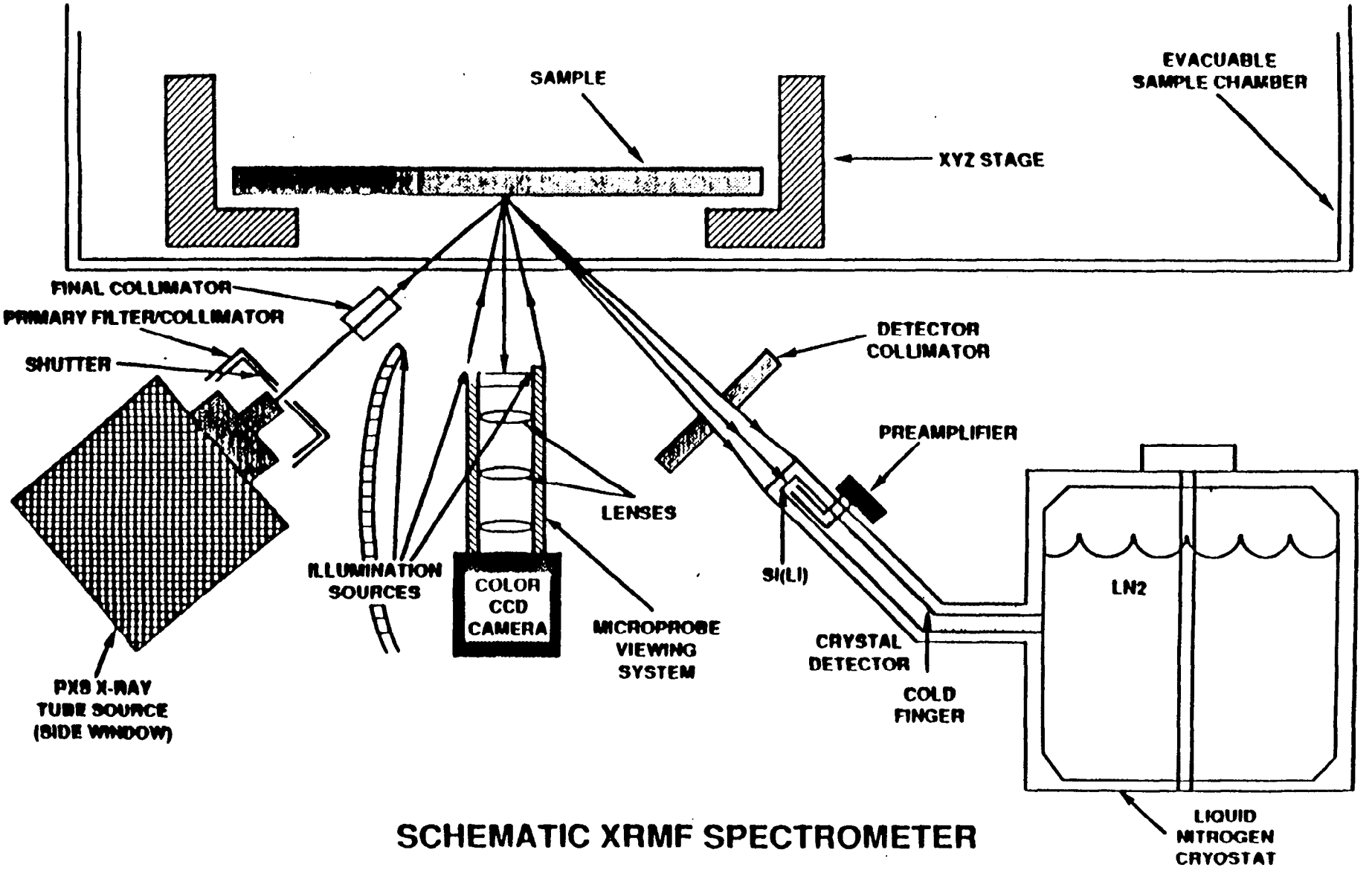
SAMPLES
- SAMPLE SCANNING
- BEAM DUMP
- Air, He, Vac

DETECTORS
- Si(Li) SSD
- WDKRF (Not used to date)
- SOLID ANGLE IS KEY

98

The Rules of X-ray Micro-Analysis

- Sample/Beam Scanning
- Chemical Feature Location
- Multiple Measurements
- Composition and Structure Interpretation



SCHEMATIC XRMF SPECTROMETER

X-RAY TUBE, COLLIMATOR, SAMPLE

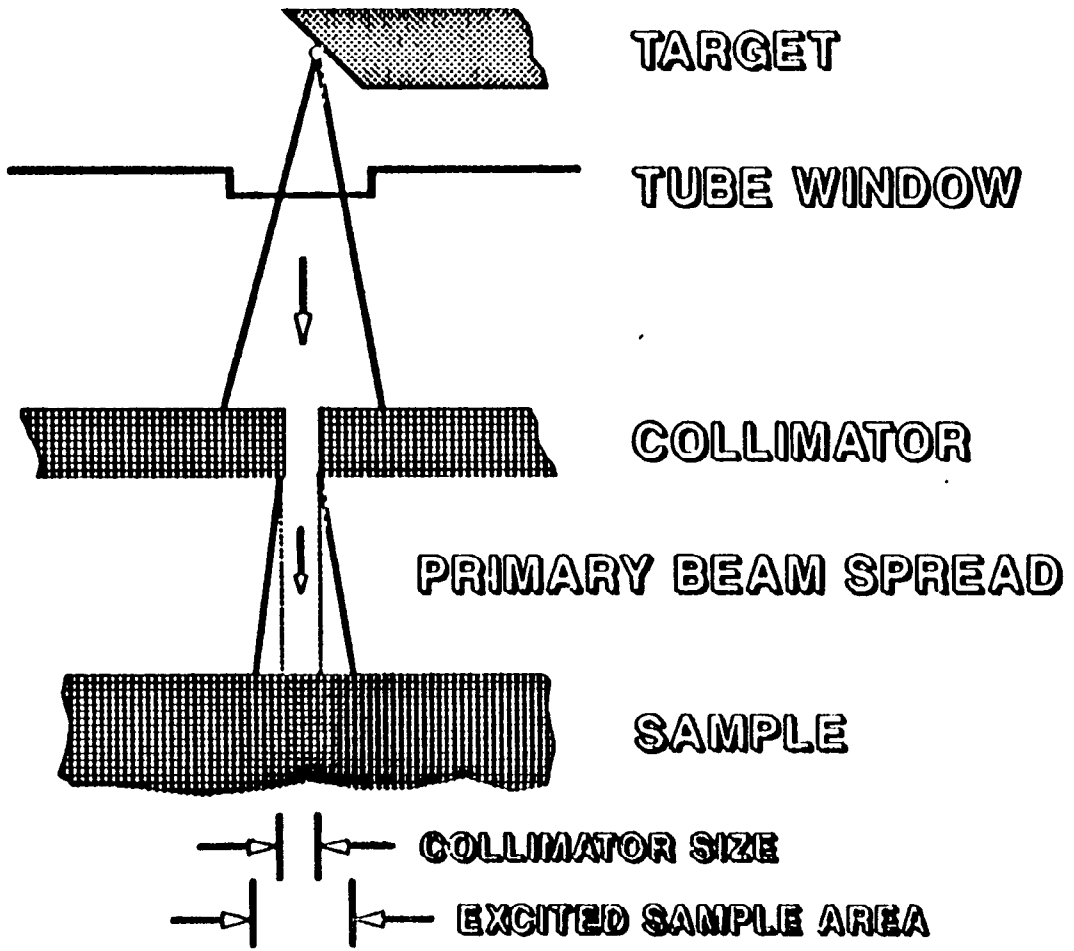


Fig. 7. Geometry of X-ray Tube to Sample Showing Primary Beam Spread

Applications of XRMF

Current---

- **Thin Films-**Composition, Thickness, Uniformity
- **Small/Structured Materials-**ID, Verify, Screen
- **Contaminant Concentrates**-Trace Analysis

Emerging---

- **Segregated Composites-**Quant Phase Analysis
- **Unique Products** Failure and Forensic Analysis

X-Ray Micro Fluorescence Applications

- **MICROELECTRONICS & SEMICONDUCTOR**
  - **DIELECTRIC FILMS for COMPOSITION and THICKNESS** (PSG, BPSG, SiO_2, SiN)
  - **METAL FILMS for COMPOSITION and THICKNESS** (Al, AlSi, AlSiCu, TiW, Pt, Cr, AlCu, Mo, TiN, Au, Cu, Pt, Ti, W, Ni, SnPb, AgPd)
  - **MULTI-LAYER FILMS** (Au/Ni, Au/Cr, Pd/Ti, Ti/Au, Ag/Ni/Ti,,Au/Ni/Ti, Sn/Cu, Au/Ni/Cu or Kovar, Alloy 42, or Monel)
  - **ORGANICS** (Resists and Polyimides-with Inorganic Additives)
  - **COATINGS on LEADFRAMES & CONNECTORS, WIRE & CABLE, and TAB TAPES**
  - **MICROELECTRONIC PACKAGES--for Process Control and Failure Analysis** (Chip on a Board, Flip Chip, MCM, and Hybrid)
  - **TRACE ELEMENTAL CONTAMINATION on WAFER SURFACES**

- **MAGNETIC RECORDING HEADS & STORAGE MEDIA**
  - **Thin Film Heads and Magnetic Media**
  - **NiFe, CoCr, NiP, Fe Oxide Films** (Composition and Thickness)
  - **Superconducting Films**

- **METALLURGICAL**
  - **Analysis of Phase Segregation** (Elemental Mapping)
  - **Analysis of Inclusions**
  - **Alloy Uniformity**
  - **Identification and Sorting of Alloys** (Small Parts & Fasteners in particular)
  - **Metal Coatings on Alloys** (Coating Composition and Thickness)
  - **Rapid Identification of Unknown Alloys**
  - **Analysis of Wear Metals in Lubricants** (Alloy Particles)
  - **Precious Metals** (Jewelery and Alloy Scrap for Precious Metal Content)

- **GEOLOGICAL**
  - **Mineral Phase Distributions** (Elemental Mapping)
  - **Nondestructive Analysis of Small Mineral Samples** (Precious Stones)
  - **Elemental Mapping of Paleontological Specimens**
  - **Micro Meteorites**
  - **Volcanic Ash and Airborne Dust Particles**
  - **Examination of All Types of Total Unknown Geological Materials**

- **FORENSICS**
  - **Nondestructive Analysis of Small Liquid and Solid Samples and Residues**
  - **Elemental Mapping and Trace Elemental Signatures** (Paper, Glass, Fibers, Paint, Ink, Gems, Alloys, Glass, Plastics, Powders, Dirt, Dust, Rocks, Drugs, and all types of Organic Materials)
  - **Identification and Tracking of Stolen and Counterfeit Goods**
  - **Nondestructive Examination of Complex Patterned Materials**
  - **Gunshot Residue Analysis**
  - **Identification of Metallic Poisons**
  - **Nondestructive Analysis of Weapon Materials**

- **GLASS**
  - **Analysis of Inclusions, Defects, and Segregation**
    - **High Value Optical Glasses** (Lasers and Analytical Instruments)
    - **Fiber Optics with Graduated Index of Refraction Materials**
  - **Optical Coatings** (Composition and Thickness)
    - **Antireflective**
    - **Filters**

- **COMPOSITE MATERIALS**
  - **Distribution & Orientation of Components** (3-Dimensional Elemental Mapping)
  - **Failure Analysis**
    - **Ceramic Matrices**
    - **Metal Matrices**
    - **Fiber Epoxy Matrices**
  - **Composition and Thickness of Metal Coatings on Composite Materials**

- **BIOLOGICAL & MEDICAL**
  - **Elemental Mapping** (Plant and Animal Tissues)
  - **Trace Elemental Analysis of Tissues and All Types of Biological Fluids**
  - **Toxic Metals in Biological Fluids** (Blood, Urine, Serum, and Saliva)
  - **Plant Toxicology**
  - **Elemental Analysis of Water Ingested by Animals and Plants**
  - **Elemental Analysis of Hair, Nails, Scales, Beaks, Bones, and Claws**

- **PETROLEUM & PETROCHEMICAL**
  - **Elements in Oils, Fuels, and Lubricants** (Residues, Deposits, & Precipitates)
  - **Residual Catalyst Metals in Polymers** (Bulk Solids and Films)
  - **Analysis of Catalysts**
  - **Petrographic Analysis (Elemental Mapping)**
  - **Prospecting** (Trace Elements in soils, water, hydrocarbons, plant tissues, etc.)

- **PHARMACEUTICAL**
  - **Trace Metals in Organics**
    - Colorants, Antioxidants, Mold Release Agents, Contaminants
  - **Material Homogeneity**
  - **Analysis of Very Small Residues and Contaminants**

- **ENVIRONMENTAL**
  - **Aerosols on Filters** (Elemental Distribution Maps)
  - **Analysis of Small Particles**
  - **Toxic Metals in Unknown Materials**

XRMF Thin Film&Coating Markets

Thickness and Composition Uniformity

- **Semiconductor Fabrication Metrology**
  - Conductive Metallic Epitaxial and Dielectric Thin Films
  - Physical and Chemical Vapor Deposition Process Control
- **Microelectronic Packaging and Connectors**
  - High density fine pitch packaging-i.e. TAB, MCM, COB
  - Hybrid, Multilayer Ceramic and Surface Mount Geometry
- **Magnetic Thin Film Heads and Media**
  - Permalloy Magnetostrictive Composition Process Control
  - Oxide and Alloy Magnetic Thin Film Media

XRMF Bulk and Micro Analysis

- **Highly Valued Large Sample Analysis**
  - 8.5" x 9.5" x 3" Maximum ---15lbs Maximum
- **Heterogeneous Segregated Bulk Materials**
  - Quantitative Principle Component Analysis
  - Line/Area Scans----Chem Imaging----X-Mapping
- **Small Structured Bulk Materials**
  - Micro-machined, Formed, Stamped and Drawn materials
- **Particulates Residues and Deposits**
  - Chem-Image, and X-Map to locate beam and Identify
- **Preconcentration --Trace Element Analysis**
  - Then Membrane Substrate ---PPB Sensitivities

XRMF Composite Material Markets

- Industrial Structural Composites
- Industrial Micromachined Composites
- Natural Geological Materials
- Natural Biological Materials
- Forensic Materials Analysis
- Failure Analysis and Reverse Engineering

The Challenges of XRMF Technology

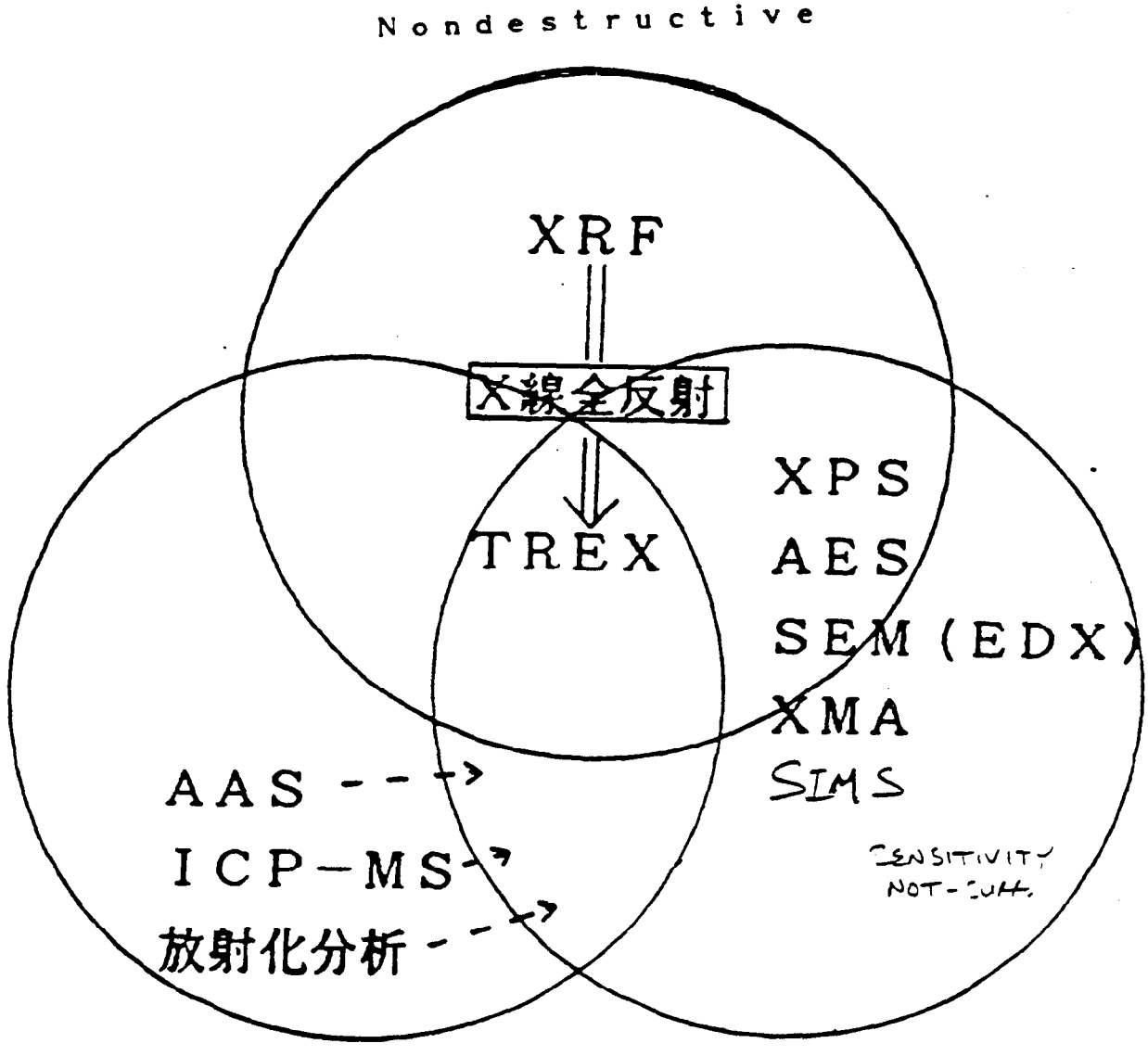
- Micro Beam X-ray Sources/Optics
- Quantitative 3-D Chemistry Imaging
- Light Element Microanalysis

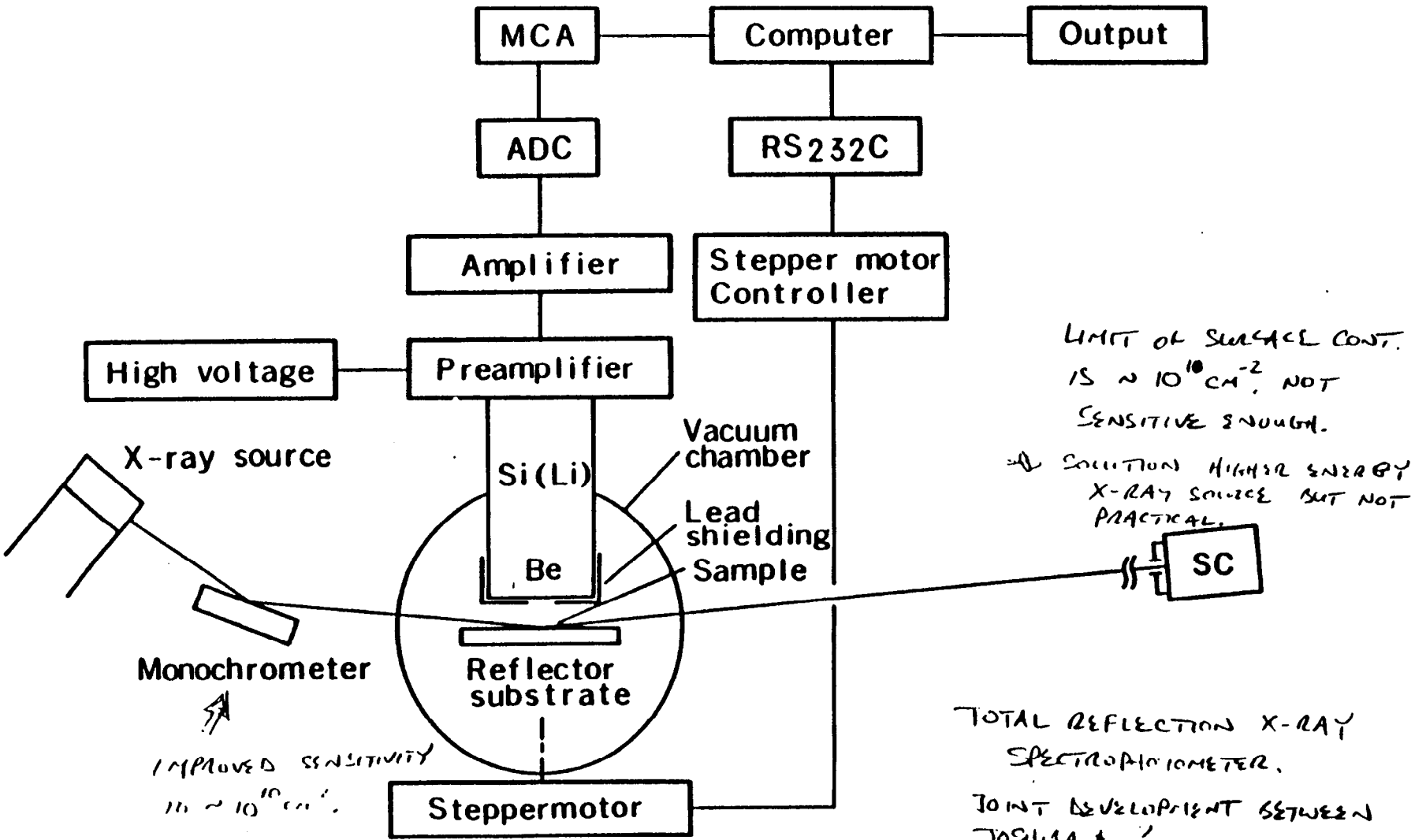
KEY TRENDS INTO NEXT DECADE
(BLIND EXTENSION)

	1981			1991				2001
MEMORY GENERATION	64K	256K	1M	4M	16M	64M	256M	1G
DIE SIZE (MM)	5	6	7	8	10	12	14	16
WAFER SIZE (INCH)	4	6	6	6	8	8	8/12	12
CAPITAL COST ($K/WSPW)	15	25	35	55	100-120	150-200	200-250	300-400
FEATURE SIZE (UM)	2.0	1.4	1.0	0.7	0.5	0.35	0.25	0.15
						====		====
						$1B FACTORY		$2B FACTORY

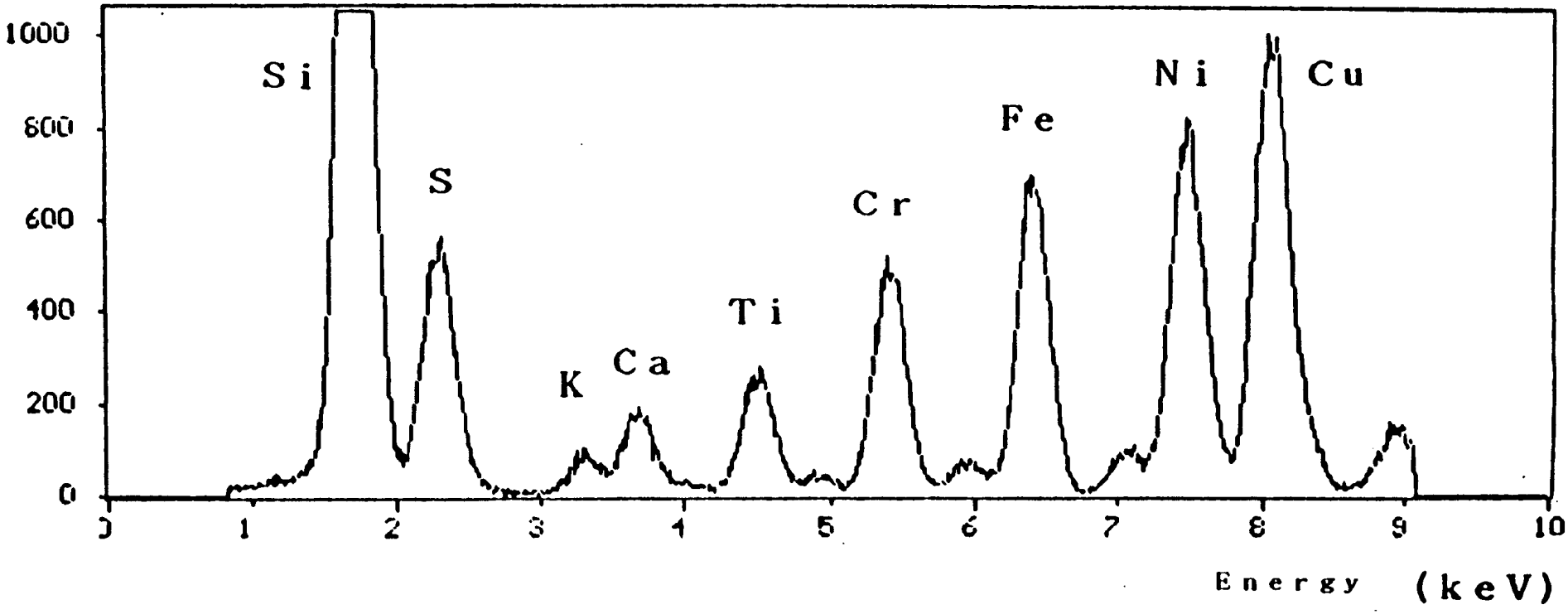
D. ROSE
10/28/91
PAGE 5

Surface Characterization Method





Schematic diagram of TREX



Contaminated Wafer (1×10^{13} at/cm²)

FOR EACH CONTAMINANT ?

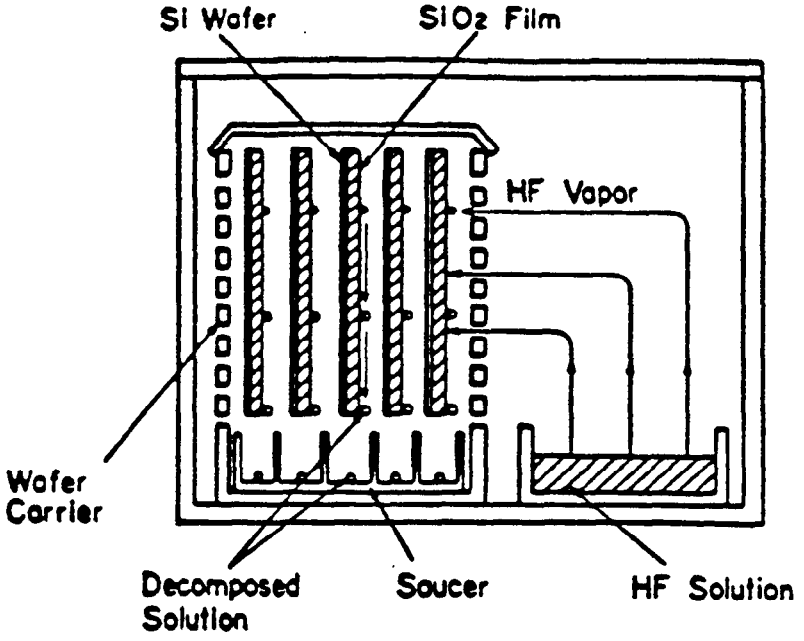


Fig. 1 Schematic drawing of instrument.

VPD USED TO REDUCE CLEANING EFFECTIVENESS

* GOOD ONLY FOR WHOLE WAFER (NON-LOCAL)
* CONFOUNDED WITH CONTAMINATION IN OXIDE FILM & METAL FOR CLEANING
* DESTRUCTIVE
* NOT SOLELY SURFACE CONT. IS MEASURED.

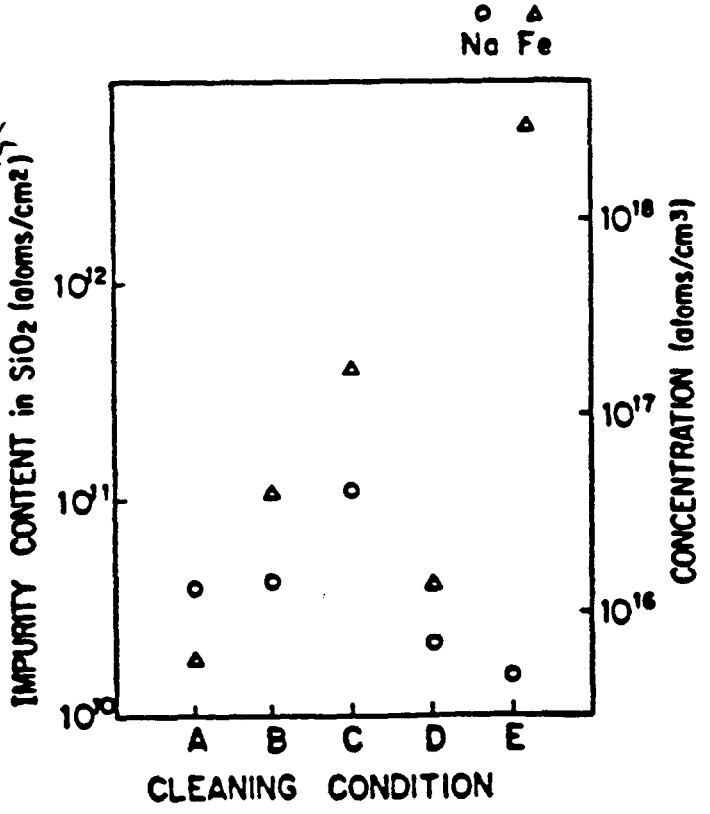


Fig. 2 Impurity content in SiO_2 vs cleaning conditions.

A. Shimazaki et al.
Ext. Abst. 16th Int. Conf. SSDM (1984)

Membrane Micro-Sample Holders

- Material----------Boron Nitride on Silicon
- Film Composition--90%Boron 10% Nitrogen
- Film Thickness-----500-2000 Angstroms BN
- CVD Processing---DiBorane + NH4
- Backside Si Etch---HF+HNO3-to BN
- X-ray Window------5mm Diameter BN
- Window Frame-----10mm OD X 0.5mm Si

Alternate Windows----Boron Carbide, Diamond

BN XRMF Sample Holders

Physical Advantages:

- Strength - 500 Angstrom X 5mm Film Supports 0.1g Mass
- Chemically Inert ---Resists Acid and O_2 Plasma attack
- Purity----No detectable "blank" from current BN Films

XRF Spectroscopy Benefits

- The Si(Li) detector Be window selectively removes BN-X-ray Fluorescence from the detected sample spectrum.
- The small Mass of Low Z BN membrane limits both scatter produced background and contaminant (blank) XRF produced within the BN film.
- A 2mm Beam interacts with $<1 \times 10^{16}$ Atoms of thin BN. Within practical (SOR) source and Si(Li) detector efficiency limits ;this Scatter Mass conservatively predicts thin film XRF detection limits of 10^{9} *to* 10^{10} *atoms* for the transition metals and lighter elements (i.e.) respectively.

Sample Preparation / Deposition

- Method requires Vapor Phase Dissolution (VPD) and quantitative droplet transfer to BN substrate.
- Method requires negligible elemental blank contribution by reagents, water and BN.
- Transition metal SOR experiments to date have used serial dilution of single element (i.e. Ti) 1000 PPM Aqueous ICP Standards. Ten microliter aliquots were deposited on 550 Angstrom Boron Nitride , 1.5 Micron Mylar and 2000 Angstrom Formvar film substrates for sensitivity comparison.

Detection of Metals by SOR XRF

Detection Limits for Ti

Technique	Absolute	Pre concentrated	
	Atoms	Atoms/cm^2	
		6" Wafer	8" Wafer
LAB TXRF	$6.8X10^{10}$	3.9X10	$2.2X10^{8}$
SOR TXRF	$3.3X10^{9}$	$1.9X10^{7}$	$1.0X10^{7}$
SOR BN 500A	$2.0X10^{9}$	$1.1X10^{7}$	$6.2X10^{6}$
SOR Formvar 2000A	$1.1X10^{10}$	$1.9X10^{8}$	$1.1X10^{8}$
SOR Mylar 1.5 Micron	$1.9X10^{10}$	$1.1X10^{8}$	$6.1X10^{7}$

Room for Improvement

Sample containment at center of BN window?

Optimum BN thickness strength vs sensitivity?

Optimize SOR Energy and Bandwidth for Io &Z

Complete Wafer Contaminant Elements

Complete Matrix Comparison with Lab XRMF

III E. TRXRF Using Synchrotron Sources

S. Laderman

TRXRF Using Synchrotron Sources

S. S. Laderman, R. D. Jacowitz, R. Smith

Integrated Circuits Business Division R&D Center
Hewlett-Packard Company

A. Shimazaki, K. Miyazaki, M. P. Scott*

Toshiba Research & Development Center
Toshiba Corporation

*on leave from Hewlett Packard

With Very Special Thanks to S. Brennan and to SSRL (DOE)

Outline

I. Why Synchrotron Radiation?

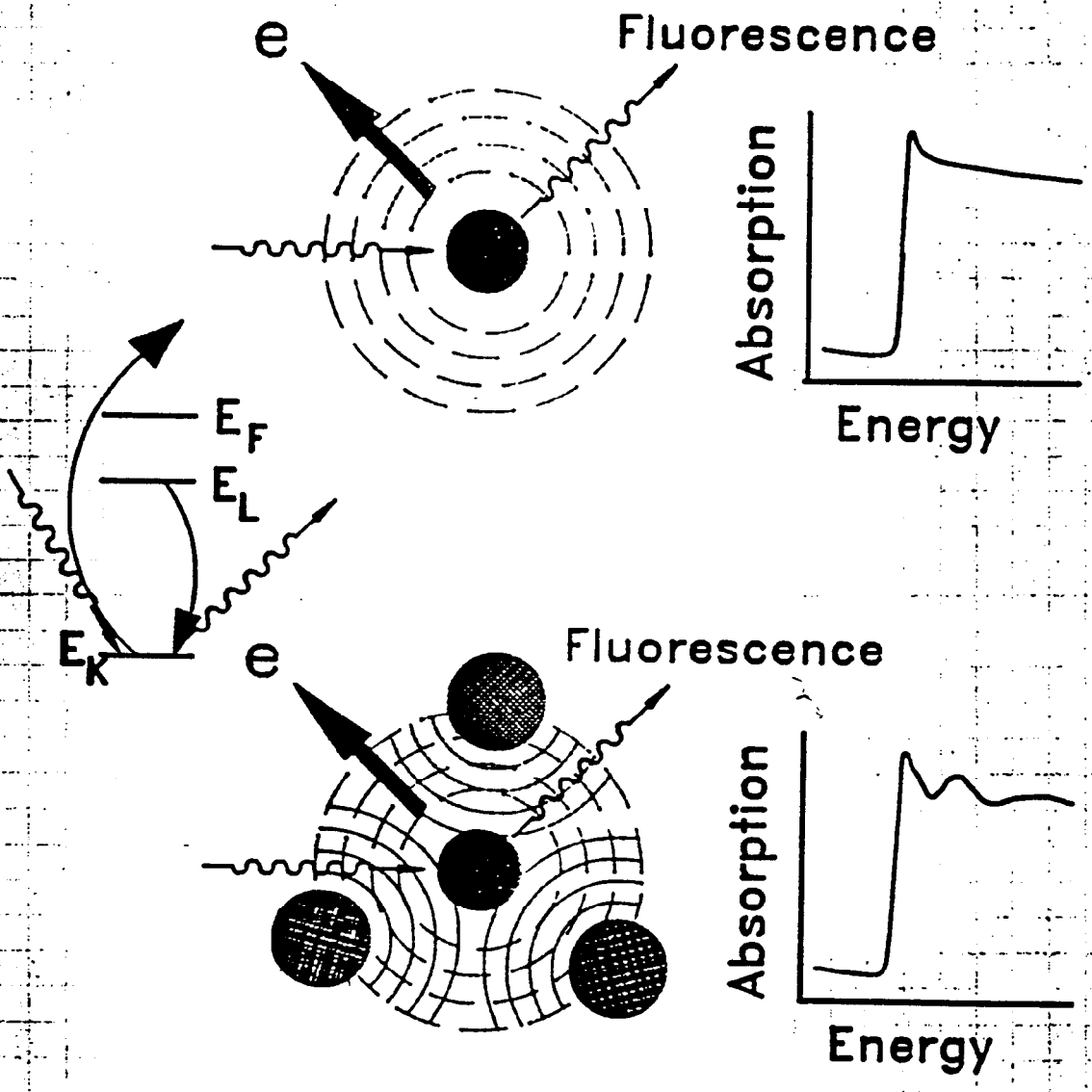
II. Element Range

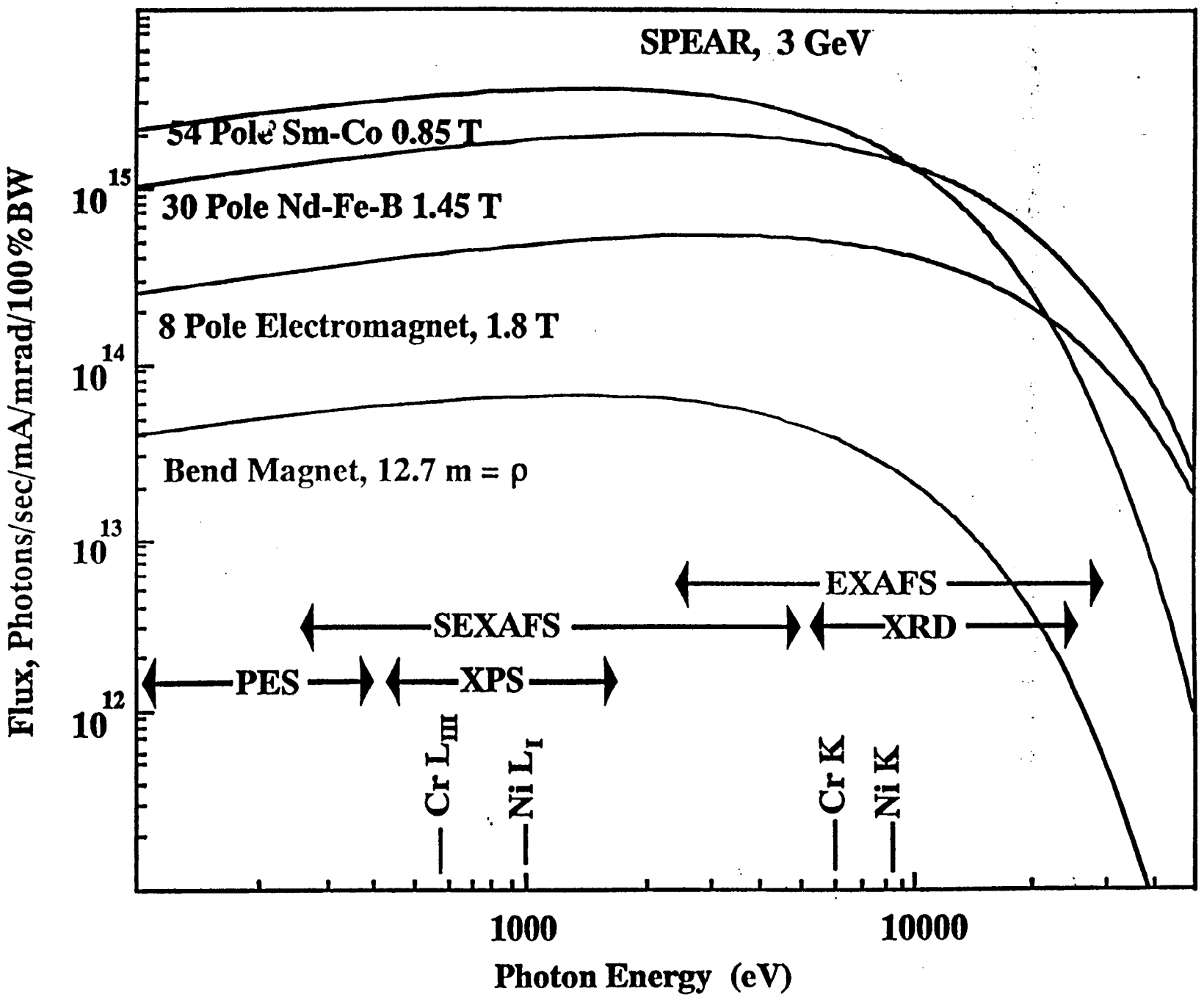
III. Depth Profiling

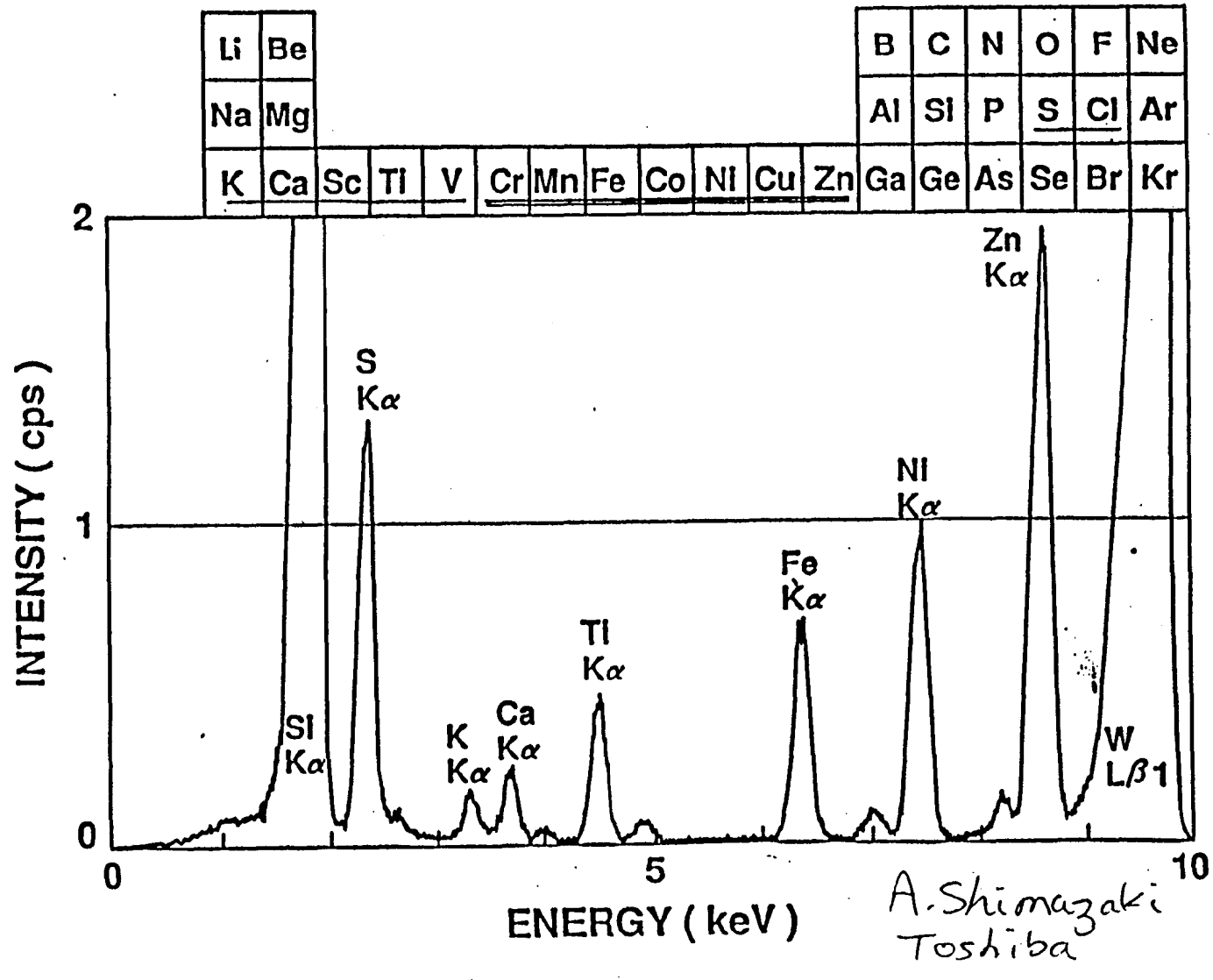
IV. Sensitivity

V. Conclusion

X-RAY ABSORPTION




SPEAR, 3 GeV
54 Pole Sm-Co 0.85 T
30 Pole Nd-Fe-B 1.45 T
8 Pole Electromagnet, 1.8 T
Bend Magnet, 12.7 m = ρ
Flux, Photons/sec/mA/mrad/100%BW
10^15
10^14
10^13
10^12
EXAFS
SEXAFS
XRD
PES
XPS
Cr L_III
Ni L_I
Cr K
Ni K
1000
10000
Photon Energy (eV)


Li Be
Na Mg
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
B C N O F Ne
Al Si P S Cl Ar
Ga Ge As Se Br Kr
INTENSITY (cps)
2
1
0
0
5
10
ENERGY (keV)
Si Kα
S Kα
K Kα
Ca Kα
Ti Kα
Fe Kα
Ni Kα
Zn Kα
W Lβ1
A. Shimazaki
Toshiba

Periodic Table of the Elements

Period	Group Ia	Group IIa	Group IIIa	Group IVa	Group Va	Group VIa	Group VIIa	Group VIII			Group Ib	Group IIb	Group IIIb	Group IVb	Group Vb	Group VIb	Group VIIb	Group O
1 1s	1 H																1 H	2 He
2 2s2p	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3 3s3p	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 4s3d 4p	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 5s4d 5p	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6 6s (4f) 5d 6p	55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7 7s (5f) 6d	87 Fr	88 Ra	89** Ac															

*Lanthanide series 4f	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinide series 5f	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

K L

W L_β

Periodic Table of the Elements

Period	Group Ia	Group IIa	Group IIIa	Group IVa	Group Va	Group VIa	Group VIIa	Group VIII			Group Ib	Group IIb	Group IIIb	Group IVb	Group Vb	Group VIb	Group VIIb	Group O
1 1*s*	1 H																1 H	2 He
2 2*s*2*p*	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3 3*s*3*p*	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 4*s*3*d* 4*p*	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 5*s*4*d* 5*p*	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6 6*s* (4*f*) 5*d* 6*p*	55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7 7*s* (5*f*) 6*d*	87 Fr	88 Ra	89** Ac															

*Lanthanide series 4*f*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinide series 5*f*	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

K L

15 keV

Periodic Table of the Elements

Period	Group Ia	Group IIa	Group IIIa	Group IVa	Group Va	Group VIa	Group VIIa	Group VIII			Group Ib	Group IIb	Group IIIb	Group IVb	Group Vb	Group VIb	Group VIIb	Group O
1 1s	1 H																1 H	2 He
2 2s2p	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3 3s3p	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 4s3d 4p	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 5s4d 5p	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6 6s (4f) 5d 6p	55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7 7s (5f) 6d	87 Fr	88 Ra	89** Ac															

*Lanthanide series 4f	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinide series 5f	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

K L

20 KeV

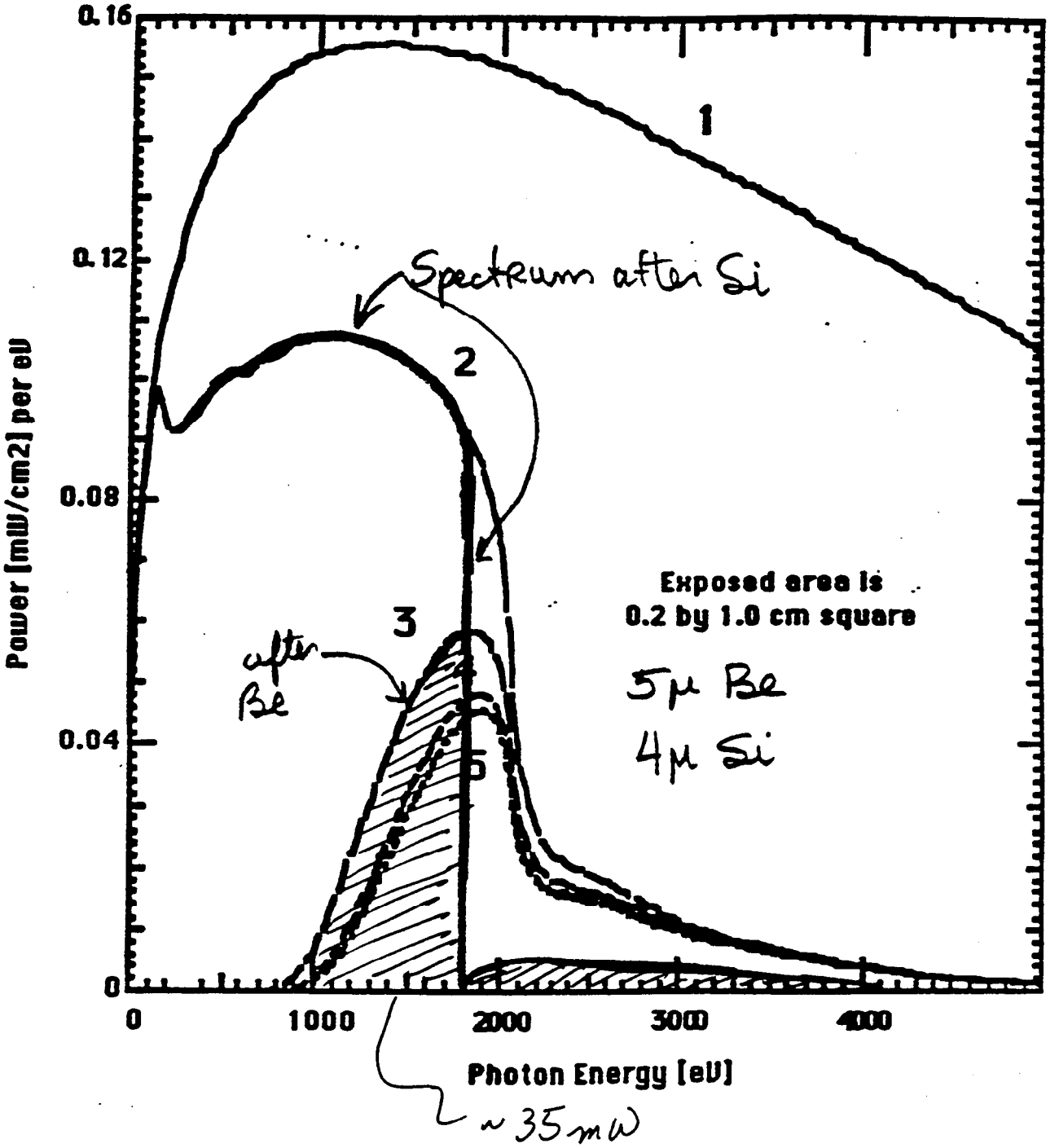
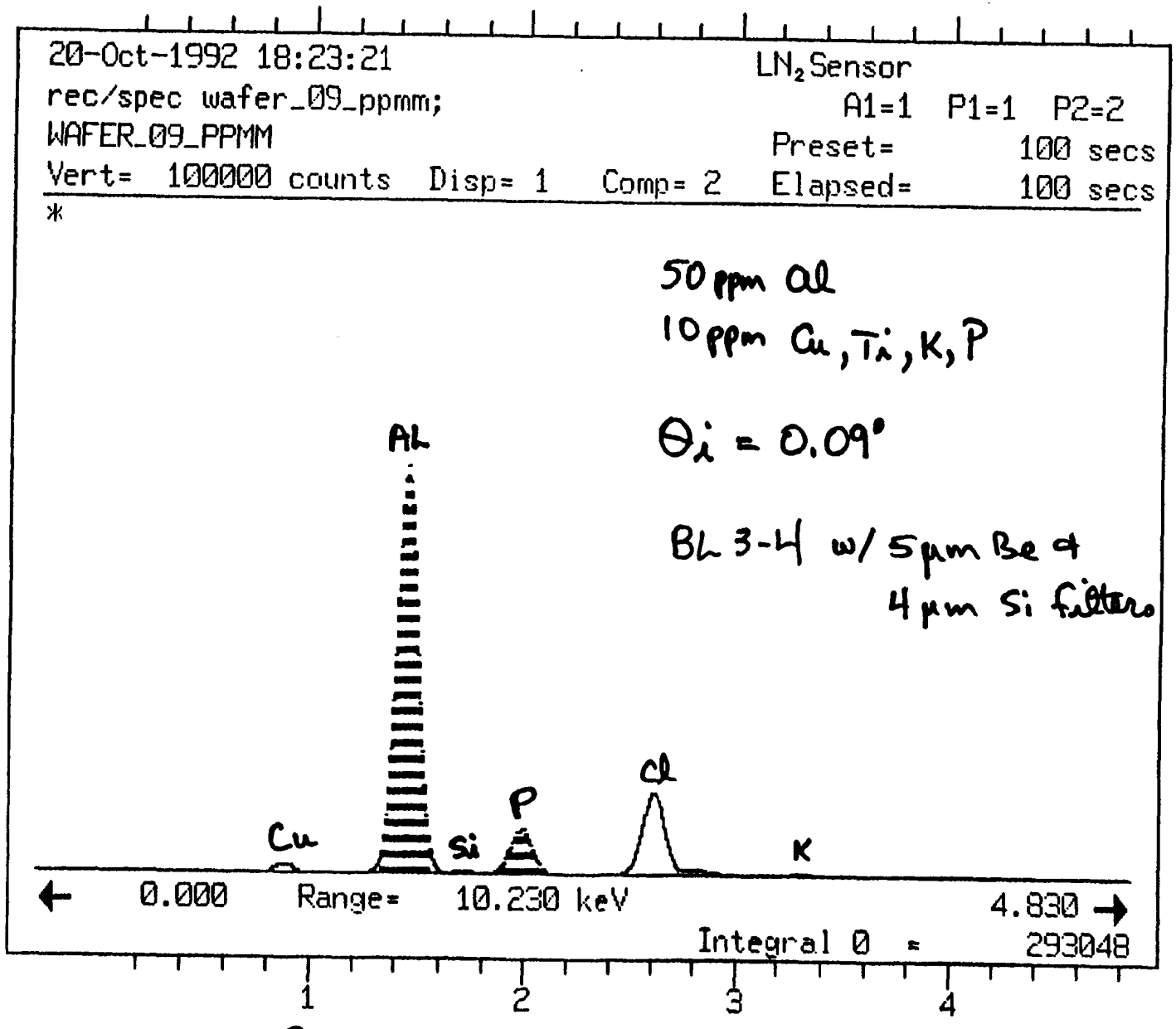
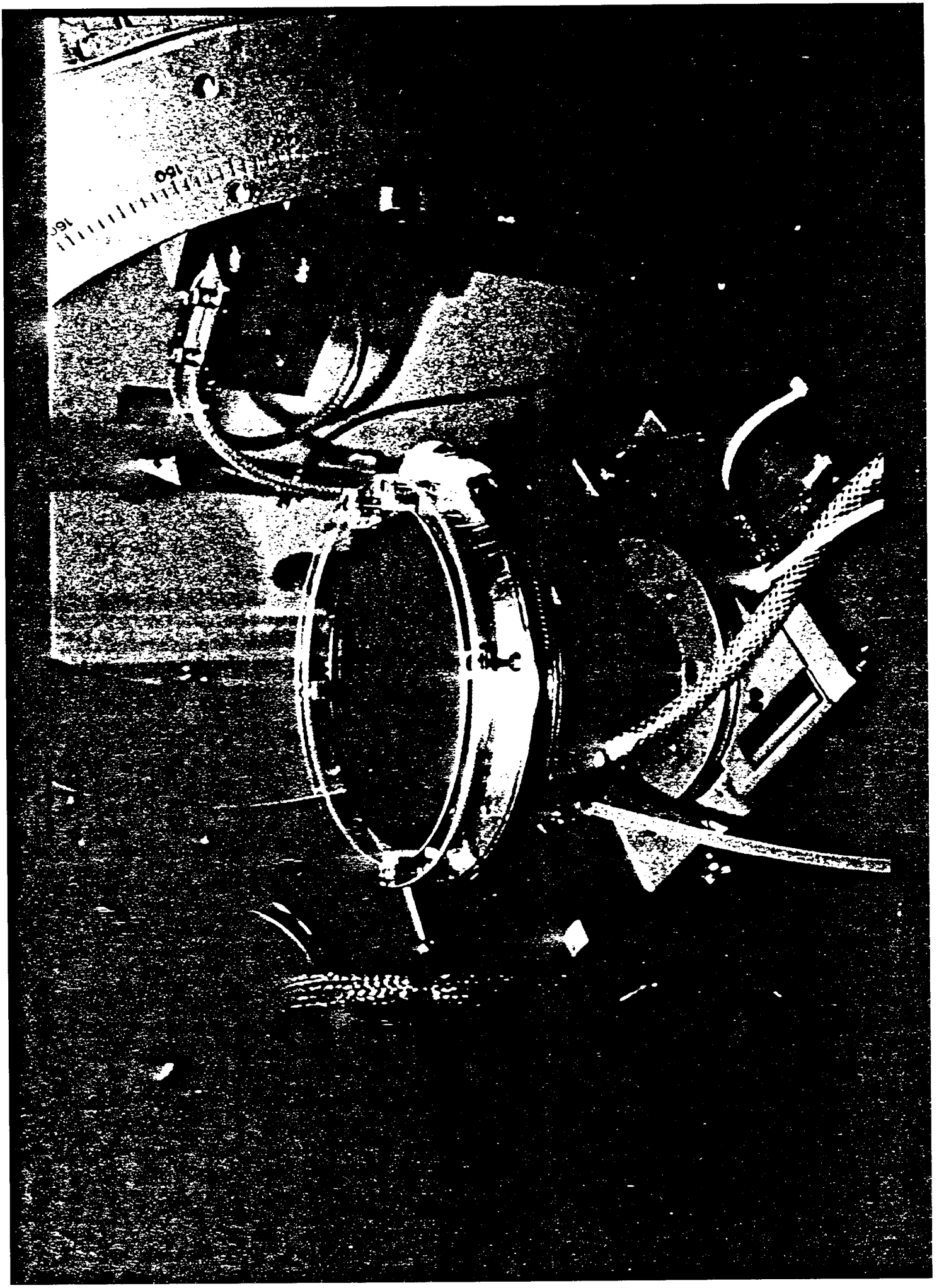

0.16
0.12
0.08
0.04
0
Power [mW/cm2] per eV
0
1000
2000
3000
4000
Photon Energy [eV]
1
2
3
Spectrum after Si
after Be
Exposed area is
0.2 by 1.0 cm square
5μ Be
4μ Si
~35mW

Figure 2



$\frac{Si}{Al}$ = 1.5% (raw data)

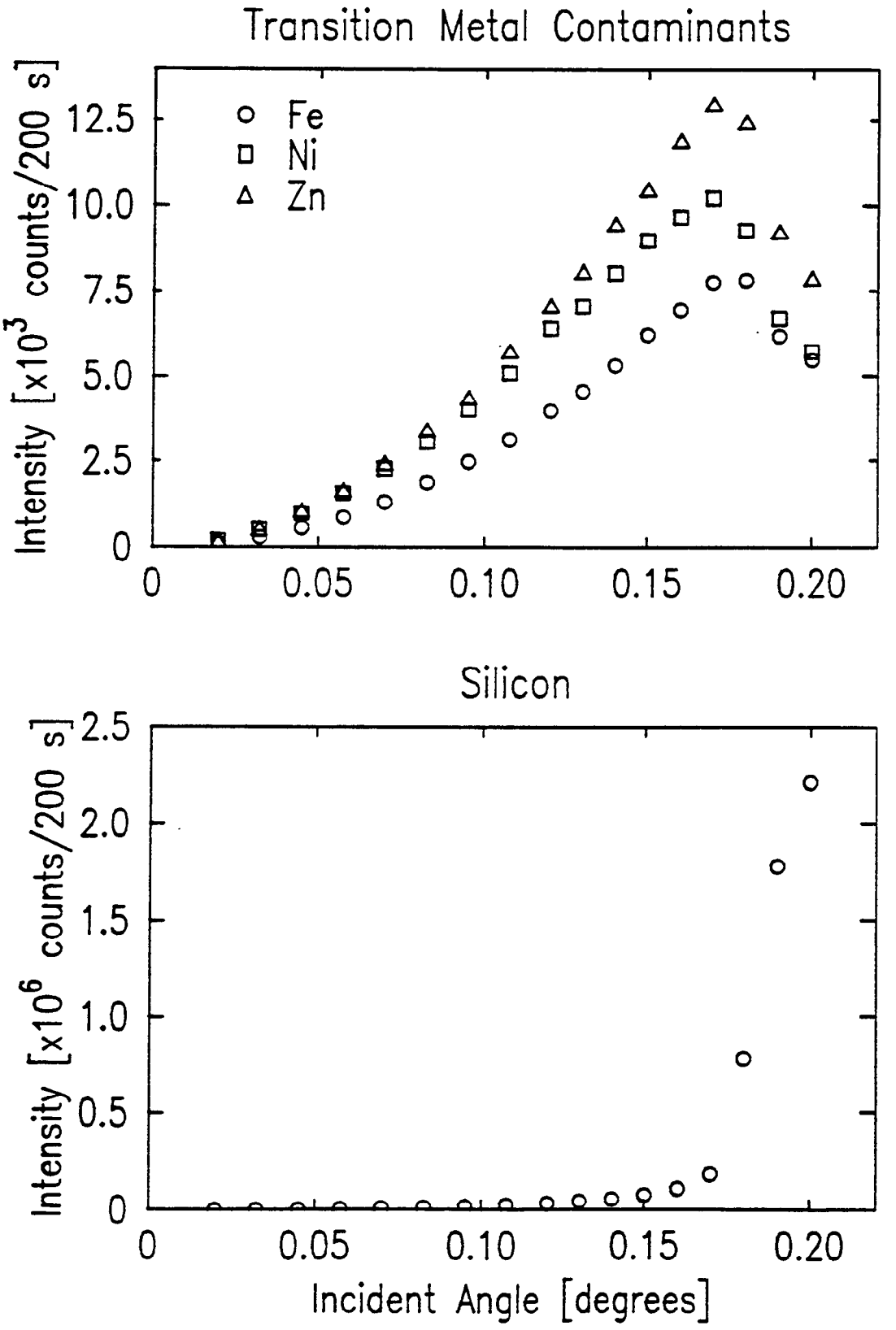
.5% (Bkgnd subtract)

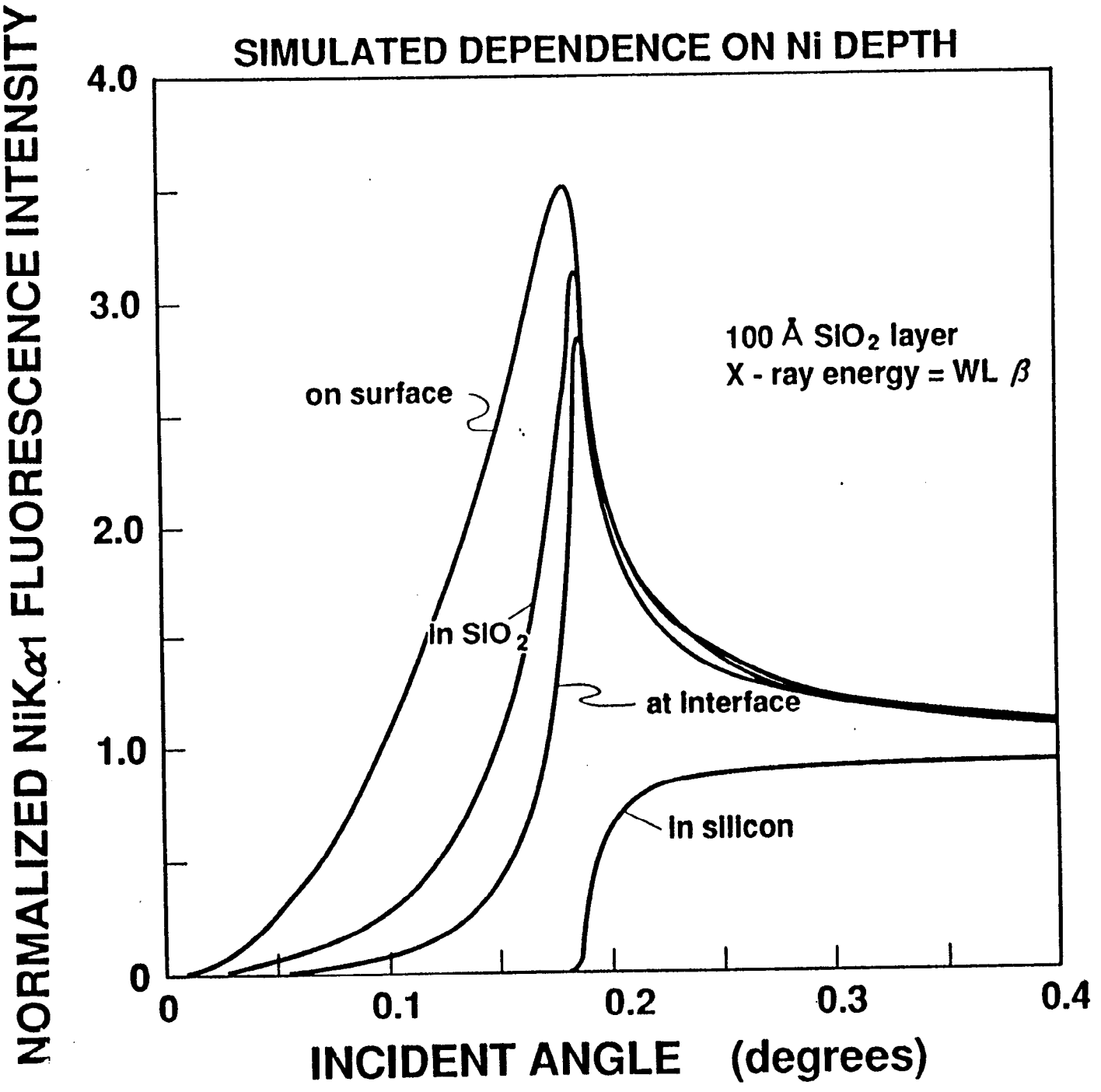


FLUORESCENCE SIGNAL DEPTH DEPENDENCE

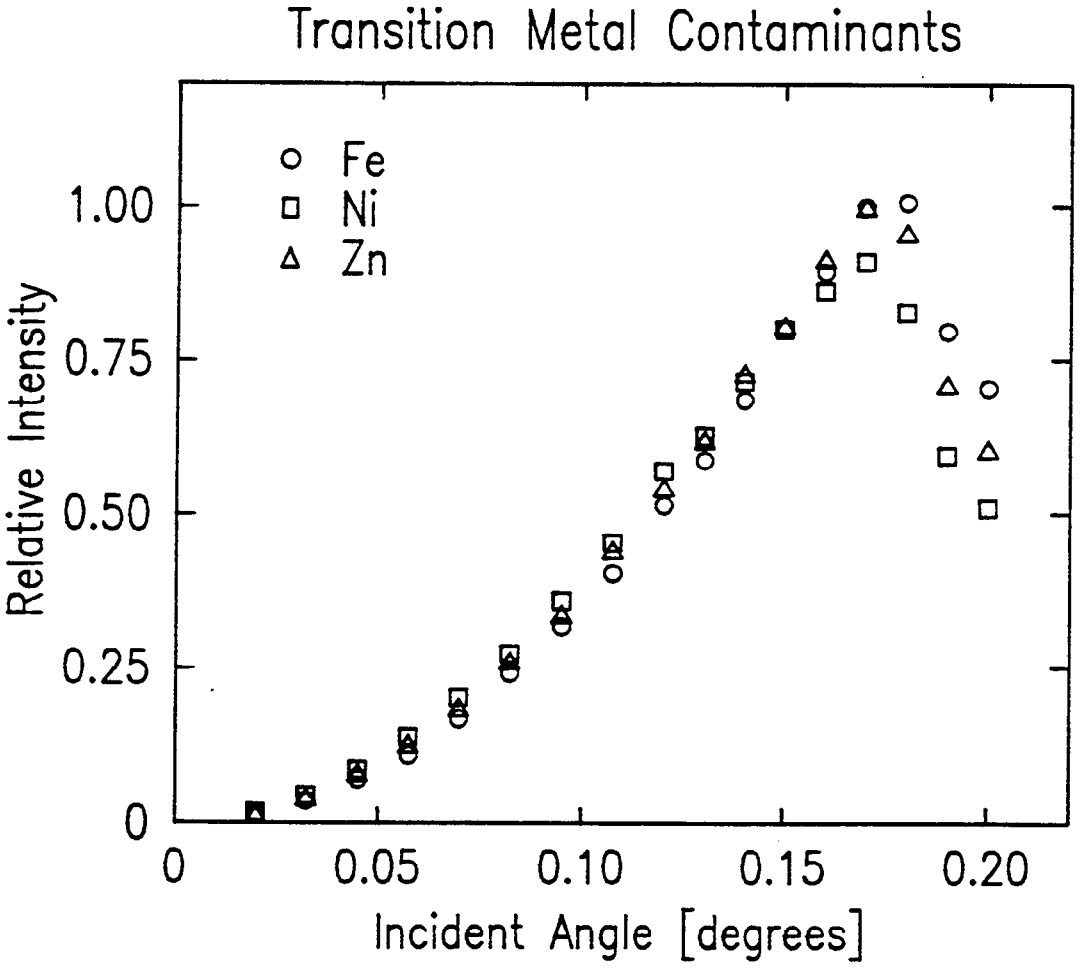
$$I(\theta) \propto I_0 \, |E_0(\theta)|^2 \times \int_0^\infty f(\theta)\, e^{-z/\delta_D(\theta)}\, dz$$

Synchrotron Radiation TRXRF Data versus Incident Angle

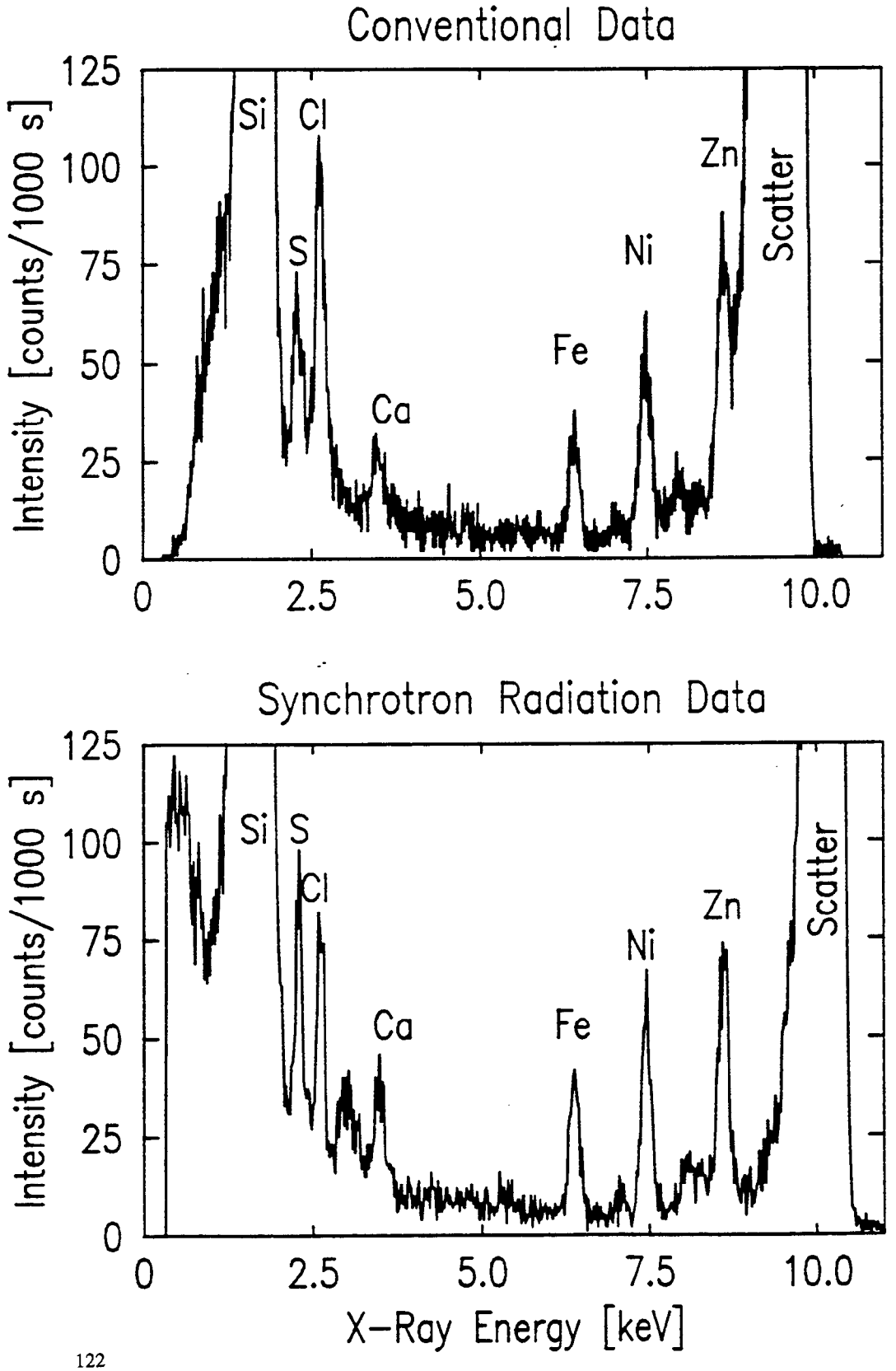



SIMULATED DEPENDENCE ON Ni DEPTH
NORMALIZED NiKα1 FLUORESCENCE INTENSITY
4.0
3.0
2.0
1.0
0
0
0.1
0.2
0.3
0.4
INCIDENT ANGLE (degrees)
100 Å SiO2 layer
X - ray energy = WL β
on surface
in SiO2
at interface
in silicon

Synchrotron Radiation TRXRF Data versus Incident Angle



Conventional & Synchrotron Radiation TRXRF Data



Synchrotron Radiation TRXRF Signal Rates

	Si	Fe	Ni	Zn	Scatter	Total
This Work	290.	0.3	0.5	0.7	13.	305.
Add 12.5 microns Teflon	14.	0.3	0.5	0.7	13.	29.
Increase Bandpass 200 X	2800.	60.	100.	140.	2600.	5500.

Today's Detection Limits

(10^{10} atoms/cm^2)

(1000 s count time)

	Fe	Ni	Zn
Rotating Anode	1.0	0.6	--
Synchrotron	1.0	0.8	0.7

Conclusion

With a Synchrotron Source, TRXRF can be Extended to:

- More Elements
- Greater Depth Resolution
- Higher Sensitivities

III F. Potential Role of Synchrotron Radiation TRXRF in Si Process R&D

M. Scott

POTENTIAL ROLE OF STRXRF IN SILICON PROCESS R&D

Martin P. Scott
Hewlett-Packard
October 21, 1992

OUTLINE

1. REVIEW OF TECHNOLOGY DRIVERS
2. CURRENT ROLE OF CONVENTIONAL TRXRF.
3. REVIEW OF ADVANTAGES OFFERED BY SYNCHROTRON SOURCES.
4. POSSIBLE ROLE OF AN SSRL TRXRF CAPABILITY.
5. CONCLUSIONS.

Drivers

- Two to three orders of magnitude reduction in particle/defect density from today's levels will be required for 1 Gbit DRAM success.
  - Defects due to homogeneous contaminants may be as important as particulates - but the mapping from contaminant levels to defect densities does not exist.
  - The nature and minimum size of defects for 0.15 micron CD is not known.
  - In some cases it is not possible to measure the likely contaminant levels required for success with 1 Gbit DRAMs.

Element Contamination from Bacteria*

Composition of Bacteria

Element	Content
C	50%
O	20%
N	14%
H	8%
P	3%
S	1%
K	1%
Na	1%
Ca	0.5%
Mg	0.5%
Cl	0.5%
Fe	0.2%
Others	~0.3%

Amount of Elements in Bacteria Cell

Elements	Weight (g)	Atoms
C	7.9×10^{-14}	3.9×10^{9}
O	3.1×10^{-14}	1.2×10^{9}
N	2.2×10^{-14}	9.5×10^{8}
H	1.3×10^{-14}	7.6×10^{9}
P	4.7×10^{-15}	9.2×10^{7}
S	1.6×10^{-15}	3.0×10^{7}
K	1.6×10^{-15}	2.4×10^{7}
Na	1.6×10^{-15}	4.1×10^{7}
Ca	7.9×10^{-16}	1.2×10^{7}
Mg	7.9×10^{-16}	2.0×10^{7}
Cl	7.9×10^{-16}	1.3×10^{7}
Fe	3.1×10^{-16}	3.4×10^{7}
Others	4.7×10^{-16}	

*K. Yabe, et al., "Responding to the Future Quality Demands of Ultrapure Water", Microntamination, p. 37, Feb. 1989.

KEY PROCESSES IN VLSI FABRICATION: CONTAMINATION CONTROL AT SURFACES & INTERFACES.

Surface Preparation

- wet immersion and vapor cleaning
- passivation
- etching

Surface Reactions

- epitaxial growth
- oxidation
- nitridation
- silicidation

Film Deposition

- chemical vapor deposition
- physical vapor deposition

Patterning

- photoresist spinning, stripping/ashing
- plasma etching
- reactive ion etching

Ion - Implantation

COMPATIBILITY OF TRXRF WITH SILICON WAFER SURFACE ANALYSIS

- UNPATTERNED WAFERS SUITABLE FOR TOTAL REFLECTION GEOMETRY.
- AUTOMATED SAMPLE HANDLING IS STRAIGHTFORWARD.
- ANALYSIS IS NON-DESTRUCTIVE
- SURFACE SENSITIVE
- ELEMENT SPECIFIC
- QUANTITATIVE (WITH APPROPRIATE STANDARD.)
- SOME SPATIAL MAPPING POSSIBLE
- PROVIDES INFORMATION ON IMPURITY DEPTH DISTRIBUTION.

CURRENT APPLICATIONS OF CONVENTIONAL TRXRF IN SILICON PROCESS R&D

- **Materials Selection**
  - starting wafers
  - chemicals
- **Equiment Development/Qualification**
  - design feedback for ultraclean processing.
  - optimization of maintenance procedures
- **Process Development/Qualification**
  - feedback without full IC processing
  - near surface thin-film analysis
- **Yield Enhancement/Quality Monitoring**
  - correlation of contamination with IC performance.
  - early detection of compromised processing.
- **Cleanroom Facilities Control**
  - ultrapure water
  - CR air
  - process gases

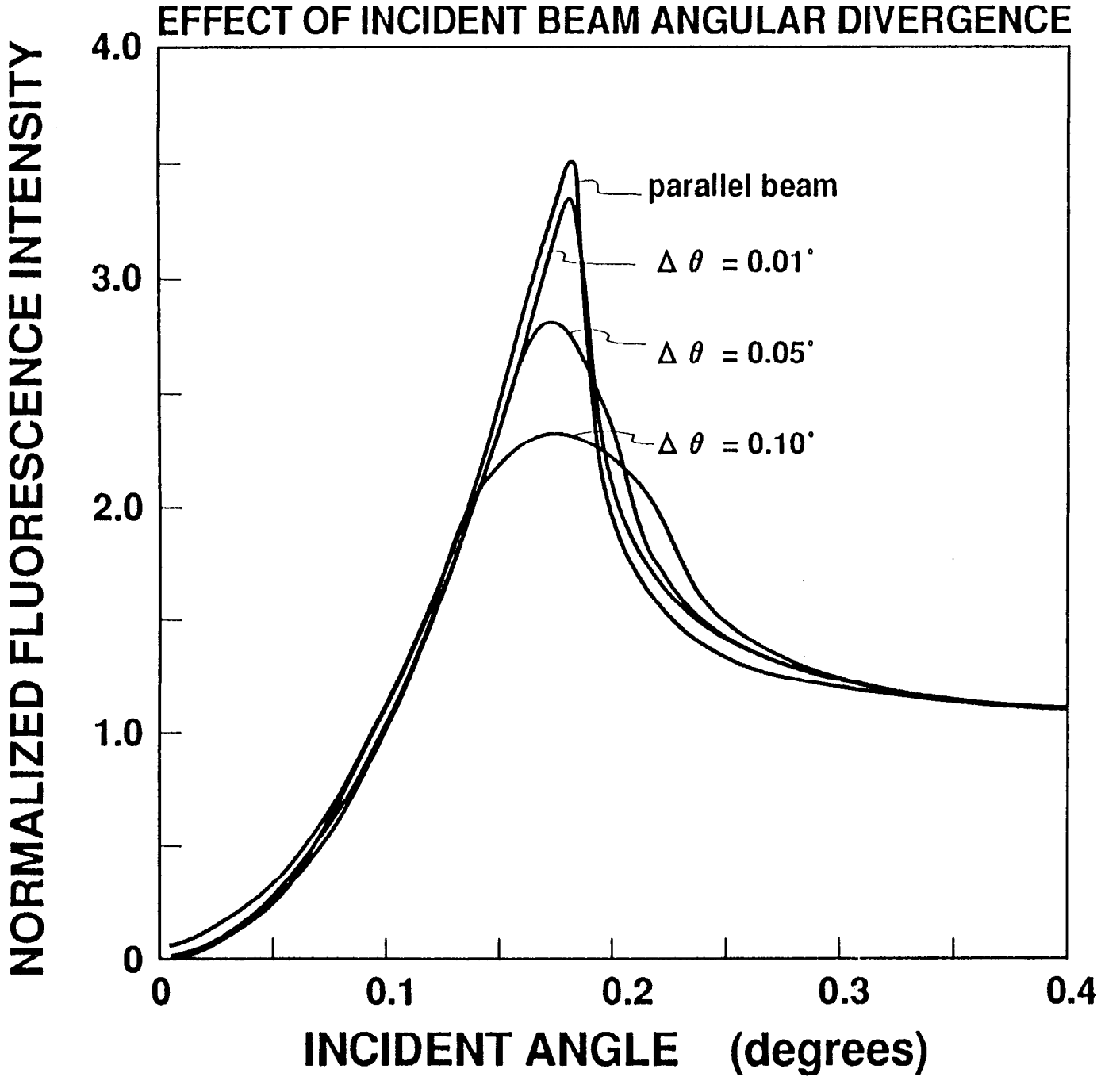
ADVANTAGES OF SYNCHROTRON TRXRF

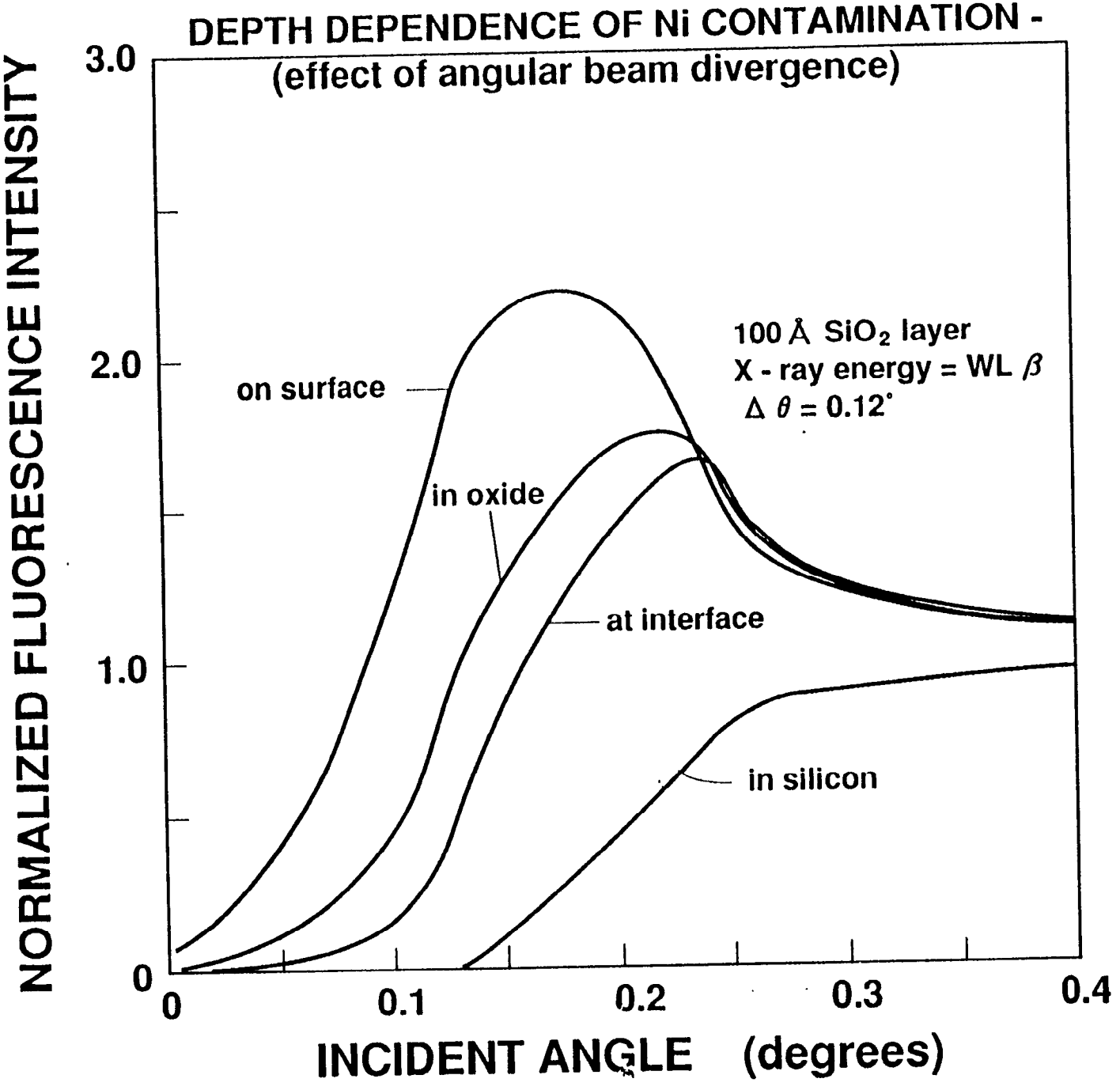
Tunability of wavelength
- selective excitation
- suppression of major components
- separation of overlapping peaks
- energy dependent analyses

High Brightness
- signal enhancement

Natural Collimation
- microanalysis (high lateral resolution)
- depth profiling

Polarization
- reduction of scatter


EFFECT OF INCIDENT BEAM ANGULAR DIVERGENCE
NORMALIZED FLUORESCENCE INTENSITY
4.0
3.0
2.0
1.0
0
parallel beam
Δ θ = 0.01°
Δ θ = 0.05°
Δ θ = 0.10°
0
0.1
0.2
0.3
0.4
INCIDENT ANGLE (degrees)


DEPTH DEPENDENCE OF Ni CONTAMINATION -
(effect of angular beam divergence)
NORMALIZED FLUORESCENCE INTENSITY
3.0
2.0
1.0
0
0
0.1
0.2
0.3
0.4
INCIDENT ANGLE (degrees)
on surface
in oxide
at interface
in silicon
100 Å SiO2 layer
X - ray energy = WL β
Δ θ = 0.12°

PRACTICAL REQUIREMENTS OF A STRXRF CAPABILITY

1. **Reliable, Timely, Easy Access**
   - low initiation costs
   - low overhead for continued interaction
   - flexible scheduling
   - high equipment and facility availability

2. **Interest at SSRL in Advanced Manufacturing Science.**

3. **Protection of Proprietary Interests**

4. **Technical Staff Support**

APPROPRIATE EXPERIMENTAL STATION

- 'Clean' sample preparation capability and measurement environment.
- Detection limits tracked with standards
- User transparent data collection/experiment automation.
- 6 and 8 – inch wafer measurement
- Detectors capable of wide elemental range
- Future capability for in-situ process chambers using corrosive gases.
- Straightforward alignment

PROVIDED SUCH A CAPABILITY EXISTS... HOW WOULD IT BE USED?

1. To extend the limits of conventional TRXRF for the same applications with:
   - lower detection limits
   - wider range of elements (especially light elements).
   - superior depth-profiling
   - higher spatial resolution

2. To make possible new kinds of experiments:
   - analyse the chemical state of surface impurities.
   - time-resolved studies of surface contamination/diffusion processes.
   - combine with surface structure determination.
   - measure under simulated process conditions.

LIKELY AREAS OF TECHNICAL CONTRIBUTION FROM STRXRF EXPERIMENTS

1. A better fundamental understanding of:
   - impurity interactions with surfaces
   - impurity diffusion near surfaces
   - wet chemical and vapor surface preparation processes.
   - the role of low level contaminants on device performance.
   - the role of light elements in IC yield
   - TRXRF quantitation and calibration
2. Non-destructive analysis of thin-film multilayers
3. Improved conventional TRXRF instrumentation
4. Information on the kinetics of contamination processes (possibly).

PROVIDED SUCH EXPERIMENTS WERE POSSIBLE...
-WHY WOULD THEY BE PERFORMED?

1. CONVENTIONAL TRXRF CAPABILITY UNABLE TO KEEP PACE WITH ULSI MICROCONTAMINAION ANALYSIS REQUIREMENTS.

2. MICROCONTAMINATION MANAGEMENT IS CRITICAL FOR FUTURE ULSI CIRCUIT FABRICATION.

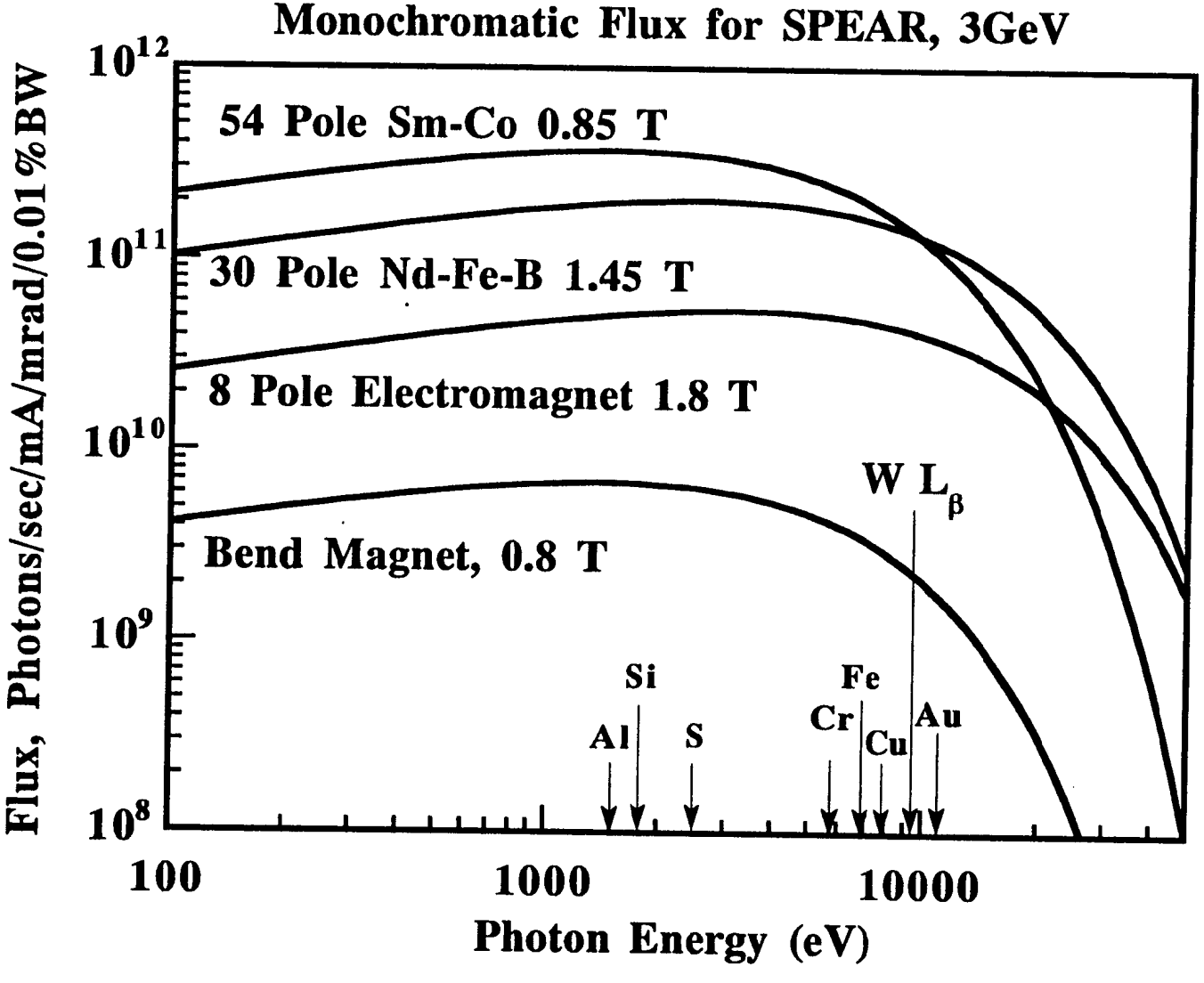
3. DESIRE FOR A BETTER FUNDAMENTAL UNDERSTANDING OF CONTAMINATION AND CLEANING PROCESSES TO GUIDE PROCESS DEVELOPMENT.

CONCLUSIONS

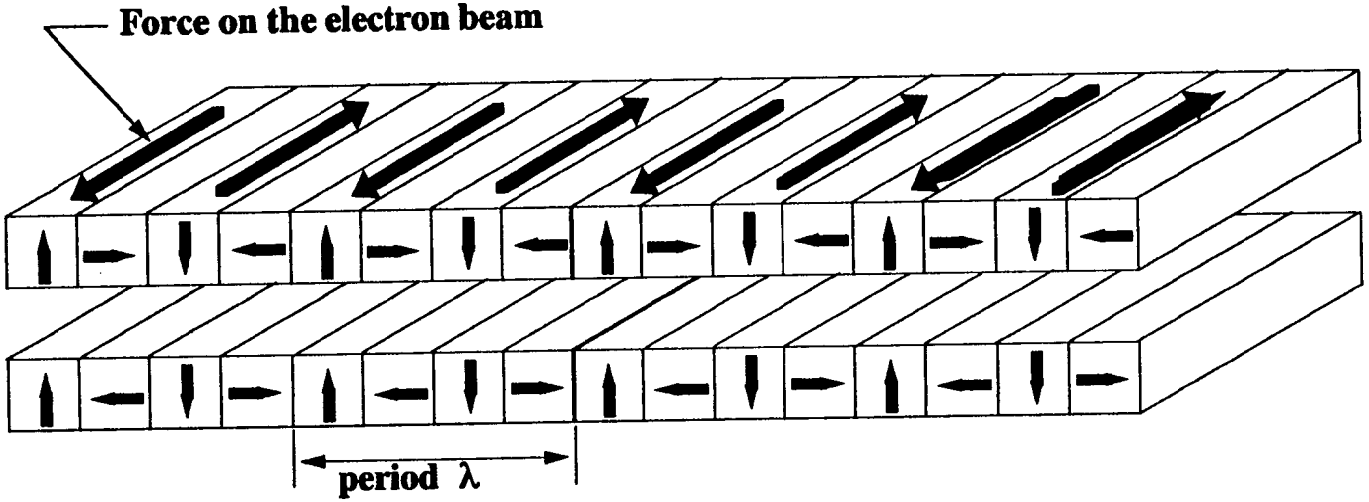
WITH SUFFICIENT AVAILABILITY AND CAPABILITY, STRXRF COULD PROVIDE CRITICAL DATA ON MICROCONTAMINATION REQUIRED FOR CONTINUED SUCCESS IN ULSI DEVELOPMENT.

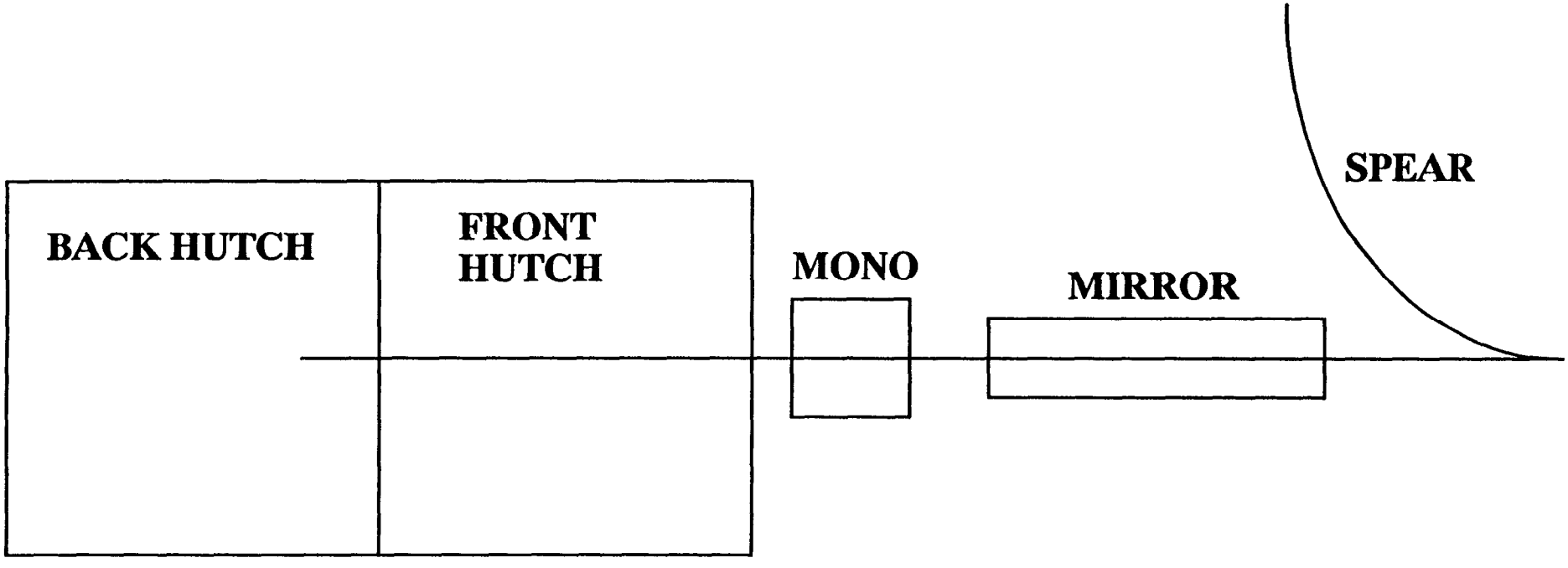
III G. Potential Developments of Synchrotron Radiation Facilities

S. Brennan


Monochromatic Flux for SPEAR, 3GeV
Flux, Photons/sec/mA/mrad/0.01%BW
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
54 Pole Sm-Co 0.85 T
30 Pole Nd-Fe-B 1.45 T
8 Pole Electromagnet 1.8 T
Bend Magnet, 0.8 T
W L_β
Al
Si
S
Cr
Fe
Cu
Au
100
1000
10000
Photon Energy (eV)

Permanent Magnet Insertion Device Structure




SPEAR
BACK HUTCH
FRONT
HUTCH
MONO
MIRROR

Scenarios for Continued Research

- **Special-purpose hutch built behind present hutch on BL 7.**

  Clean room
  Wafer handling equipment

- **If standard Si(111) crystals, somewhat easier to schedule time.**

- **Installation of multilayers would require scheduling blocks of times.**

Scenarios for Continued Research

- **Special Multilayers**

  25-40 Å d-spacing Rh-C plane optic would replace the current Si(111).

  E/dE ~ 100-150.
  ~ 100x more flux.
  Divergence unchanged.

- **Would work both for 10-13 keV (25Å) and for 1-1.5 keV (40Å) range.**

Scenarios, Other Beam Lines

Beam Line 6:

54 pole 10 kG permanent magnet wiggler.

- **High-vacuum monochromator**
- **Differentially pumped**
- **No Be windows prior to mono**
- **Energies as low as 1keV possible**

Beam Line 10

30 pole 14.5 kG permanent magnet wiggler

Mobile Clean "box"

Rather than building special hutch on Beam Line 7 (or any other BL), Build

> **Cleanliness**
> **wafer-handling,**
> **wafer-positioning**
> **etc**

into "box" that can be installed in any of several hutches, as each beam line has special capabilities.

III H. Identification of Goals, Needs and Concerns

M. Garner

Application of Synchrotron Radiation For Trace Impurity Analysis Advanced Silicon Processing

Who would use this?

Researchers

Materials Technologist

Process Development Engineers

Technicians

Analytical Services? (Charles Evans, Surface Science Analysis Ass....)

Semiconductor Companies

Others

System Capability

Ease of Use
*Automated Operation
*Manual Operation
*User Interface

TXRF

Surface Micro-roughness

Transmission

Application of Synchrotron Radiation For Trace Impurity Analysis Advanced Silicon Processing

Administration Issues:

Ease of Access

Time Allocation

Convenience

Training

Computer Reservation System?

Cost