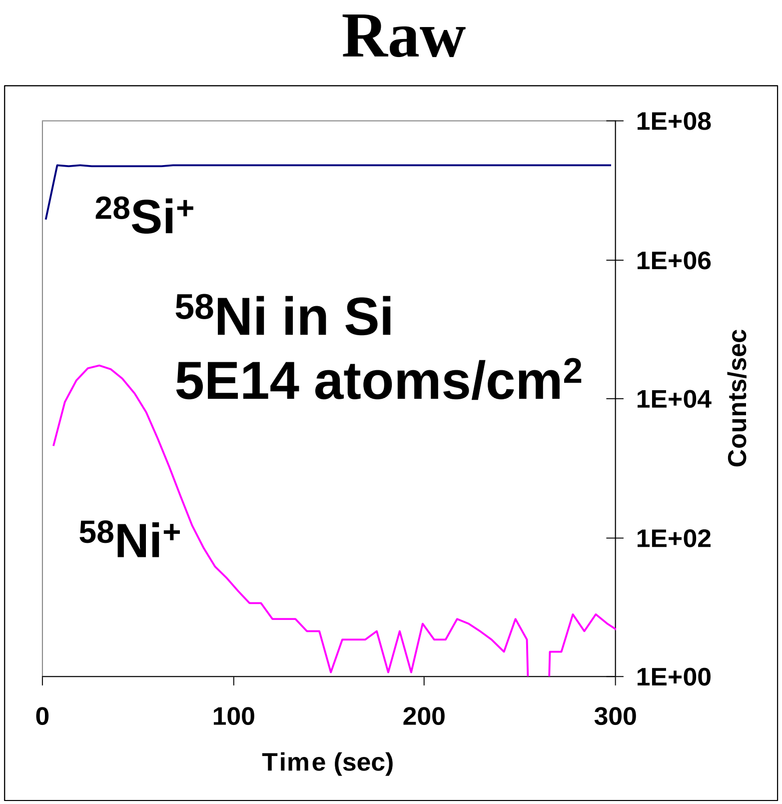
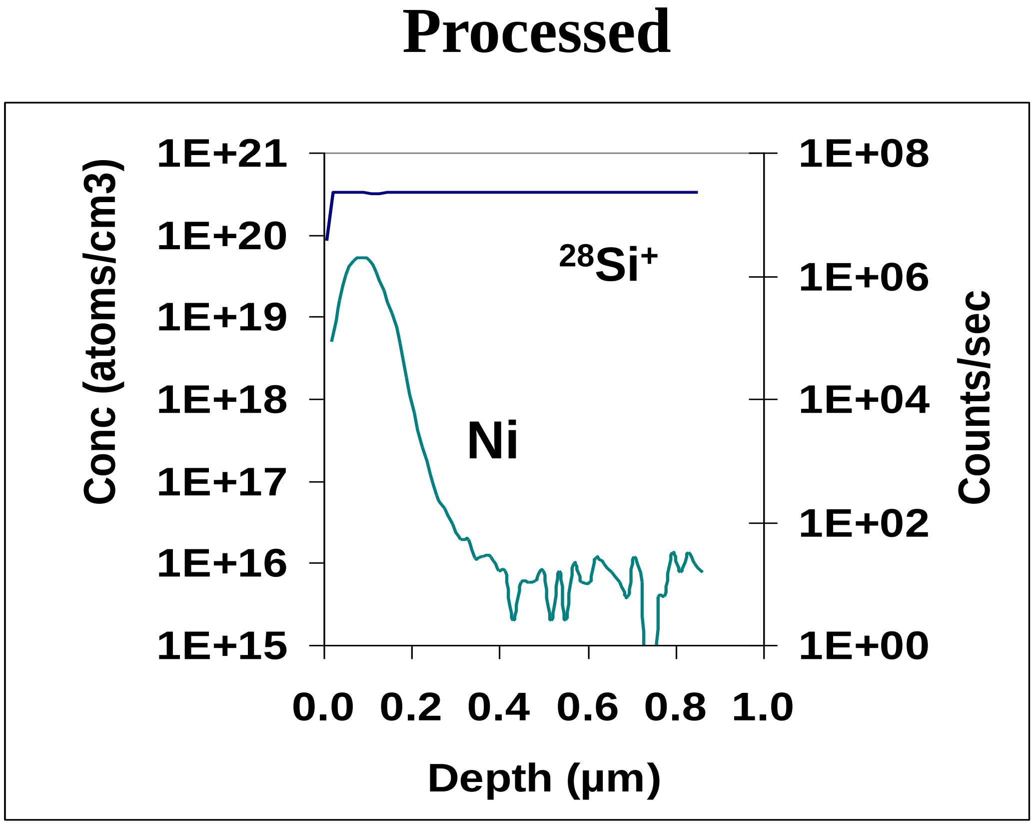
Quantification

- RSF method
- RSF calculation
- Profilometer measurement
- Bulk doped standards
- Ion implanted standards
- Yield variations by element and matrix
- RSF patterns
- Surface and near surface
- Image depth profile

Conversion of Raw to Processed Data





- Raw data in counts versus time or cycles
- Convert to reduced data in concentration versus depth
- Concentration axis uses RSF
- Depth axis uses crater depth

Why Use RSFs?

- SIMS requires standards for calibration
- Prediction without standards
  - physical models for secondary ion emission
  - thermodynamic - all sputtered species are in local thermal equilibrium
- Instrument dependent numbers
  - absolute sensitivity
  - useful yield (ions detected/atoms sputtered)
- Relative sensitivity factors (RSFs)
  - more accurate than models
  - require many standards

RSF Calculation

RSF = $(D \times C \times I_m \times t)/(z \times I_s)$

where D is implanted dose in atoms/cm^2

- C is number of data cycles
- I_m is matrix isotope secondary ion intensity in counts/s
- t is count time/cycle for species of interest
- z is depth of crater in cm
- I_s is summation of secondary ion intensity of species of interest in counts

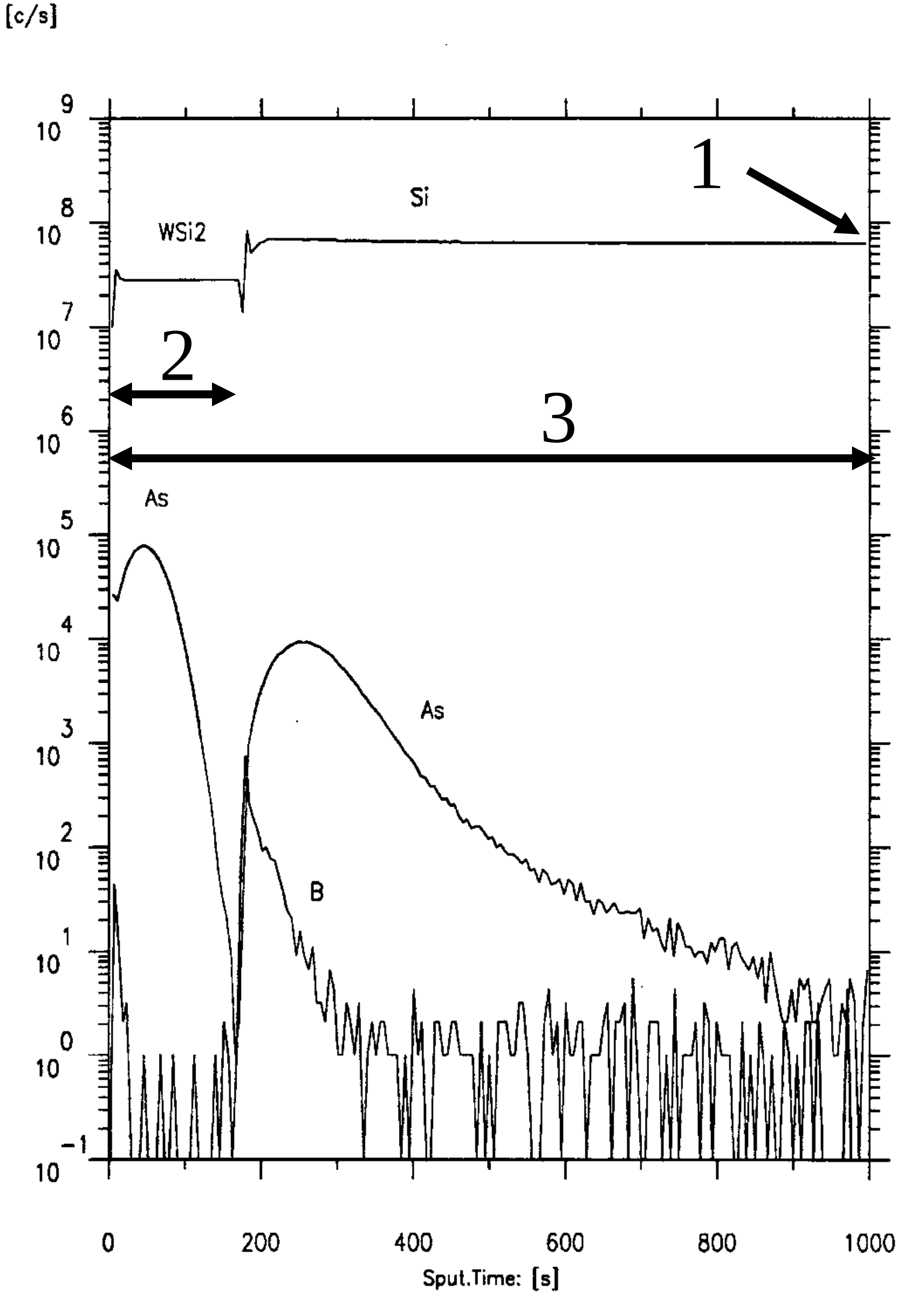
Assumptions: Implanted dose is correct, sputtering rate is uniform

Depth Measurement

Profilometer used to measure depth
1% error and ~0.1 µm min depth for older systems
<1% error and <20 nm min depth for newer systems

Example: Tencor P10
Measurement repeatability: 1 nm
Vertical Range +/-6.5 µm, resolution 0.1 nm
Vertical linearity 1 nm for measurement <0.2 µm
0.5% for measurement >0.2 µm
or 5 nm for 1 µm crater

Normalization



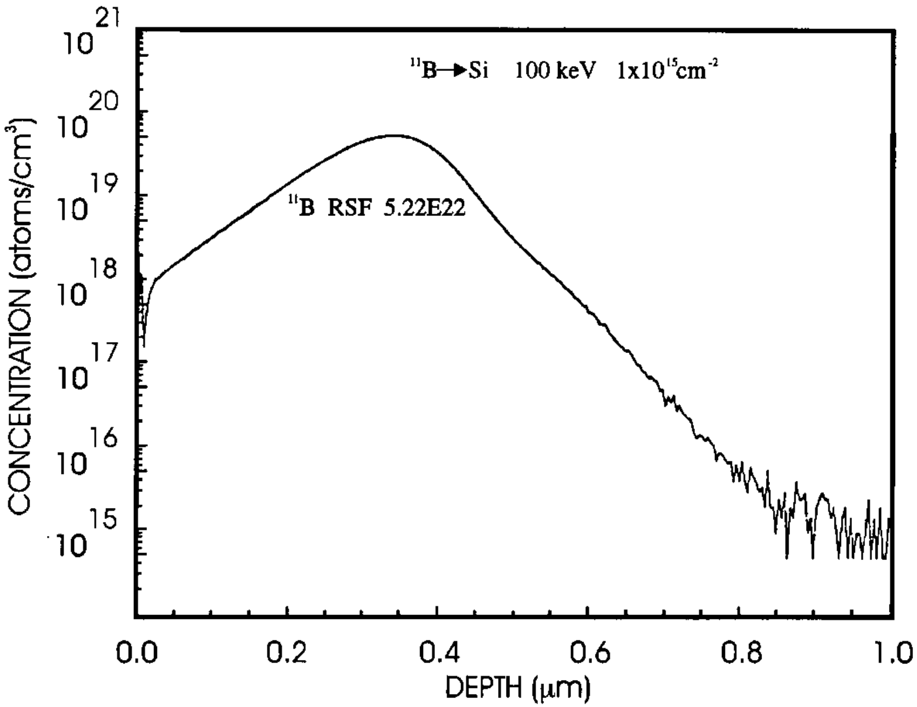
Measure matrix species to accommodate analysis variations
e.g., sample position on holder

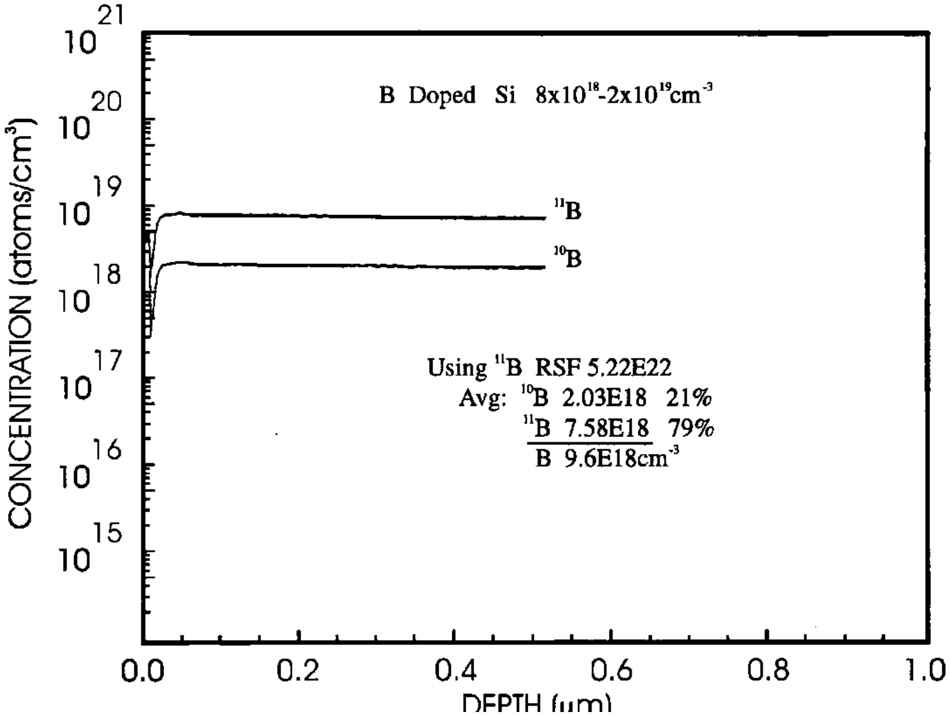
Three Methods:
1 Measurement at end of profile
2 Average over region of interest
3 Point by point

Bulk Doped Standards

- Provide constant concentration with depth
- RSF determined quickly
  - sputter until secondary ion yield is constant
- Limited number elements available
  - B, P, As in Si
  - B, P in SiO_2
  - (e.g., borophosphosilicate glass - BPSG)
- May not be accurate near surface

Implant - Bulk Doped Comparison





Implanted standard usually contains only one isotope

Bulk doped standard usually contains all isotopes at natural abundances

Quantification Using Ion Implantation

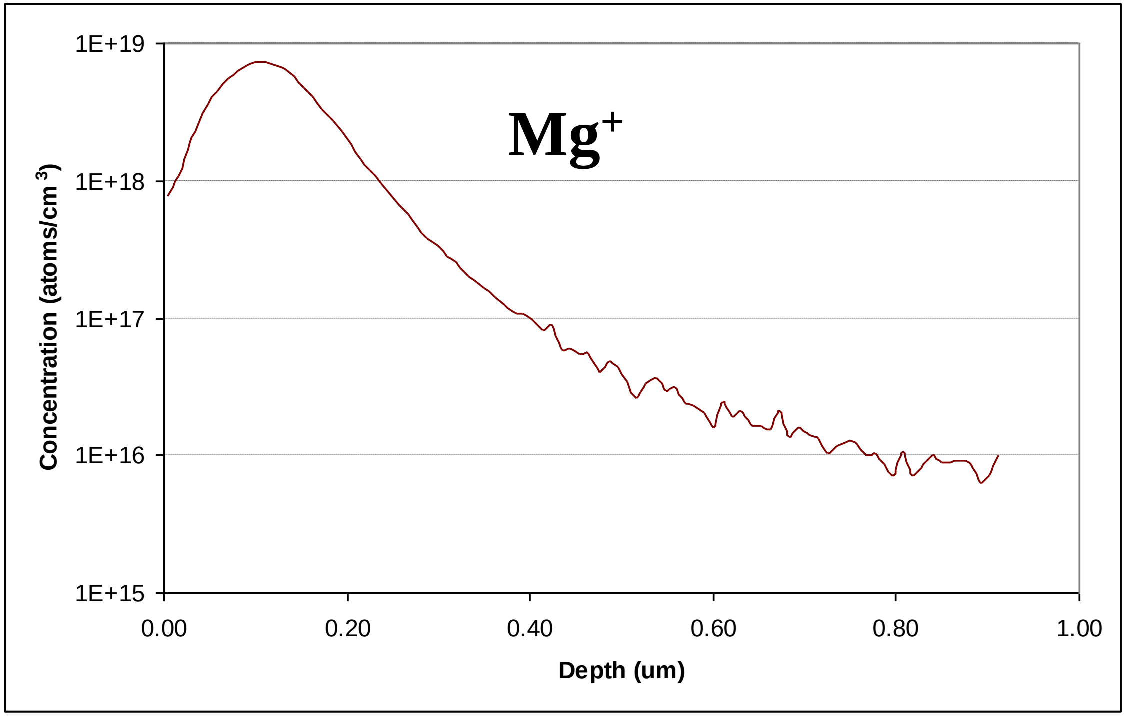
- Ion implant into same matrix as specimen
- Depth profile through implanted region of standard
- Determine RSF and detection limit
- Use RSF to quantify specimen of interest

Concentration Conversion

Conc. (%)	**Conc. (atoms/cm^3)**
100.00	**5E22 (for Si)**
10.00	**5E21**
1.00	**5E20**
.1	**5E19**
.01	**5E18**
.001	**5E17**
.0001	**5E16 (1ppma)**

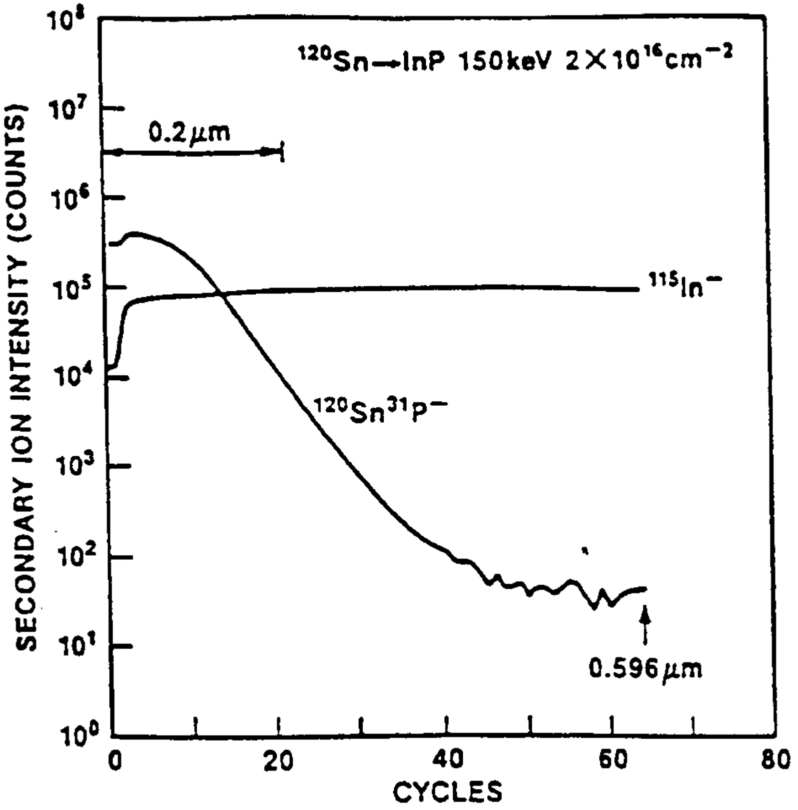
Ion Implanted Standards

- All elements and isotopes can be implanted
- Depth can be varied with implant energy
- Peak concentration can be varied with dose
- All substrates and structures can be implanted
- Multiple elements can be implanted
- Provides a detection limit
- Need to verify dose and check for isotopic contamination

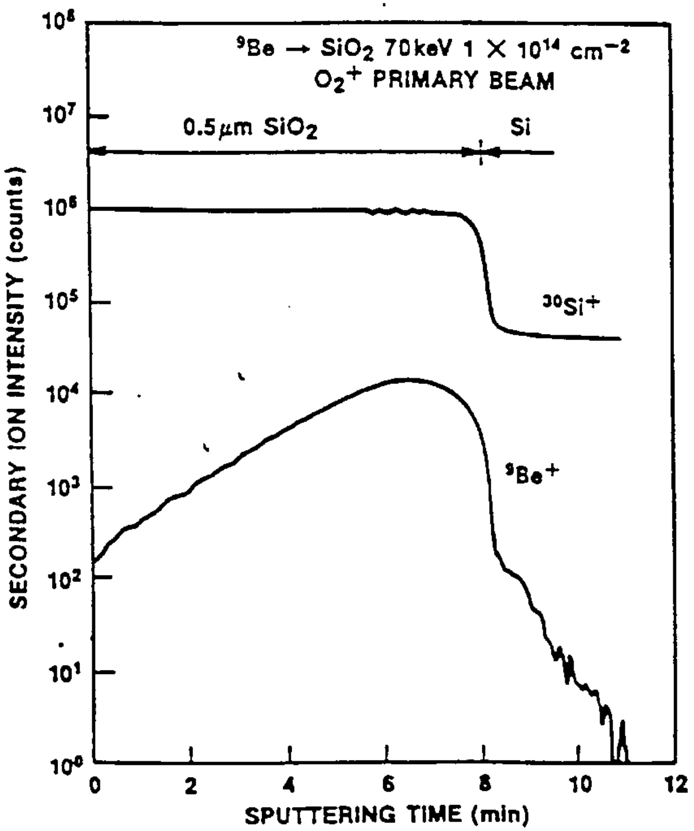


Mg in GaN
9.9E13 atoms/cm^2

Implant Energy



Implant energy too low
for Sn → InP
Dose error near surface



Implant energy too high for
Be → SiO_2 layer on Si, much of
the Be is beyond the SiO_2

SIMS, R. G. Wilson, F. A. Stevie, and C. W. Magee, Wiley, New York (1989)

Concentration (Dose)

- Dose for standard matched with sample to be analyzed
- Too high
  - different analysis conditions for standard and sample
    - FC and EM considerations
- Too low
  - contaminants in sample can affect result
- Typical dose for SIMS: 1E14 atoms/cm^2
  - (peak concentration ~1E19 atoms/cm^3)
- Match dose and depth with samples to be analyzed

Species

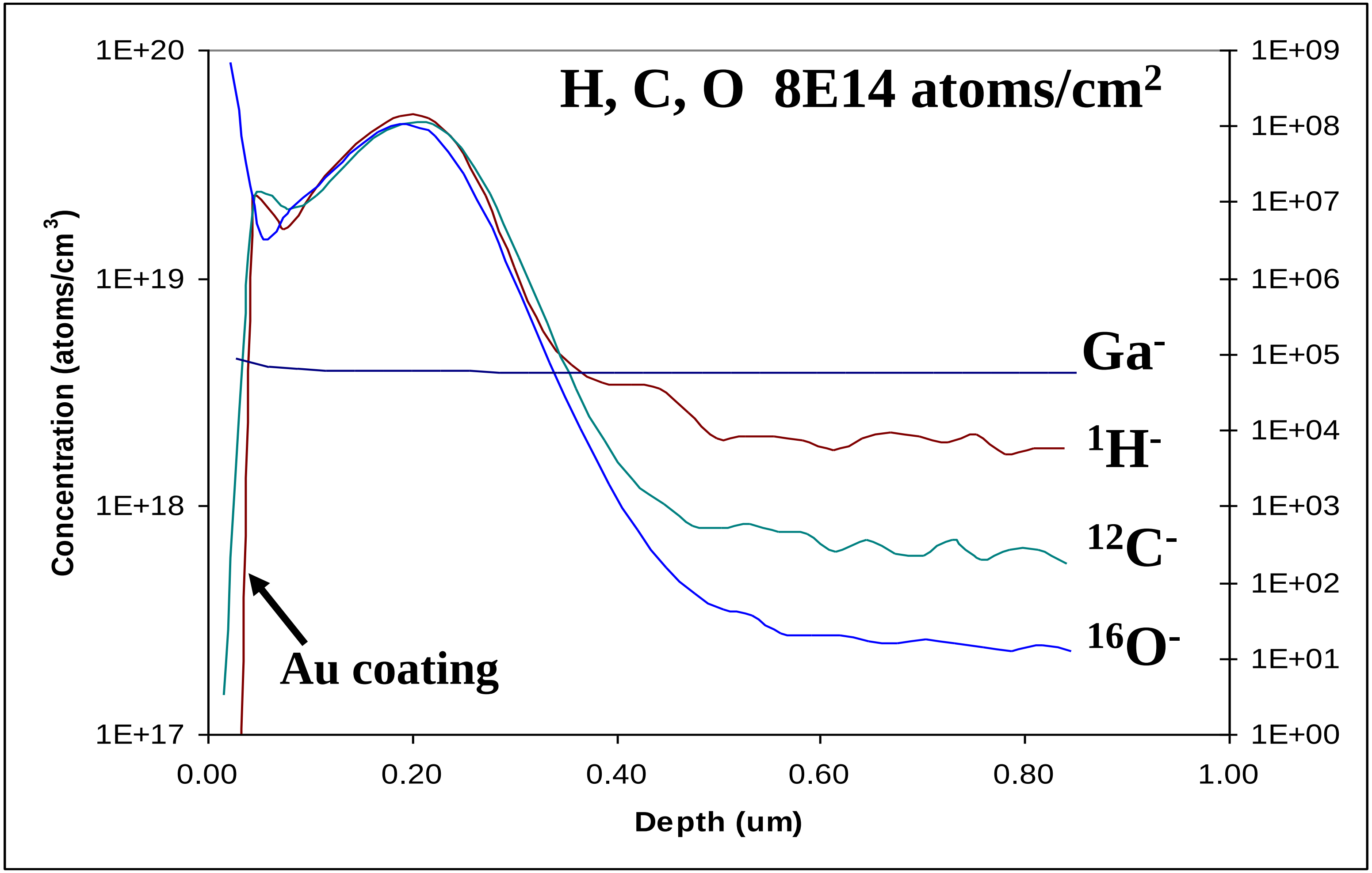
- Choose one isotope (usually best)
- Multiple isotopes may be implanted
- Avoid mass interferences if possible
  - Most implanters use low mass resolution
  - Why complicate your SIMS analysis?

  Example:

  Implantation of Si

    - Possible ^{28}Si and ^{12}C^{16}O interference
    - Use ^{29}Si

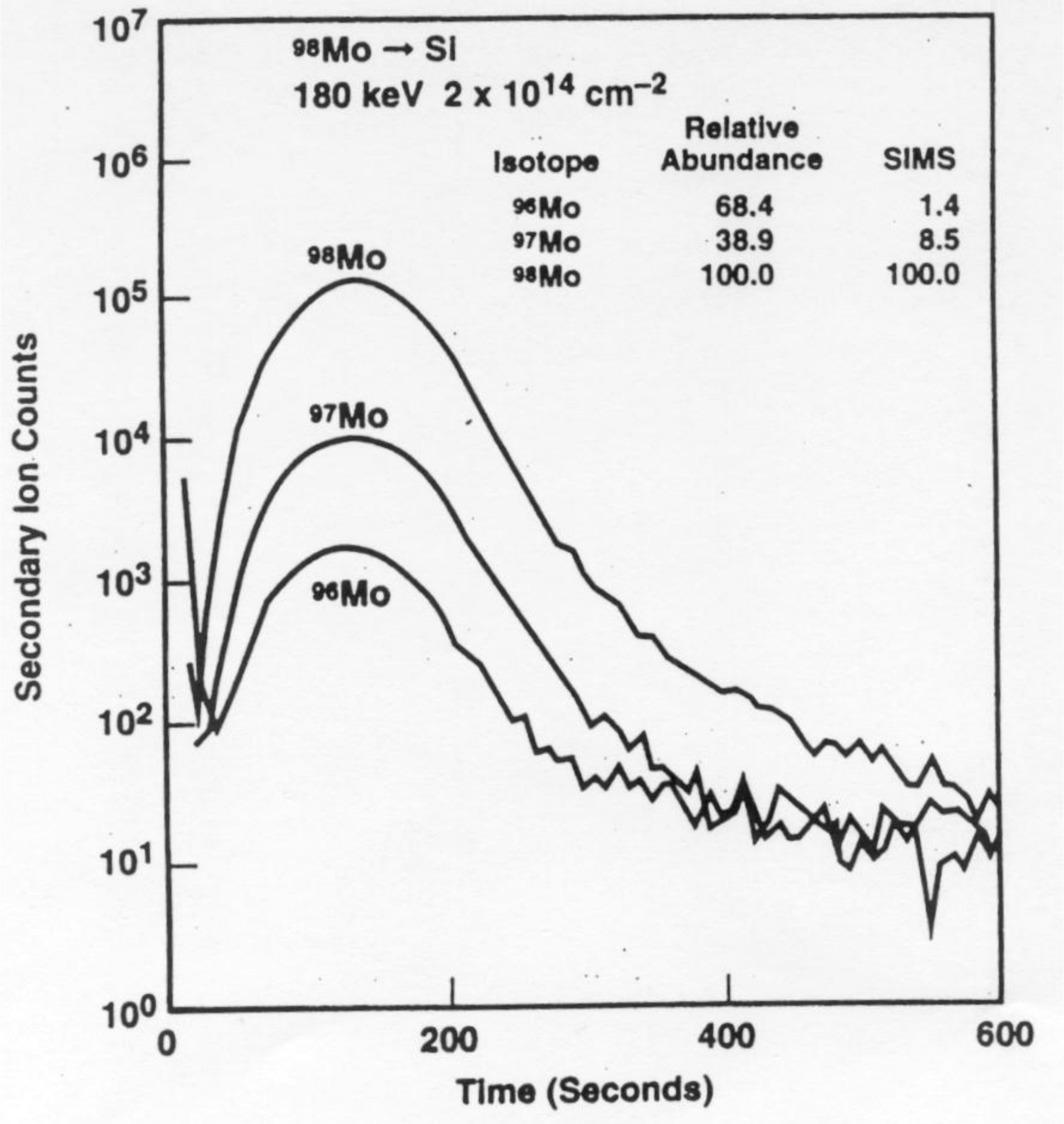
Multiple Implants in GaN



Sample is Au coated to reduce charging

Checking Standards

- Implanter dose can be inaccurate
  - Implanter dose not absolute measurement
  - Mass interferences not resolved by implanter
- Check dose of implant into Si
  - Use RBS if possible
  - Compare with known implant in Si
    (if implanting Si, use GaAs)
  - Charging for implantation of insulators
  - Non-uniform dose – rotate target during implant
- Check isotope distribution with SIMS



Isotope Check

Check isotopic distribution using SIMS profiles

Apportion dose from SIMS isotopic data
^{96}Mo = 2%
^{97}Mo = 6%
^{98}Mo = 92%

^{98}Mo = 0.92 x 2E14
= 1.8E14 atoms/cm^2

Dose - Peak Concentration Conversion

Peak Concentration can be estimated from implant dose

$\sim 10^5$ x dose

Assume implant range distribution is Gaussian

$n(x) = n_0 \exp(-(x-R_p)^2 / 2\Delta R_p{}^2)$

where $n_0 = \Phi / (\sqrt{(2\pi)}\, \Delta R_p) \sim 0.4\Phi / \Delta R_p$

Φ = dose, ΔR_p is straggle

Typical $\Delta R_p = 0.01$ to $0.1\mu m$

$n(R_p) = (0.4 / 0.1 \text{ to } 1\text{x}10^{-4} \text{ cm})\, \Phi = 0.4\text{x}10^5 \text{ to } 4\text{x}10^5\, \Phi \text{ cm}^{-3}$

P in Si, 100keV, $\Delta R_p = 0.04\mu m = 0.04\text{x}10^{-4}$ cm

$n(R_p) = 0.4\Phi / 0.04\text{x}10^{-4} = 1\text{x}10^5\, \Phi \text{ cm}^{-3}$

Reference Materials

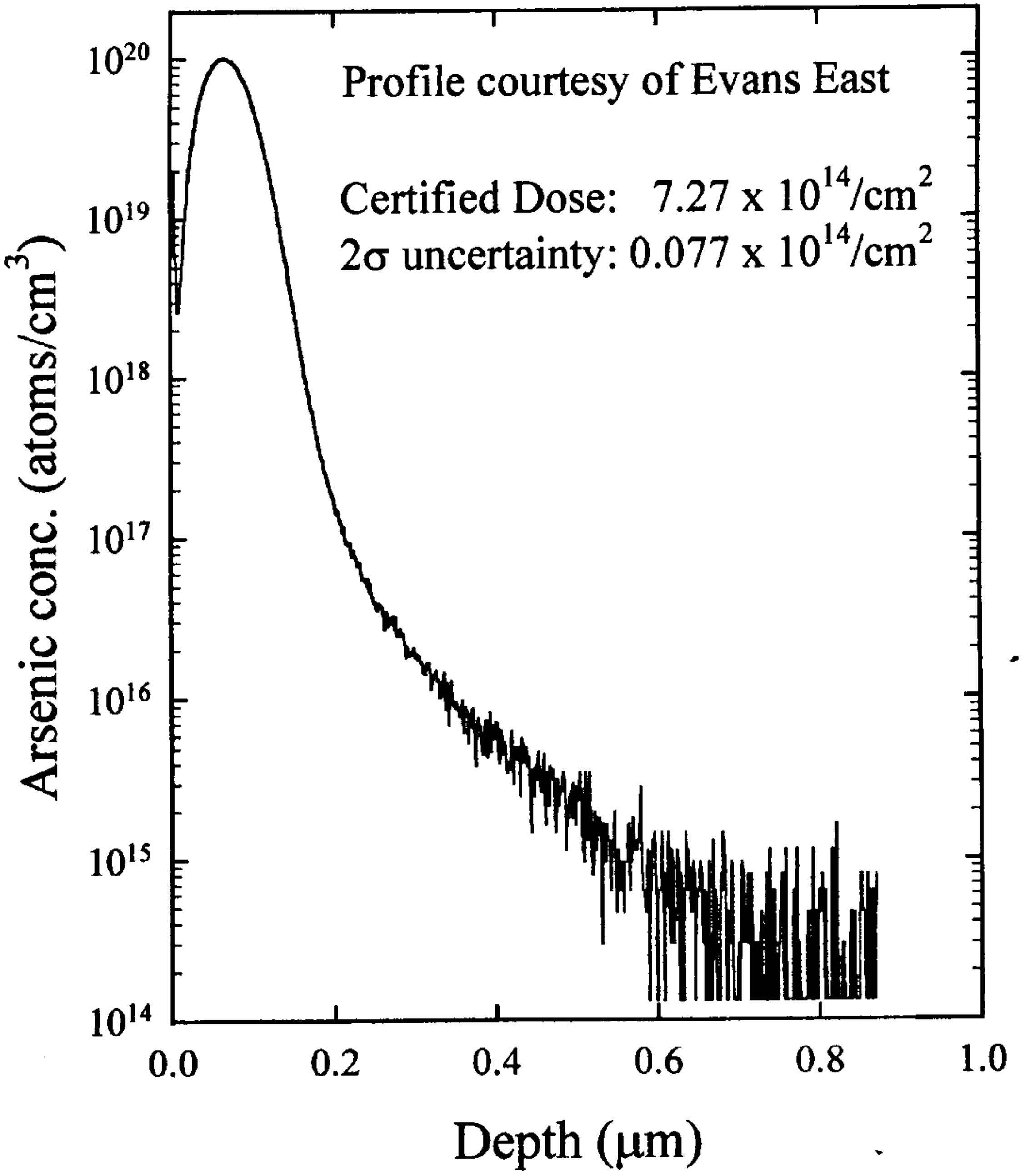
- Certified reference material
  - B, P, As in Si from NIST

- Commercial reference material
  - certified by vendor

    e.g.: Evans Analytical Group standards

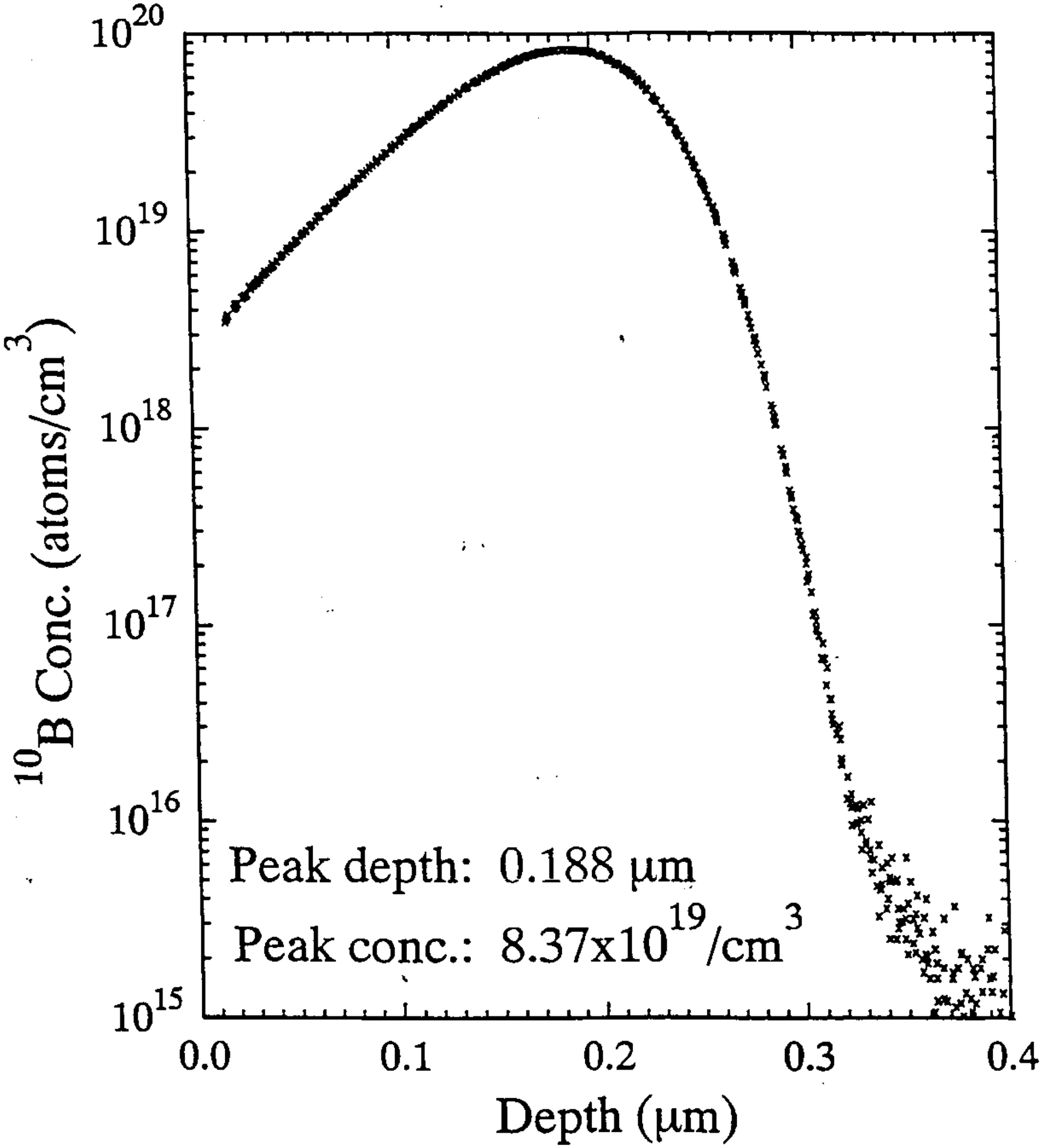
- Reference standard (home grown)
  - implanted or bulk doped material
  - check using another method (RBS)
  - compare with other standards

NIST Standard for As



SRM 2134
100 keV As implant in Si
90ng/cm^2

Precision (Reproducibility)



Eight superimposed SIMS depth profiles of ^{10}B in SRIM 2137 using 3 keV O_2^+ ion bombardment at 52° from normal

D. S. Simons, NIST SRIM 2137 Documentation

Magnetic Sector Reproducibility

Relative Standard Deviation (RSD) <1%

can be achieved for low and high mass resolution

High mass resolution

As varied doses (0.25-0.51%)

P (0.38%)

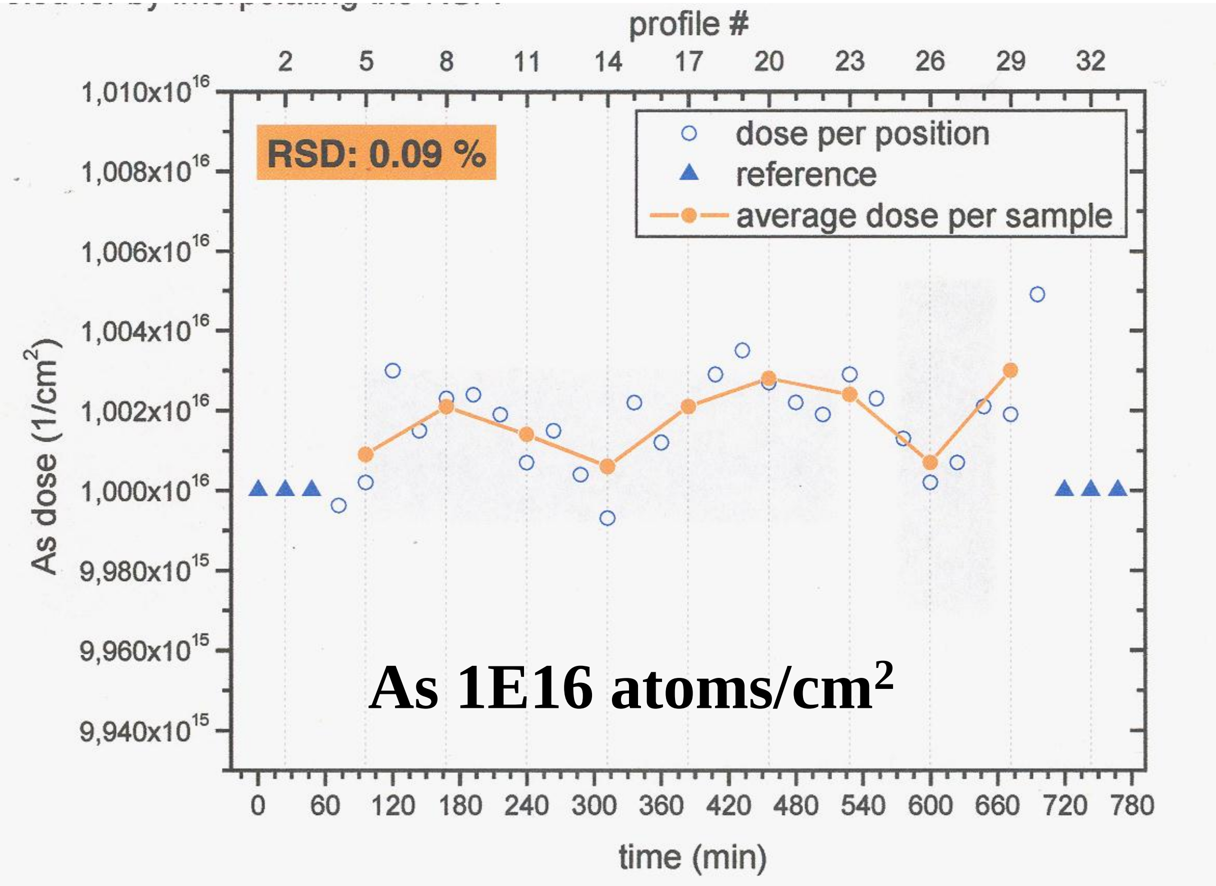
A. Budrevich and J. Hunter
Characterization and Metrology for ULSI Technology
D. Seiler et al., eds., AIP, Woodbury, (1998) 169

Low mass resolution

BF_2 (0.92%)

F. A. Stevie et al., SIMS XI Proceedings
Wiley, Chichester (1998) 1007

High Reproducibility TOF-SIMS Dose Meas.



As 1E16 atoms/cm^2

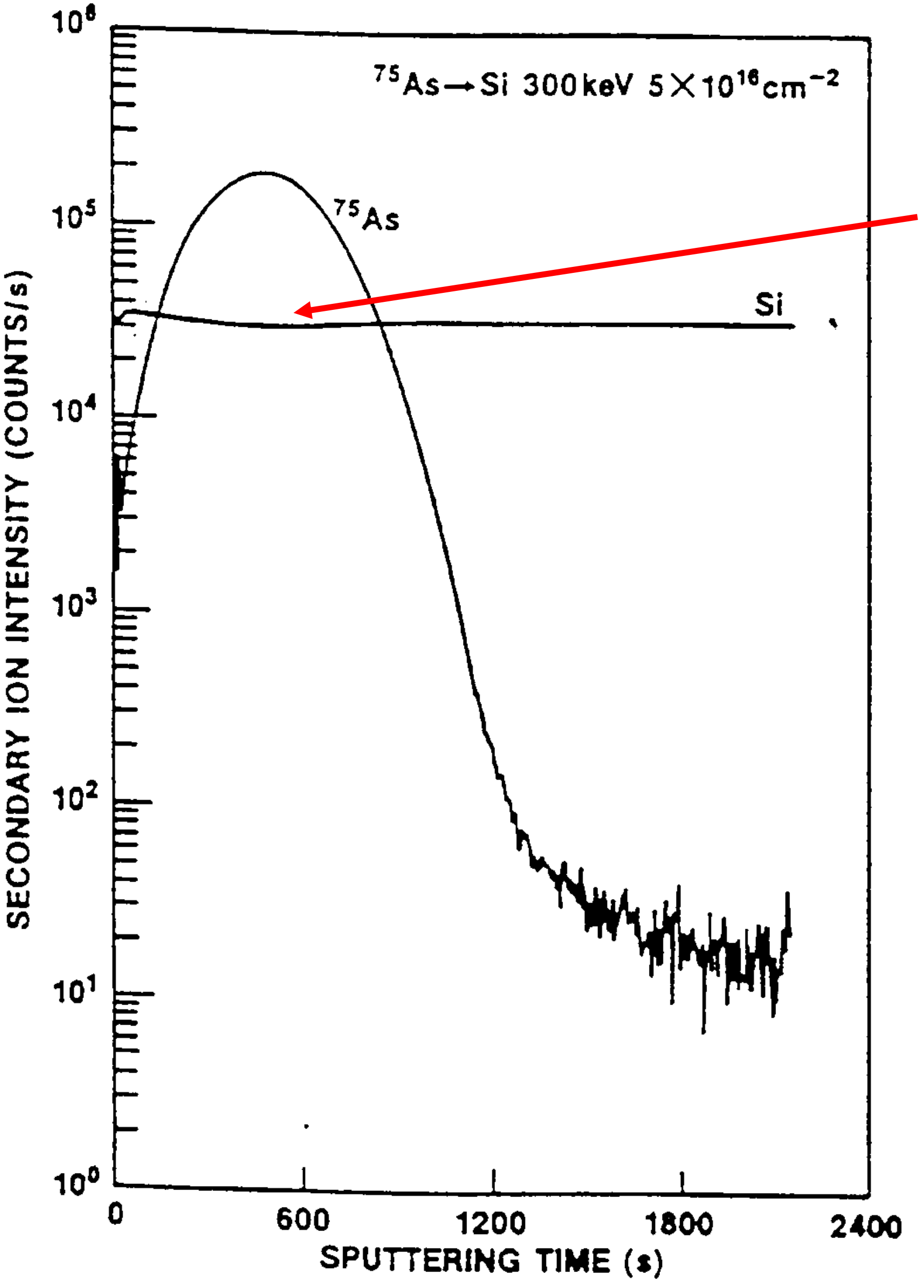
B, P, As reproducibility <0.1% RSD

T. Grehl, R. Mollers, E. Niehuis, D, Rading
20th SIMS Workshop, May 2007

Linearity Limitations

- Counts vs concentration linear from ppt to ~1%
- Concentrations in percent range may have inaccuracy because substrate (matrix) is different)
- Can implant at high dose or use other analytical methods to provide accurate numbers for concentrations >1%

Nonlinear Region

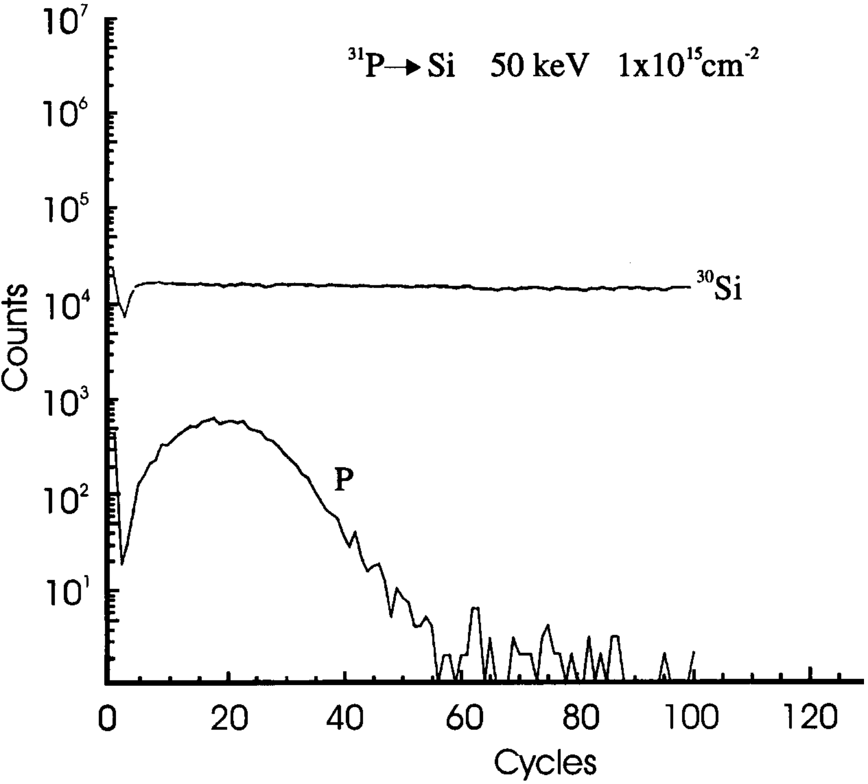


Change in Si relative intensity
at peak of high dose As implant

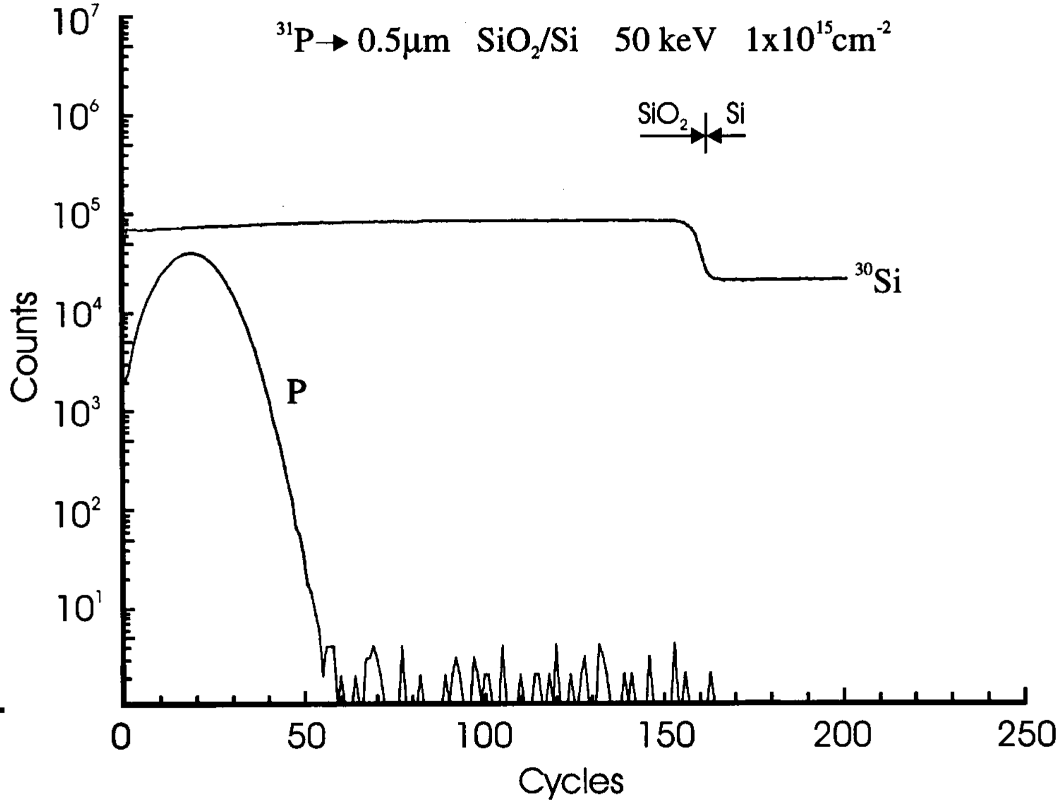
As peak concentration ~5E21 cm^{-3}
or ~10% atomic

SIMS, R. G. Wilson, F. A. Stevie, and C. W. Magee, Wiley, New York (1989)

Matrix Effects



P in Si

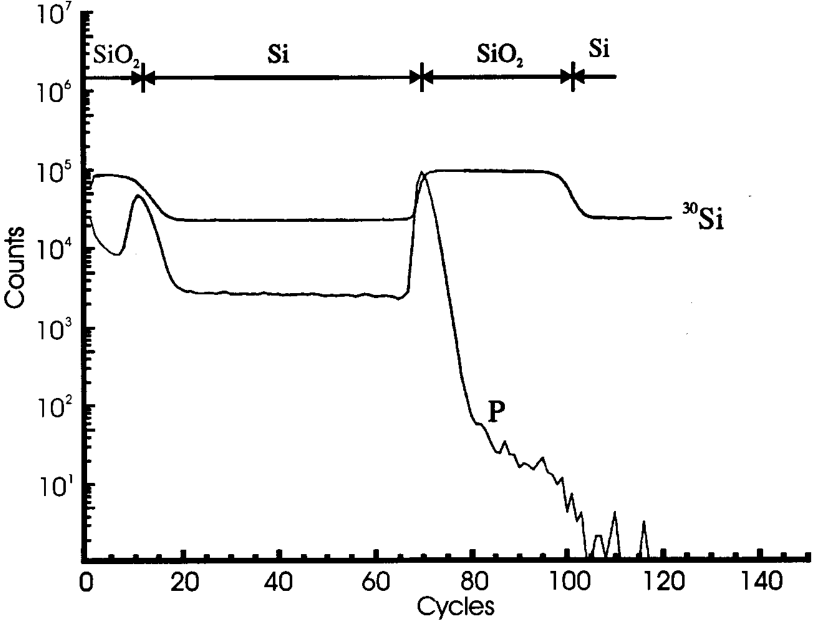


P in SiO_2 layer on Si

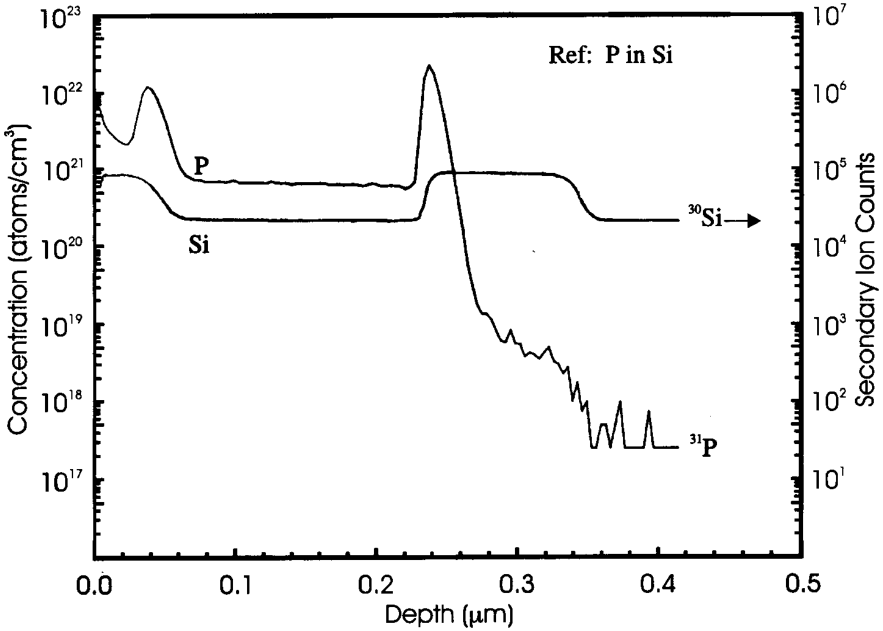
Same phosphorus dose for both samples

Note: x-axis scale is not the same

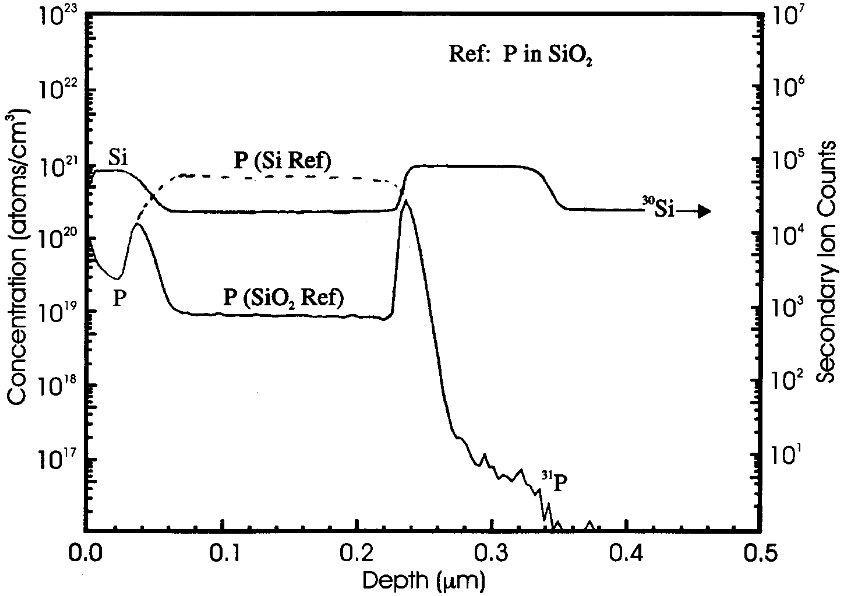
Matrix Effects



Raw data shows P peaks at interfaces



Referenced to P in Si



Referenced to P in SiO_2

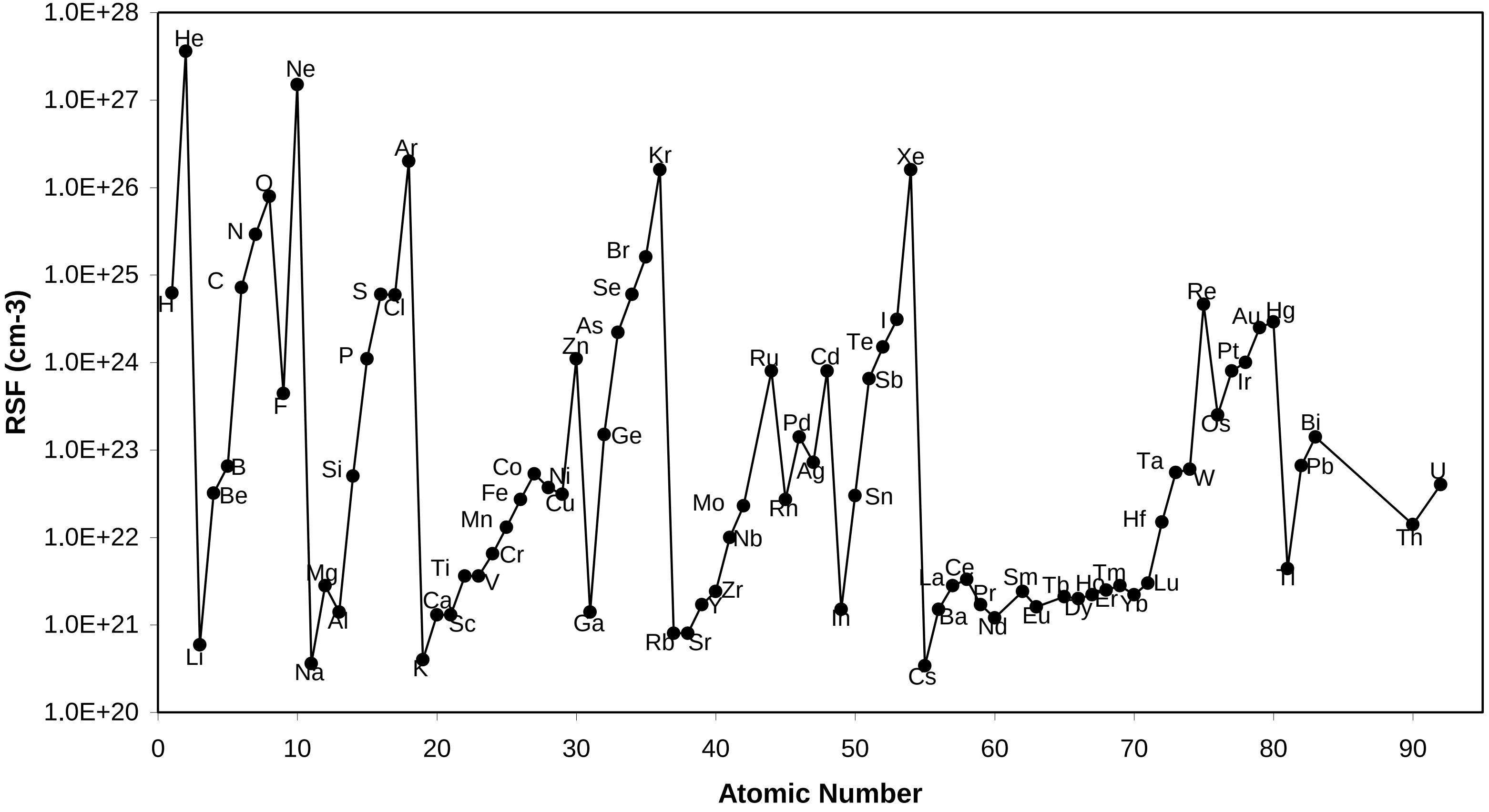
Dashed line composite shows no P peaks. P in Si increased because ion yield lower than in SiO_2

Secondary Ion Yield Variations

- Secondary ion yields vary by orders of magnitude over periodic table
- Secondary ion yields vary for different matrices
- RSFs are inversely proportional to secondary ion yields

Positive Secondary Ion Yields

O_2^+ 8keV, 80 elements implanted into silicon



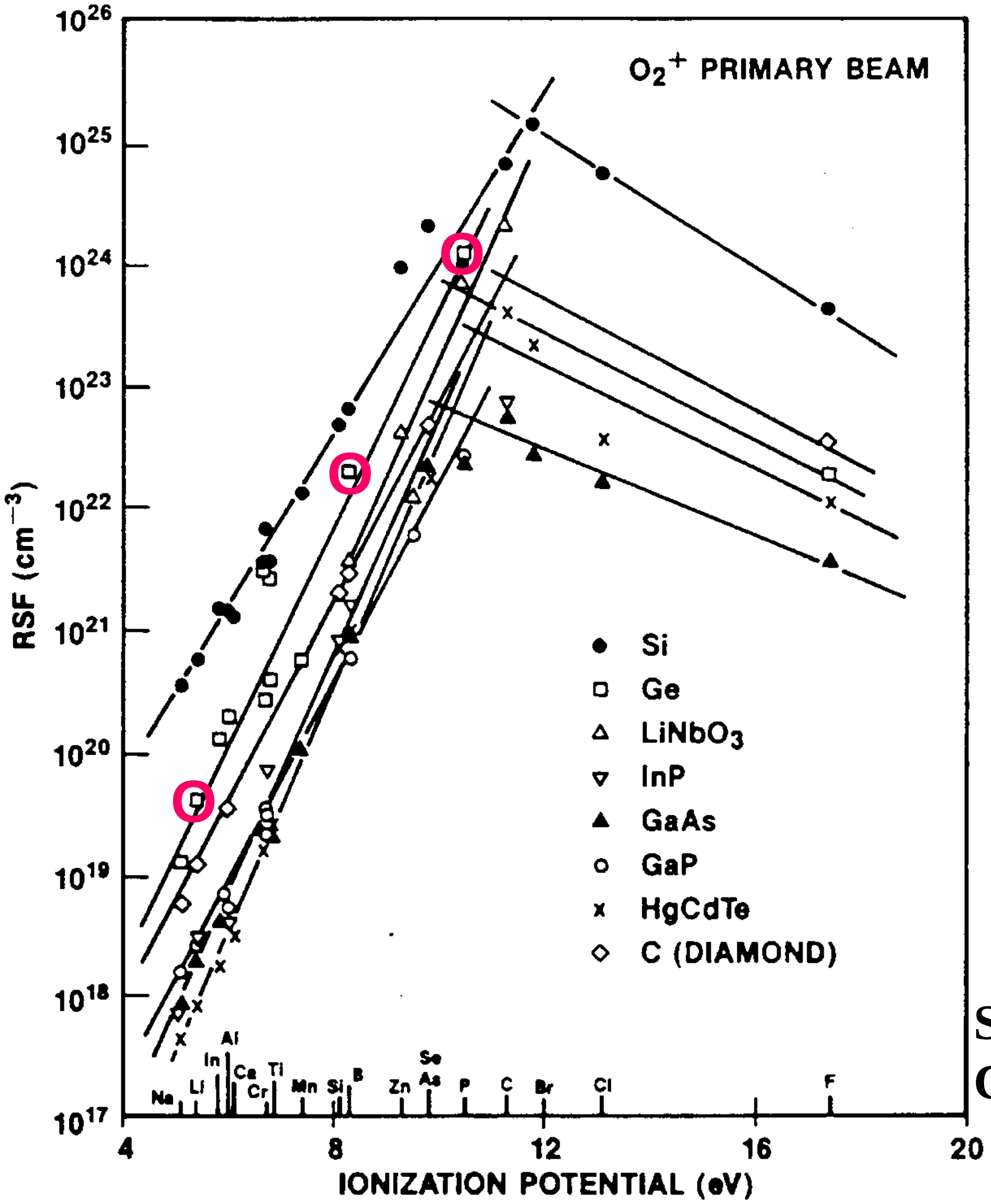
SIMS, R. G. Wilson, F. A. Stevie, C. W. Magee, Wiley, New York (1989)
F. A. Stevie and R. G. Wilson, J. Vac. Sci. Technol. A9 (1991) 3064
R. G. Wilson, F. A. Stevie, S. L. Chryssoulis, R. B. Irwin,
J. Vac. Sci. Technol. A12 (1994) 2415

RSF Patterns

Systematic patterns observed for

- secondary positive ions & ionization potential
- secondary negative ions and electron affinity

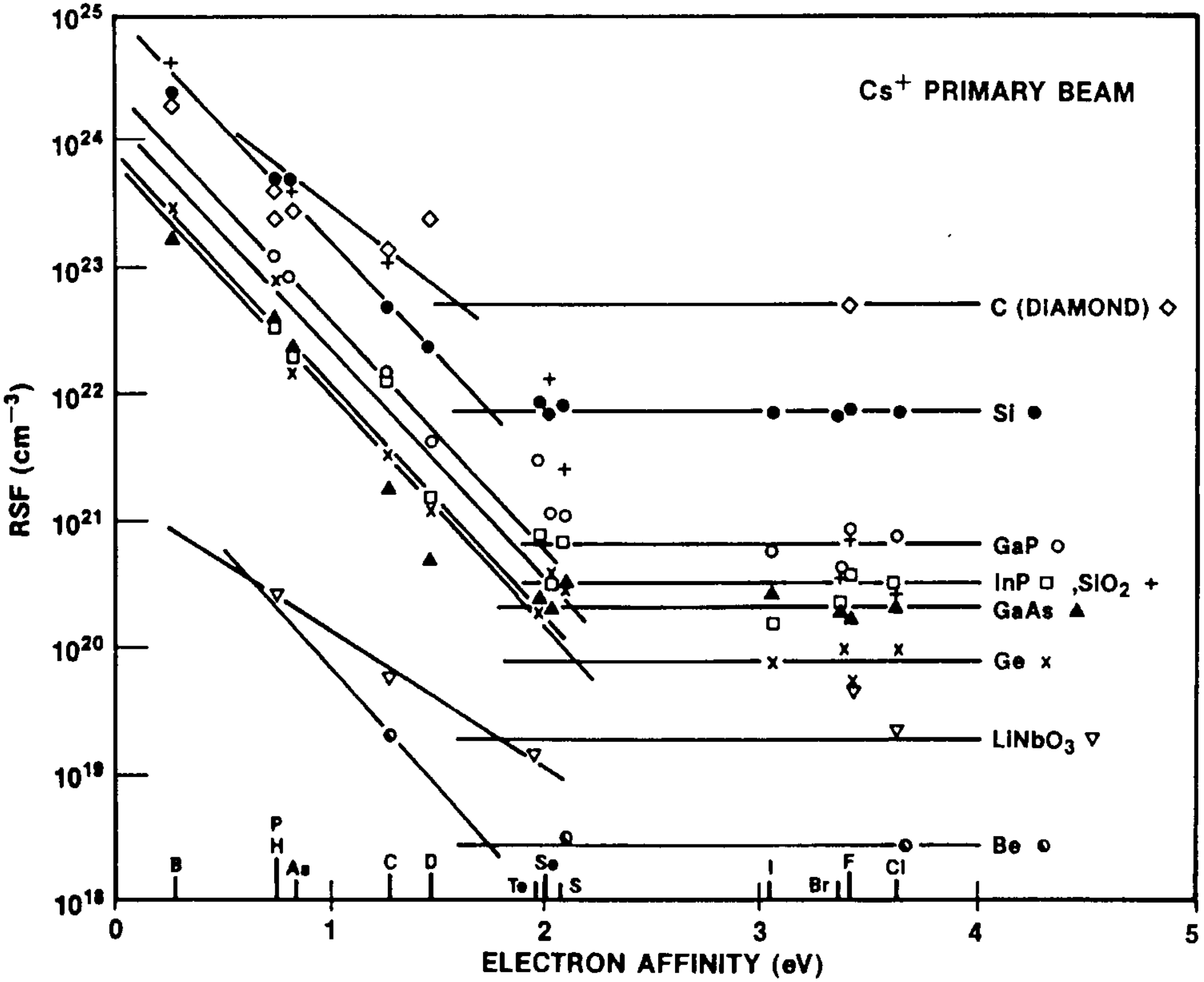
RSF Patterns



- O_2^+ bombardment positive secondary ion RSFs vs. ionization potential for 8 matrices
- Same pattern observed for all 8 matrices
- Implant three elements to define major line

SIMS, R. G. Wilson, F. A. Stevie, and C. W. Magee, Wiley, New York (1989)

RSF Patterns

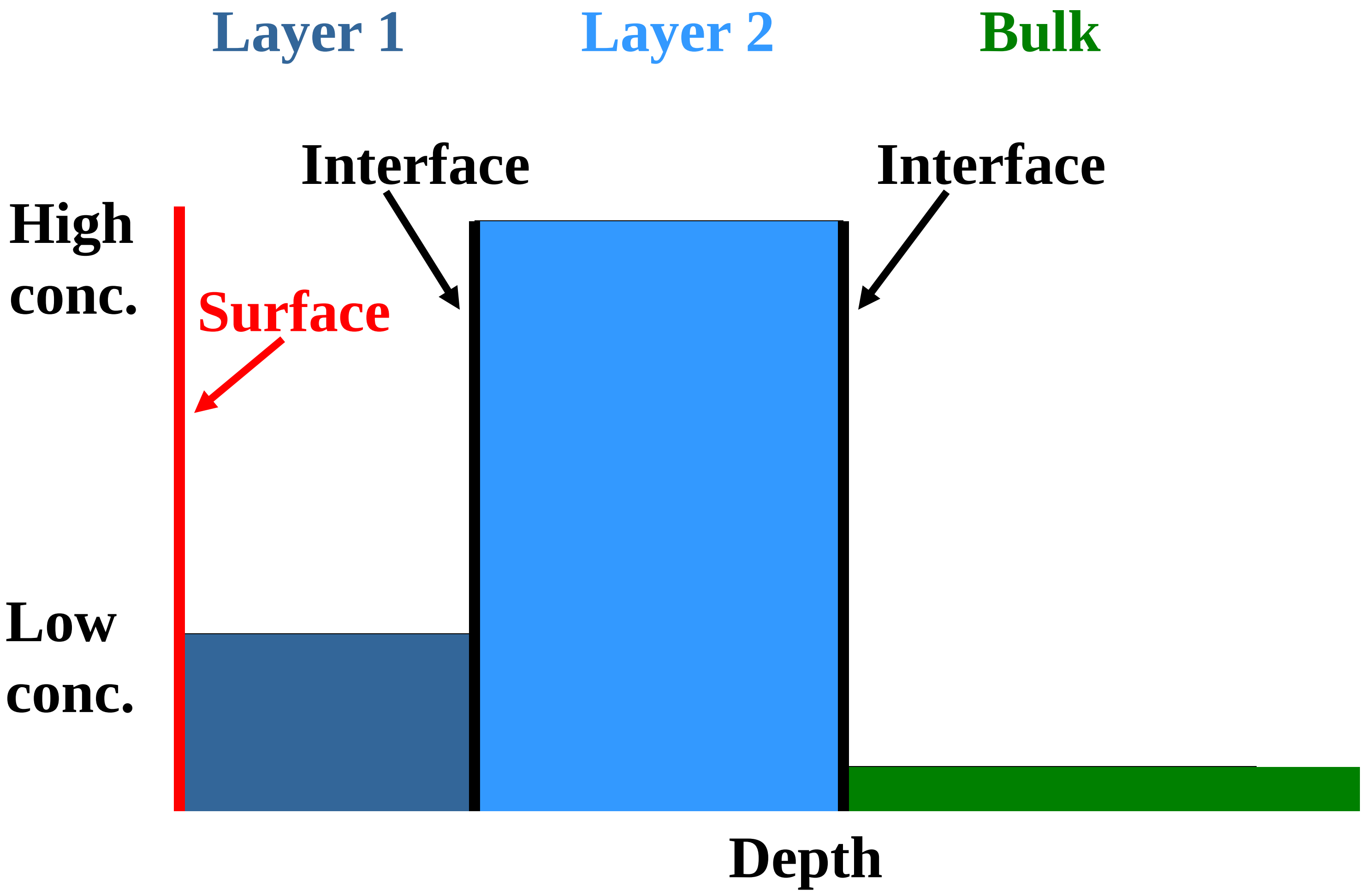


Cs$^+$ bombardment negative secondary ion RSFs vs electron affinity for 8 matrices

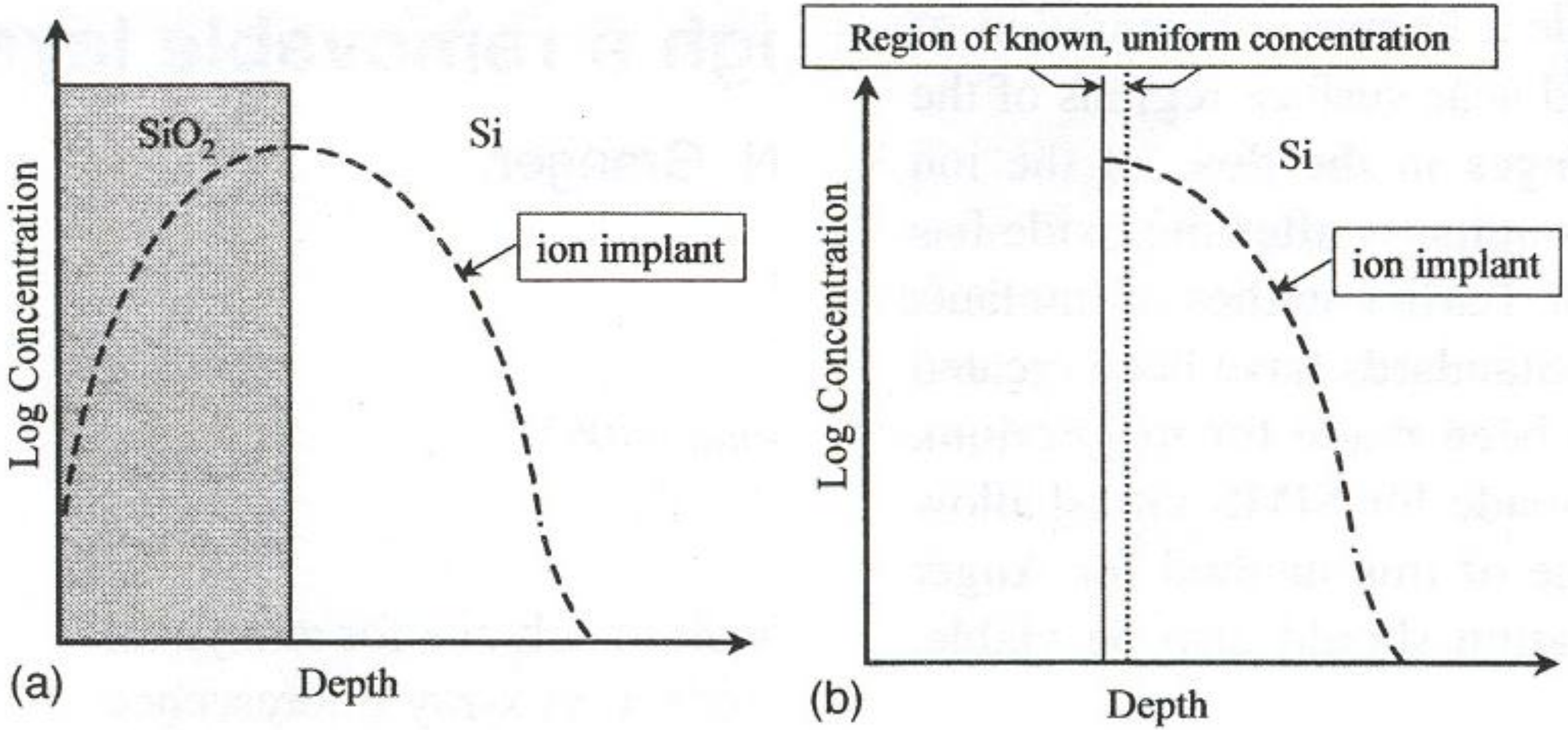
Same pattern observed for all 8 matrices

SIMS, R. G. Wilson, F. A. Stevie, and C. W. Magee, Wiley, New York (1989)

Quantification Regions



Implant Through Removable Layer



(a) Implant energy chosen to place implant peak at interface between layer and substrate

(b) After layer removed, known concentration at surface and near surface

F. A. Stevie, R. F. Roberts, J. M. McKinley, M. A. Decker, C. N. Granger, and R. Santiesteban, J. Vac. Sci. Technol. B18, 483 (2000)

TOF-SIMS of Implants Through SiO_2

Quantified with existing standards

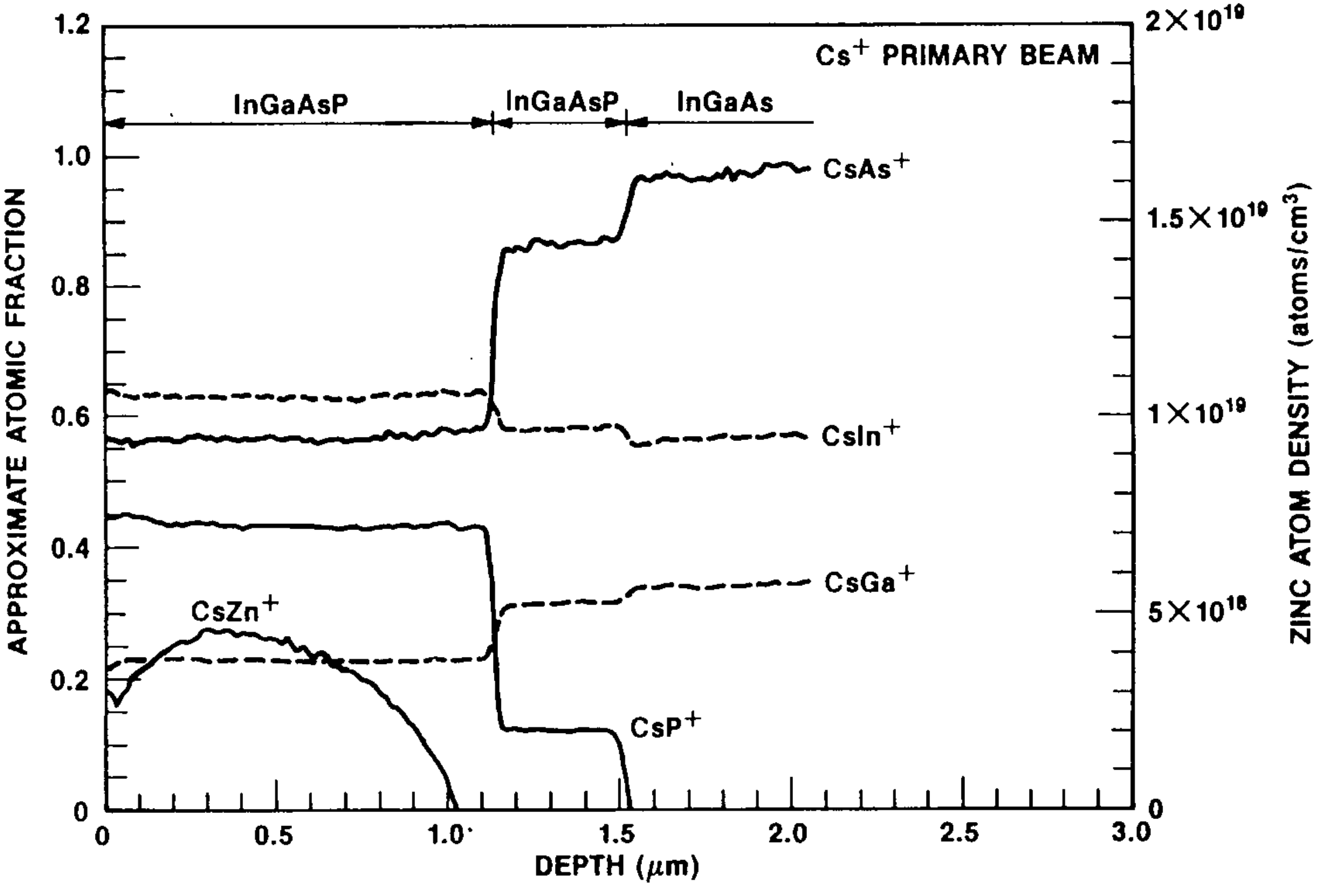
Species	Energy (keV)	Total Dose (at/cm^2)	Calc Dose 1nm	Meas Dose 1nm
^{31}P	74.5	1E14	1E12	9.1E11
^{75}As	160	1E14	1E12	1.0E12
^{24}Mg	56	1E14	1E12	8.6E11
^{27}Al	62	1E14	1E12	6.9E11
^{39}K	96	1E14	1E12	1.2E12
^{58}Ni	141	1E14	1E12	5.6E11
^{40}Ca	100	1E14	1E12	6.8E11
^{59}Co	137	1E14	1E12	7.2E11
^{48}Ti	110	1E14	1E12	6.3E11
^{56}Fe	131	1E14	1E12	8.9E11
^{63}Cu	147	1E14	1E12	1.7E12

0.1µm SiO_2
layer removed

Results within
factor of 2
for 11 elements

B. Schueler, Physical Electronics; I. Mowat, Evans Analytical Group

Matrix and Impurity Species Using Cs Molecular Ions



SIMS major element depth profile for In, Ga, As, and P, as well as trace depth profile for Zn. Use of Cs$^+$ primary beam with detection of positive secondary ions permits compositional analysis of matrix elements. Analyzed using a quadrupole instrument.

SIMS, R. G. Wilson, F. A. Stevie, and C. W. Magee, Wiley, New York (1989)

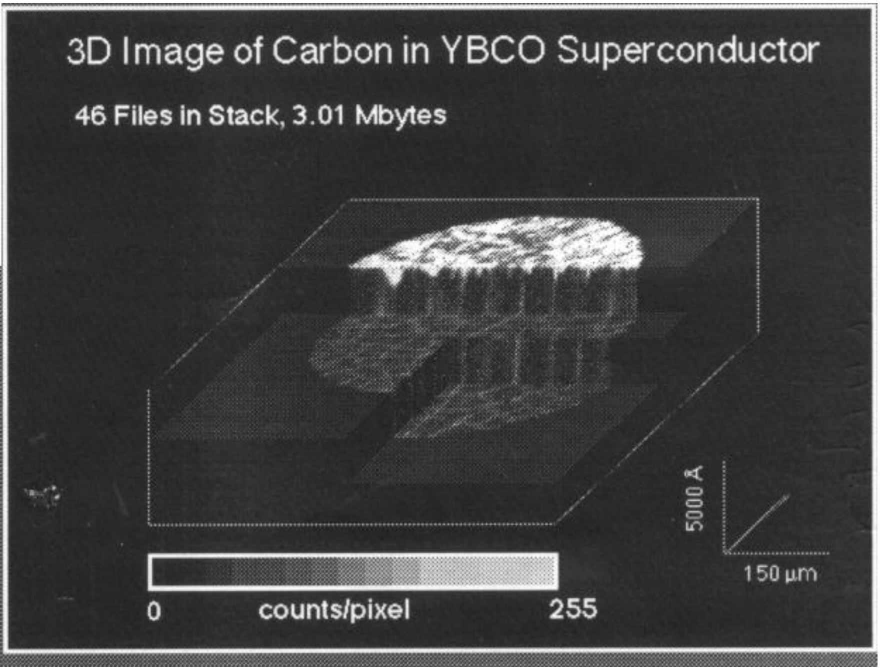
Quantitative 3-D Imaging

- Acquire image depth profile on implant, determine RSF
- Acquire image depth profile on sample of interest
- Images normalized to matrix ion species
- RSFs used to convert per pixel secondary ion intensity to concentration

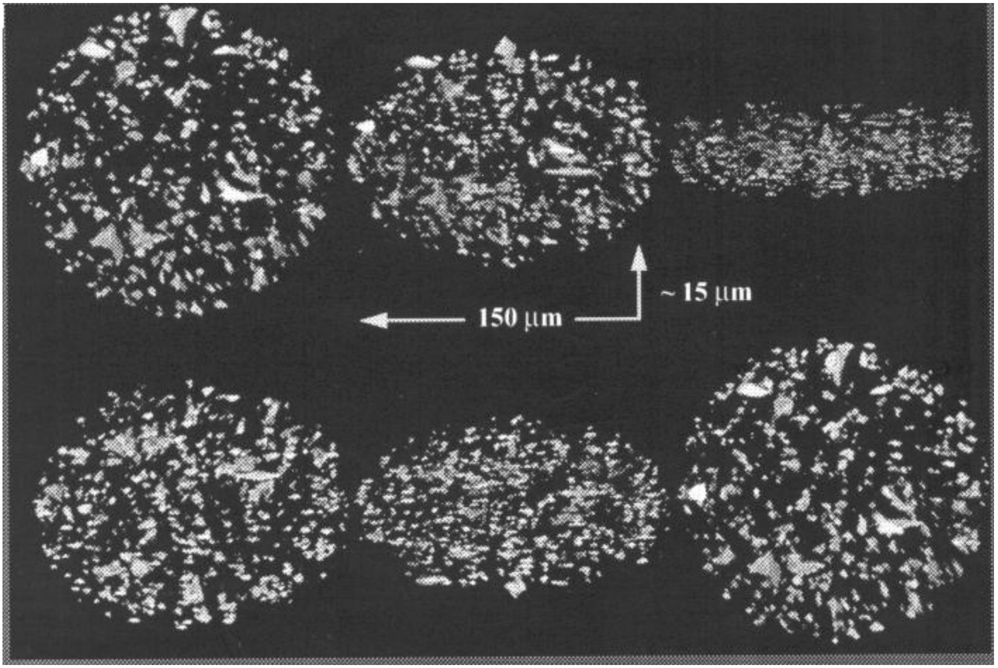
G. Gillen and R. L. Myklebust, SIMS VIII (1992) 509

Quantitative 3-D Image Depth Profiling

CAMECA IMS-3F or 4F; Microscope imaging with RAE (3F) or fast RAE/slow scan CCD camera (4F)



C in YBCO superconductor



Li particles in Ag (CCD camera)

G. Gillen and D. Bright, NIST

Quantitative 3-D Image Depth Profiling

Images normalized to matrix ion species

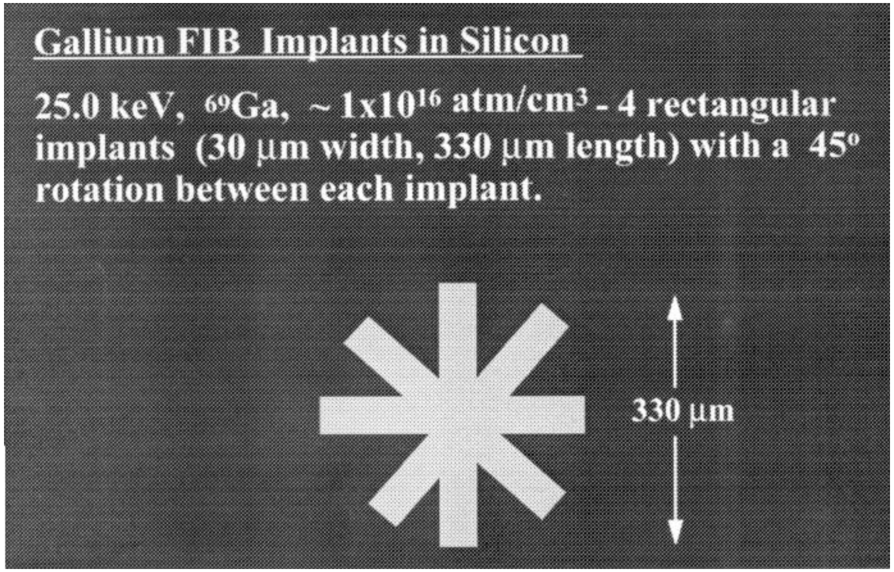
RSFs used to convert per pixel secondary ion intensity to atom density

Impurity density in atoms/cm^3 = $I_i/_m$ x RSF

where I_i = impurity isotope intensity (counts/s)

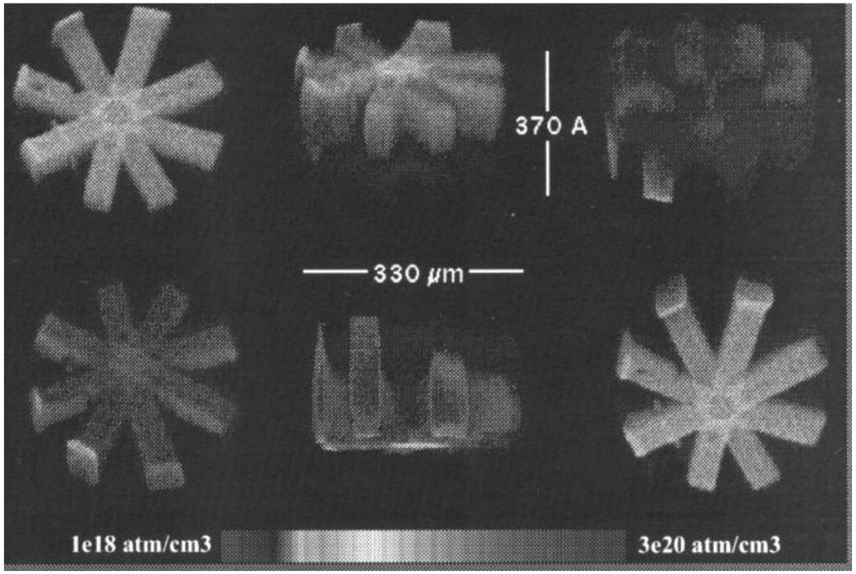
I_m = matrix isotope intensity (counts/s)

Gallium FIB Implants in Silicon



Gallium FIB Implants in Silicon

25.0 keV, ^{69}Ga, ~ 1x10^{16} atm/cm^3 - 4 rectangular implants (30 µm width, 330 µm length) with a 45° rotation between each implant.



G. Gillen and D. Bright, NIST