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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR.550 -16

SPRING COLLEGE IN MATERIALS SCIENCE ON
"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS SCIENCE AND ENGINEERING"
(6 May - 7 June 1991)

"STATIC AND DYNAMIC SIMS"

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These are preliminary lecture notes, intended only for distribution to participants.

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SIMS

Secondary Ion Mass Spectrometry

© Mark Dowsett
Dept of Physics
University of Warwick

Information Content

Ion Scattering

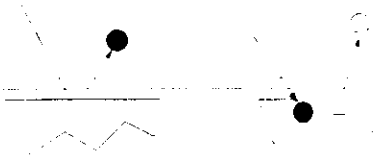
- *(Crystalographic) Structure*
- *(Lattice) Damage*
- *Atomic Composition*
  (Bulk ~1%)
  (Depth Profile or Surface)

Sputtering/MS

- *(Molecular) Structure*
- *Chemical Composition*
  (Bulk ~1:10^{10})
  (Depth Profile, Surface, 3-D Mapping)

Ion Beam Analysis
Techniques

Ion Scattering	Sputtering/ Mass Spectrometry
Acronyms	
LEIS	SIMS
ICSS	SSIMS
MEIS	FAB(MS)
RBS	SNMS(3 versions)
NRA	RIMS
PIXE	
Parameters	
Energy	Mass
Angle	Energy
Species (usually same in and out)	X,Y,t (Angle)



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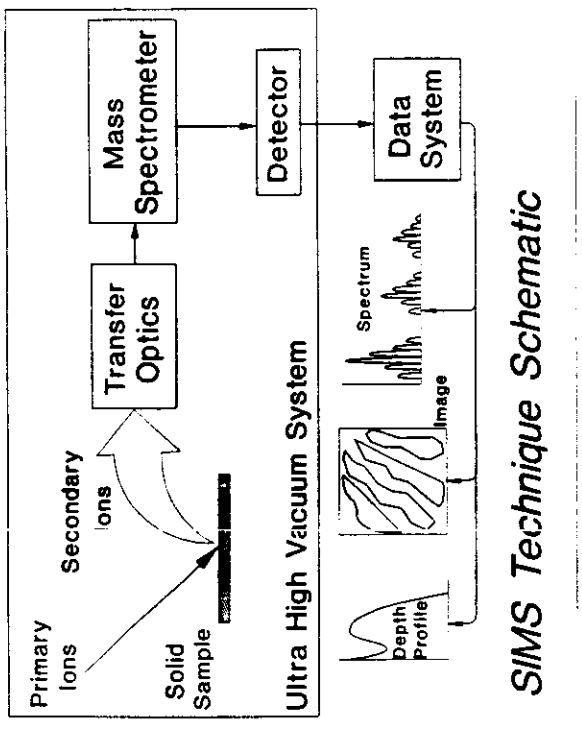
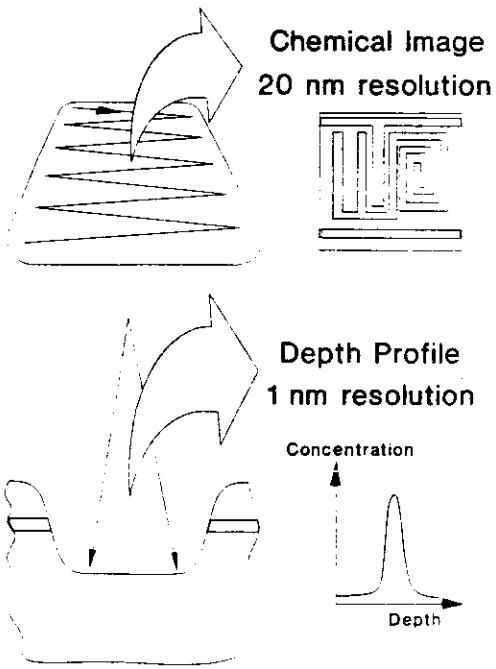


Depth Profiling and Imaging



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The SIMS Signal

$I_{X_i}^{\pm}$ = positive or negative ion flux detected for the i^{TH} isotope of element X

(similar considerations apply for molecular ions)

$$I_{X_i}^{\pm} = \dot{\Phi}_p Y A C_X \gamma_{X_i} \eta_X \epsilon_X \int_{\Delta E} \int_{\Omega} \alpha_X^{\pm}(\epsilon, \psi, \theta \ldots) n_X \, d\epsilon \, d\Omega$$

where

$\dot{\Phi}_p$ = flux density of primary ions (ions $m^{-2} s^{-1}$)

Y = total sputter yield (atoms/ion incident)

A = field of view (m^2)

C_X = fractional concentration of X in sample

γ_{X_i} = abundance of i^{TH} isotope of X (or equiv. for molecular ions)

η_X = transmission for X

ϵ_X = detector efficiency for X

$\alpha_X^{\pm}$ = degree of ionisation for X (ions/sputtered X) (for a particular energy and angle ψ, E)

Techniques

Destructive or Non-Destructive?

Destructive Technique

Sample consumption is intrinsic to analysis (i.e. determines analytical precision)

Non-Destructive Technique

Sample consumption is incidental to the analysis (but almost always limits analytical precision)

Useful Yield

$$\tau_x = \Gamma_x \, \alpha_x^{\phi} = n_x^{\phi} / N_x$$

τ_x - *useful yield of species X*

Γ_x - *instrumental collection/transmission/detection*

α_x^{ϕ} = $\frac{\text{no of X produced in charge state } \phi}{\text{total X in sputtered volume}}$

SIMS SIGNAL/CTD.

$n_x = n_x(E, \psi, \theta \ldots)$ = NORMALIZED ENERGY AND ANGULAR DISTRIBUTION OF SPUTTERED PARTICLES:

$$\left(\int n_x(E, \psi, \theta \ldots) \, dE \, d\Omega = 1 \right)$$

To SIMPLIFY:-

~~$I_{x_i}^{\pm} = C_{x_i} \gamma_{x_i} Y \langle \alpha_x^{\pm} \rangle \Gamma_x^{\pm} \dot{\phi}_p$~~

~~WHERE $\Gamma_x^{\pm}$ IS AN INSTRUMENT AND SPECIES DEPENDENT PARAMETER~~

~~USEFUL YIELD $\tau_x = \langle \alpha_x^{\pm} \rangle \Gamma_x^{\pm}$~~

$$I_{x_i}^{\pm} = C_x \gamma_{x_i} Y \langle \alpha_x^{\pm} \rangle \Gamma_x^{\pm} \dot{\phi}_p$$

WHERE $\Gamma_x^{\pm}$ IS AN INSTRUMENT COLLECTION/TRANSMISSION/DETECTION EFFICIENCY FOR SPECIES X

τ_x = USEFUL YIELD = $\langle \alpha_x^{\pm} \rangle \Gamma_x^{\pm}$

Precision and Sensitivity

$$C_x = \frac{n_x}{N \Gamma_x \alpha_x}$$

C_x - *fractional atomic concentration of species X*

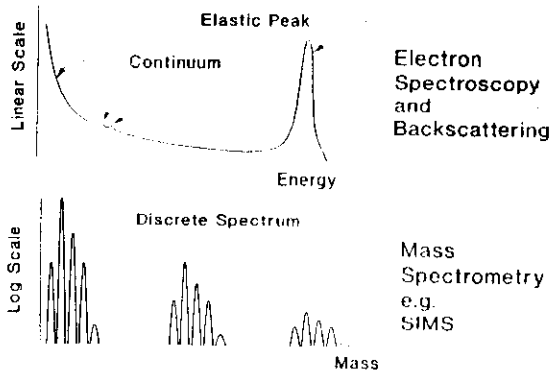
n_x - *no. of ions of X detected*

N - *no. of sample atoms consumed*

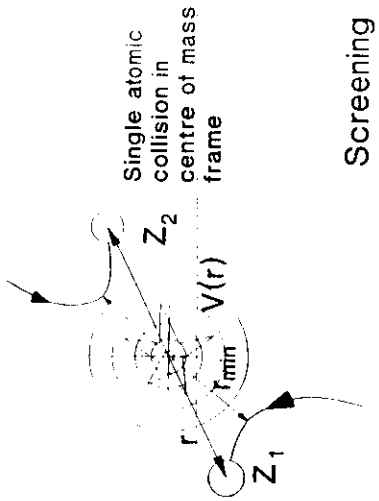
Γ_x - *instrumental collection/transmission/detection*

α_x - *emission probability for ion detected*

SIMS has a much larger dynamic range and sensitivity than most other techniques, because a mass spectrum is discrete and inherently background free. In competeing techniques, the data often appear as small perturbations on a continuum....



Interatomic Potential (Energy)



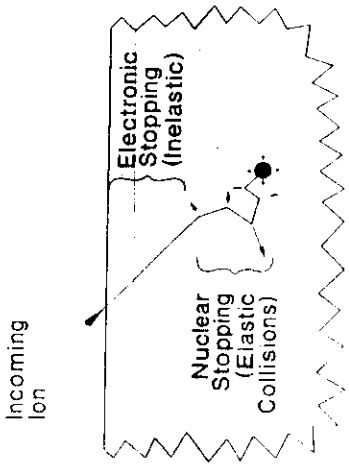
Screening Function

— Coulomb Term

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \Phi(r)$$

For calculation of $\Phi(r)$ see Zeigler et al.

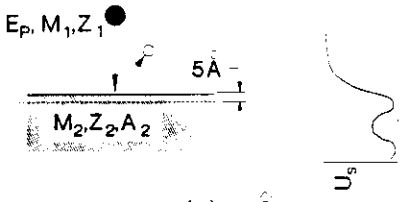
Stopping of keV ions in a solid



In the energy range used in SIMS (0.5-20keV), the nuclear stopping is dominant

For more information see "The Stopping and Range of Ions in Solids" F F Ziegler, J P Biersack, and U Littmark, Pergamon Press (1985).

Sputtering: Sigmunds Formula



$$Y = 0.7\, A_2\, \alpha(\mu)\, \frac{S_n(\epsilon)}{U_s}\, \frac{\hat{\rho}}{\hat{\epsilon}} \text{ atoms/ion}$$

A_2 - atomic no. of target

μ - M_1/M_2 where M_1 and M_2 are masses of ion and target atoms resp. (gm!)

$\alpha(\mu)$ - see below

$S_n(\epsilon)$ - reduced nuclear stopping cross section - see below

$$\epsilon = \frac{32.5\, E_p\, M_2}{(M_1+M_2)\, Z_1 Z_2 (Z_1^{2/3}+Z_2^{2/3})^{1/2}} \qquad \hat{\epsilon} = \frac{\epsilon}{E_p}$$

E_p - primary ion energy (/keV)

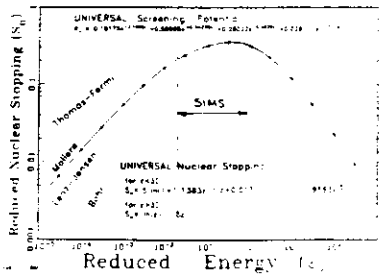
Z_1, Z_2 - atomic no. of ion and target resp.

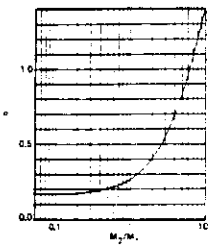
U_s - surface binding energy

$$\rho = \frac{166.8\, M_1 R}{(M_1+M_2)(Z_1^{2/3}+Z_2^{2/3})} \qquad \hat{\rho} = \frac{\rho}{R}$$

R - ion range ($\mu g/cm^2$) = $10^5 \times N M_2$, where x=range (cm) and N=no of atoms/cm^3

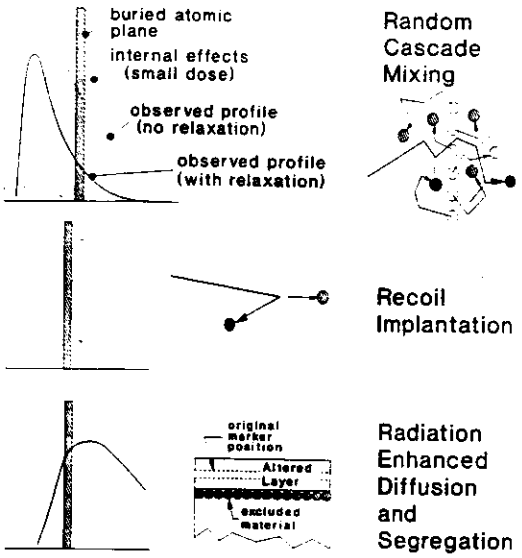
Sputtering contd...



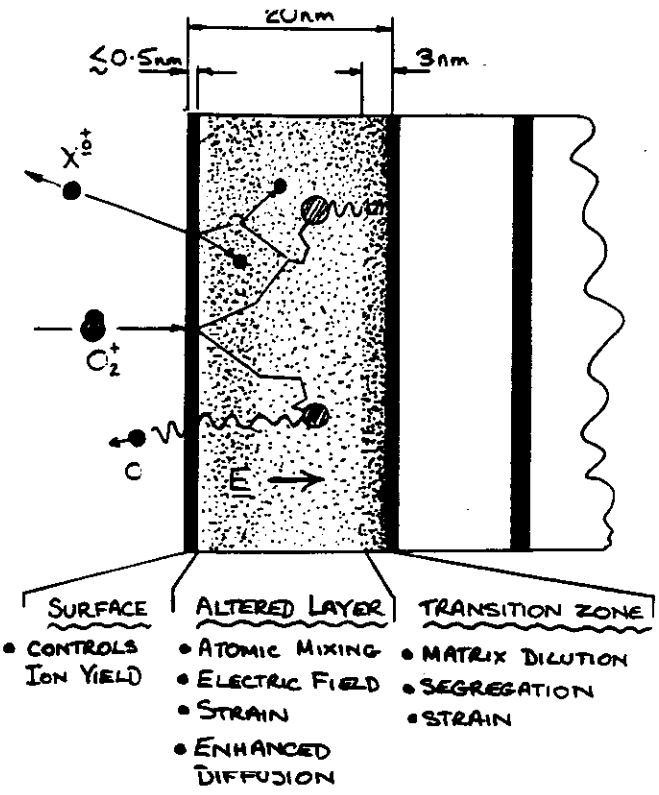


See: P Sigmund, Phys Rev 184 1969 383-415
J Lindhard, M Scharff and H E Schiott: Mat Fys Medd Dan Vid Selsk 33 (1963) 1-42
Ziegler et al op cit.

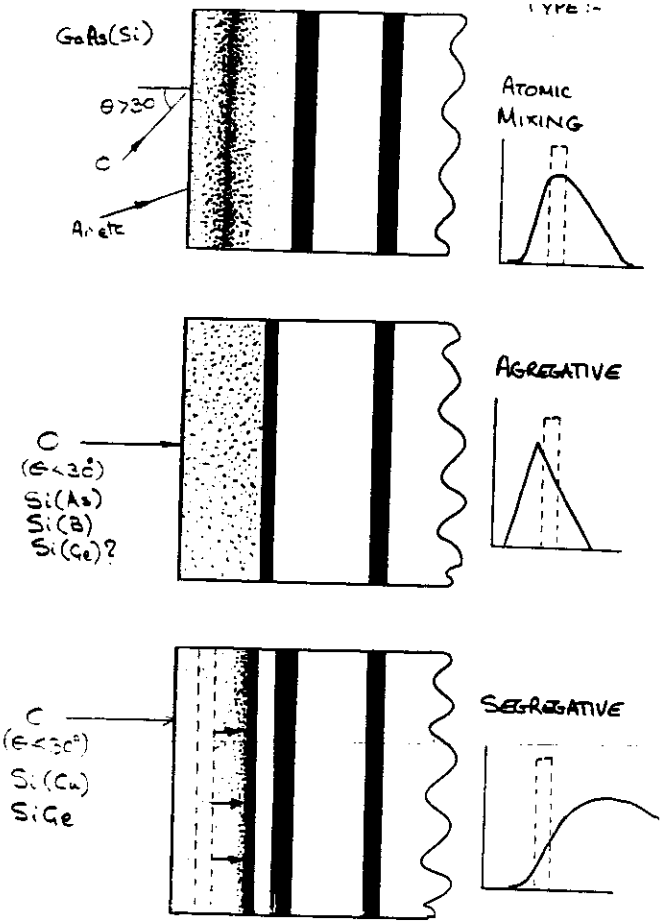
Atomic Mixing Effects - Schematic

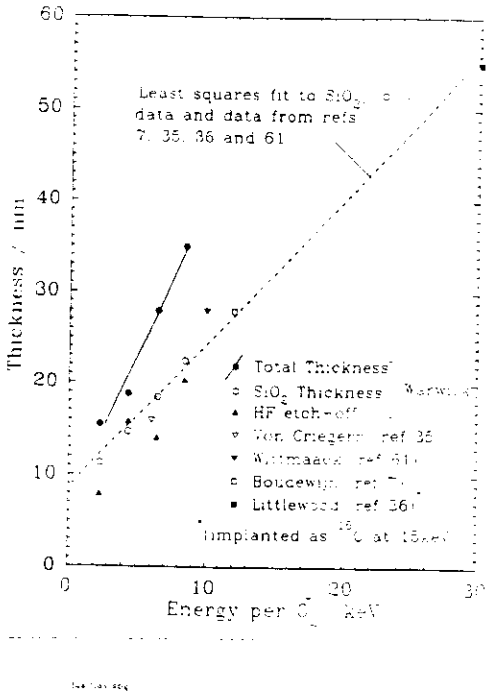


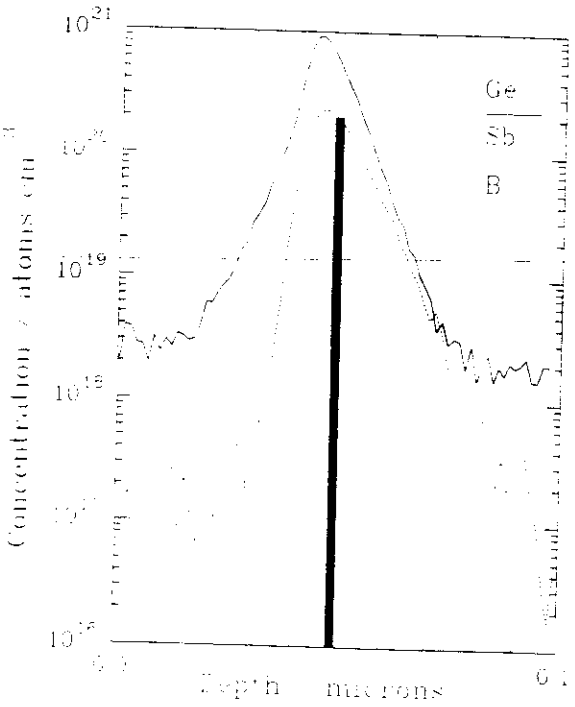
See: U Littmark and W O Hofer, NIM 168 (1980) 329-342
P Sigmund and A Gras-Marti, NIM 182/183 (1981)25-41
B V King and I S T Tsong, J Vac Sci Technol A2(4) (1984) 1443-1447
K Wittmaack and N Menzel, Appl Phys Lett 50 (1987) 815-817

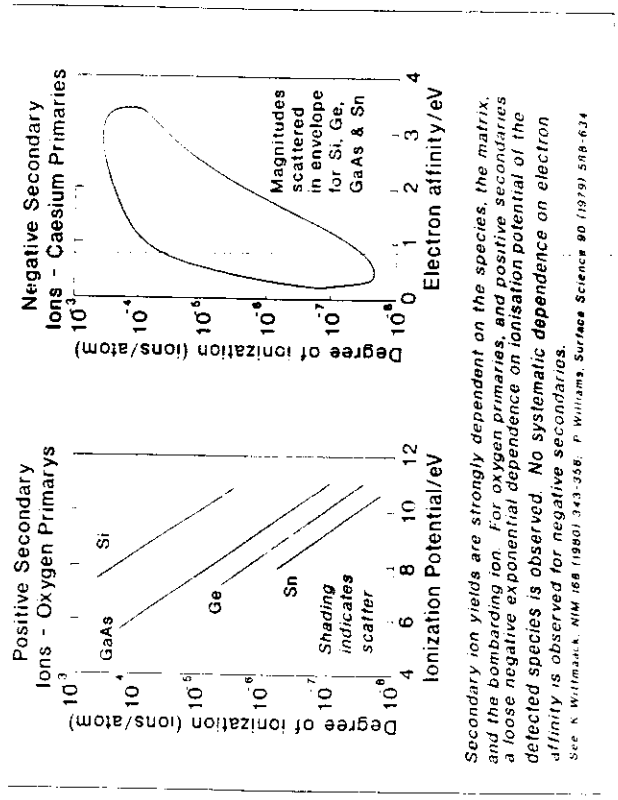


EFFECT OF THE ALTERED LAYER









Secondary ion yields are strongly dependent on the species, the matrix, and the bombarding ion. For oxygen primaries, and positive secondaries a loose negative exponential dependence on ionisation potential of the detected species is observed. No systematic dependence on electron affinity is observed for negative secondaries.

See K. Wittmaack, NIM 168 (1980) 343-358. P. Williams, Surface Science 90 (1979) 588-634

Newton's and Helmholtz-Lagranges' Equations

Linear Magnification = h'/h = -x'/f' = -f/x

So xx' = ff' (Newton's Eqn.)

And nhtan α = n'h'tan α' (Helmholtz-Lagrange Eqn.)

Simple Einzel Lens

Principal and Focal Planes

Example of Secondary Ion Emission Process

"Kinetic" model of Joyes

● clean metal surface.
●● inert gas bombardment
●●● E_s>30eV

[P Joyes, J de Phys (Paris) 30 (1969) 365.

For further details of secondary ion emission models see A Benninghoven, F G Rudenauer, and H W Werner: "Secondary Ion Mass Spectrometry", John Wiley and Sons, New York, (1987) Chapter 3.

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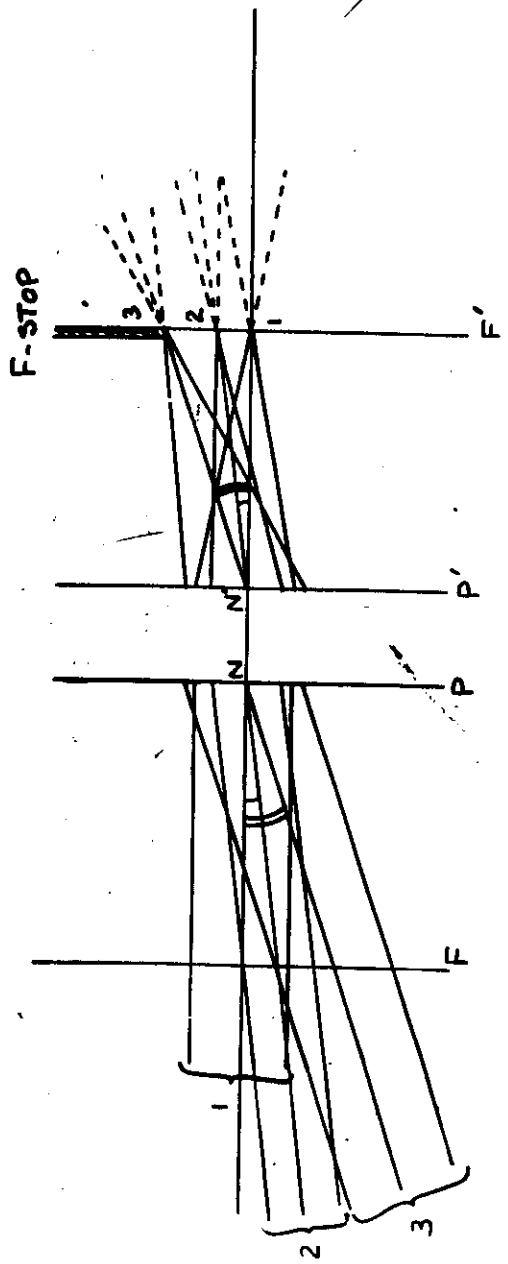
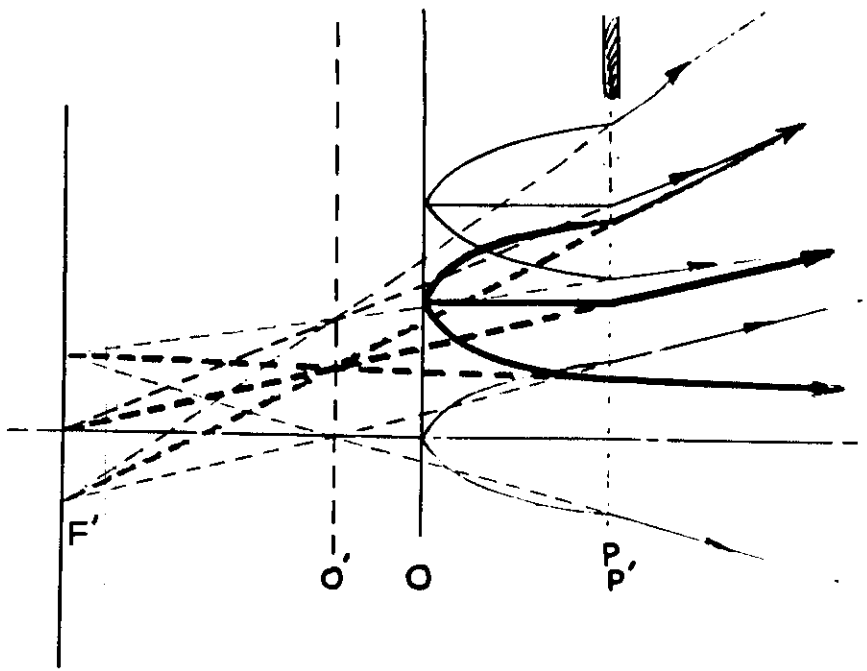
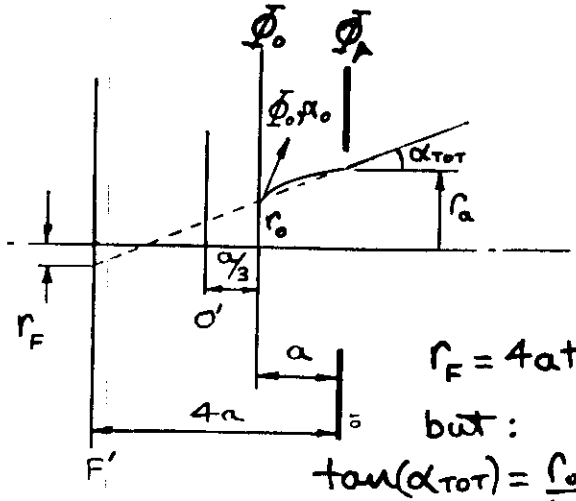
See K Wittmaack, NIM 168 (1980) 343-356. P Williams, Surface Science 90 (1979) 588 634



ANGLE DEFINING APERTURE IN FOCAL PLANE OF SYSTEM





$$r_F = 4a\tan(\alpha_{TOT}) - r_a$$

but:

$$\tan(\alpha_{TOT}) = \frac{r_o}{4a} + \frac{3}{2}\sin\alpha_o\sqrt{\frac{\Phi_o}{\Phi_A}}$$

and $$r_a = r_o + 2a\sin\alpha_o\sqrt{\frac{\Phi_o}{\Phi_o}}$$

REAL IMAGE OF PUPIL

Solving eqns of motion directly:-

$$r = \frac{-2a\Phi_0 \sin^2\alpha_0}{(\Phi_A-\Phi_0)\tan\alpha_0} + \frac{2a\Phi_0\sin^2\alpha_0}{(\Phi_A-\Phi_0)}\sqrt{\frac{1}{\tan^2\alpha_0} + \frac{(\Phi_A-\Phi_0)z}{\Phi_0\sin^2\alpha_0}} + r_0$$

if $\Phi_0/\Phi_A \ll 1$ as before and putting $\sqrt{\frac{\Phi_0}{\Phi_A}} = n$

$$r = -\frac{2an^2\sin^2\alpha_0}{\tan\alpha_0} + 2an^2\sin^2\alpha\sqrt{\frac{1}{\tan^2\alpha} + \frac{1}{n^2}\frac{z}{\sin^2\alpha}} + r_0$$

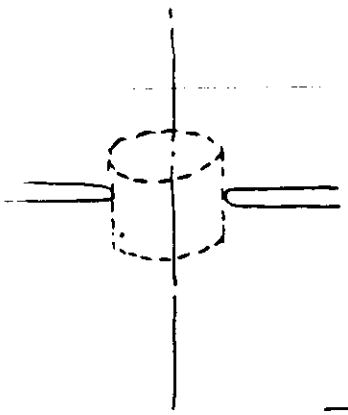
neglecting terms containing n^2 and higher powers...

$$r = r_0 + 2\sin\alpha_0\sqrt{\frac{\Phi_0}{\Phi_a}}\sqrt{az}$$

$$\text{also} \quad r' = \sin\alpha_0\sqrt{\frac{\Phi_0}{\Phi_A}}$$

} i.e. as before but with $\sin\alpha_0$ in place of r_0' $(\tan\alpha_0)$

CV



P.T.O.

(ii) In the aperture:

$$r_a = r_0 + 2r_0'\sqrt{\frac{\Phi_0}{\Phi_a}}\,a \quad \text{when } \Phi_0 \text{ now} = \bar{\Phi}_0$$

and $r_a' = r_0'\sqrt{\frac{\Phi_0}{\Phi_a}}$

is great then

If voltages are measured with respect to Φ_A (but emitted particle have small energy spn of emission $\Phi_{0_A} \neq 0$ and $\frac{\Phi_{0_A}}{\Phi_a} \ll 1$ ie total acceleration

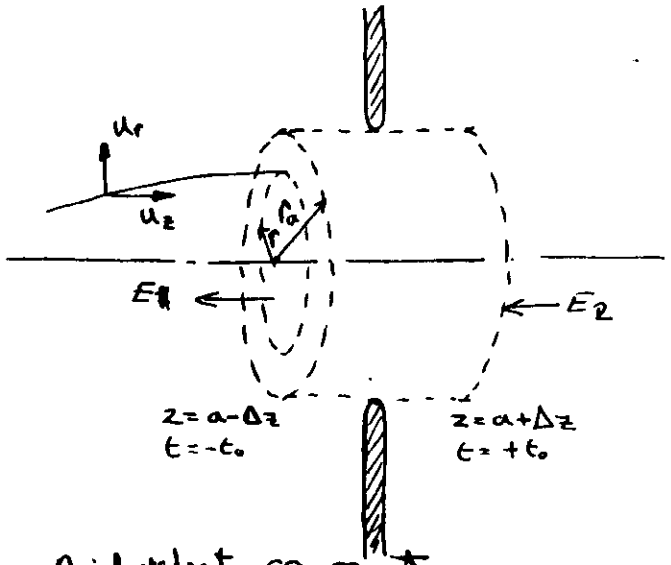
PARTICLE 0 energy

$$r(a) = \frac{2r_0'\sqrt{\Phi_0}\sqrt{k.a+\Phi_0}}{k} + r_0 \quad \left(\text{remember } k = (\bar{\Phi}_a - \bar{\Phi}_0)\right.$$

$$= r_0 + \frac{2r_0'\sqrt{\Phi_0\bar{\Phi}_0}}{\bar{\Phi}_a - \bar{\Phi}_0}\cdot a \quad (5)$$

At the anode $r(2) = r(a) = r_a$.

OF COURSE, IF $\bar{\Phi}_0 = 0$ THEN $r'(a) = 0$ and $r(a) = r_0$ SINCE TRAJECTORIES WILL BE STRAIGHT LINES.



Axial velocity component

$$u_z^2 = \frac{2e}{m}(\bar{\Phi}_A - \bar{\Phi}_0) = \frac{2e}{m}\bar{\Phi}_A \quad \text{; } \int \text{ paths measured}$$

Radial force acting on particle in cylindrical zone:

$$\frac{d}{dt}(mu_r) = -eE_r \qquad \frac{dr}{dt} = f$$

$$u_r = \frac{-e}{m}\int_{-t_0}^{+t_0} E_r\, dt$$

need to rewrite integral using fact that $u_z = \frac{dz}{dt} = \text{const}$

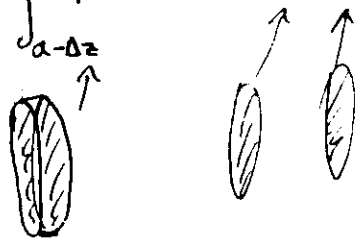
(8) $$u_r = \frac{-e}{mu_z}\int_{-z_0(=a-\Delta z)}^{+z_0(=a+\Delta z)} E_r\, dz$$

since $\frac{dz}{u_z} = \frac{dt}{dt}$ etc

Now:

Apply Gauss' theorem to aperture region $\int_{S'} E\cdot da' = \Phi_0$ for no charge enclosed

$$2\pi r \int_{a-\Delta z}^{a+\Delta z} E_r \cdot dz + \pi r^2 (E_1 - E_2) = 0$$



so $$-\int_{a-\Delta z}^{a+\Delta z} E_r \cdot dz = \frac{r}{2}(E_1 - E_2) \qquad (9)$$

substituting for (8) $\int$ in 8 get

$$u_r = \frac{\pm e}{mu_z}\cdot\frac{r}{2}(E_1 - E_2) \qquad (10)$$

if $E_2 = 0$ then $u_r = \frac{e}{mu_z}\frac{r}{2}\cdot E_1$ (10a)

but $u_z^2 = \frac{2e}{m}(\bar{\Phi}_a - \bar{\Phi}_0)$ from Newton's law (11)

dividing 10a by 11

$$\frac{u_r}{u_z} = \frac{E_1}{4(\bar{\Phi}_a - \bar{\Phi}_0)}\, r$$

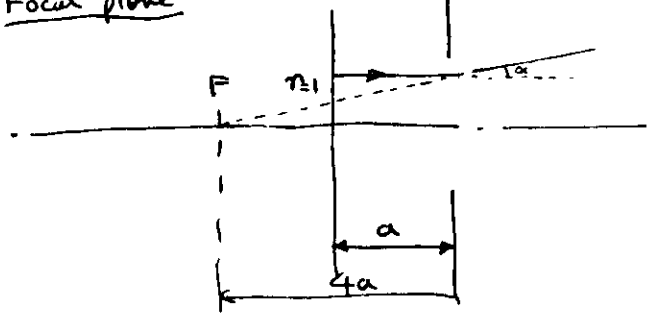
$\frac{u_r}{u_z} = r'$ (= slope by definition) $= r_{a+}$

so $r'_{a1} = \frac{E_1 r}{4(\bar{\Phi}_a - \bar{\Phi}_o)} = \frac{r}{4a}$ ie (12)

ie r'_{a+} (= $\tan\alpha$) $= \frac{r}{4a}$ ie $-\frac{1}{f} = \frac{1}{4a}$

Imaging properties:-

Focal plane



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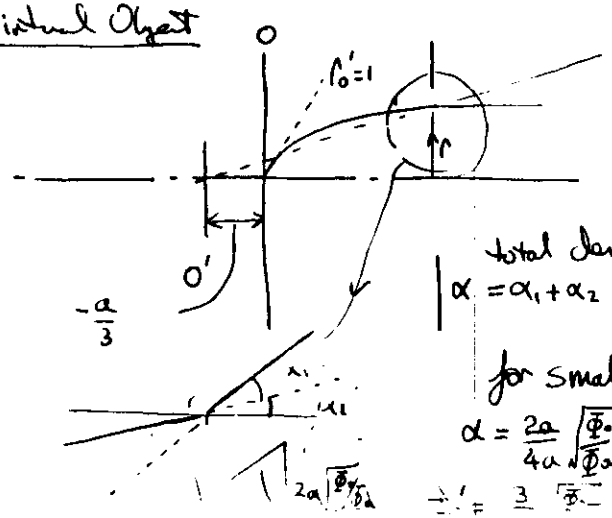
Virtual Object



from (6) + (7)

$r = 2a\sqrt{\frac{\bar{\Phi}_o}{\bar{\Phi}_a}}$

$r'_{(a)} = \sqrt{\frac{\Phi_o}{\Phi_a}} = \alpha_2$

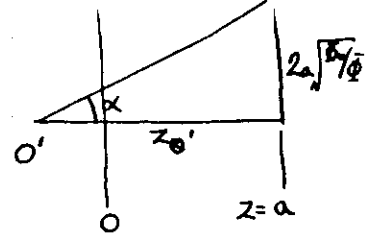
total deviation

$\alpha = \alpha_1 + \alpha_2 = \frac{r}{4a} + \sqrt{\frac{\Phi_o}{\Phi_a}}$

for small angles.

$\alpha = \frac{2a}{4a}\sqrt{\frac{\bar{\Phi}_o}{\bar{\Phi}_a}} + \sqrt{\frac{\Phi_o}{\Phi_a}} = \frac{3}{2}\sqrt{\frac{\bar{\Phi}_o}{\Phi_a}}$

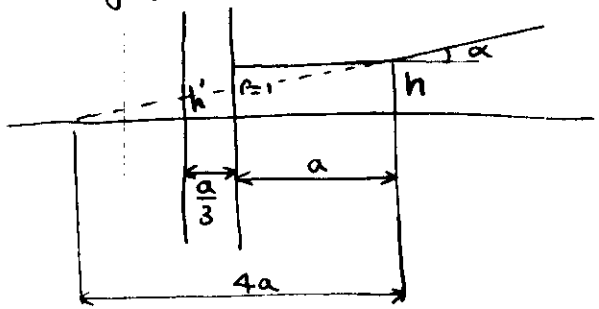
$\therefore r' = \frac{3}{2}\sqrt{\frac{\bar{\Phi}_o}{\Phi_a}}$



$z_o = 2a\sqrt{\frac{\bar{\Phi}_o}{\bar{\Phi}}} \Big/ \tan\alpha = \frac{4a}{3}$

$\therefore O'O = \frac{4a}{3}$.

Magnification. — similar Δs



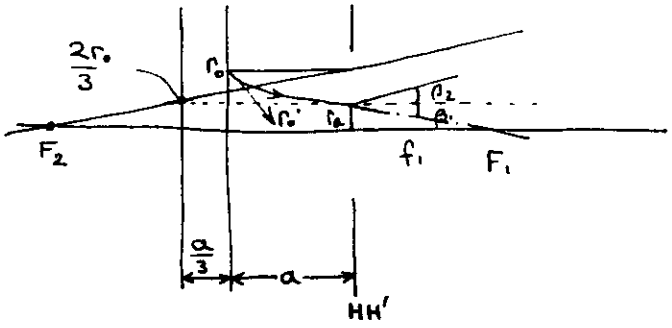
$\frac{h'}{h} = \frac{3a - a/3}{4a}$

$= \frac{8a}{3.4a}$

$= \frac{2}{3}$

Meaning Pupil Behavior.

Both Focii and Principal Planes of D-C lens.



$$r_a = \frac{2r_0}{3} = r_0 + 2a\sqrt{\frac{\Phi_0}{\Phi_A}}\,\sin\alpha_0$$

$$\therefore \quad \sin\alpha_0 = -\frac{r_0}{6a}\sqrt{\frac{\Phi_A}{\Phi_0}}$$

$$\beta_1 = r_{a-} = \sin\alpha_0\sqrt{\frac{\Phi_0}{\Phi_a}} = -\frac{r_0}{6a}$$

$$\beta_2 = \frac{r_a}{4a} = \frac{r_0}{6a}$$

$$\Rightarrow \quad \frac{r_a}{f_1} = \frac{r_0}{6a}$$

$$\therefore f_1 = 4a$$

Types of Mass Spectrometer Used in SIMS

	Double Focussing Magnetic Sector	Quadrupole	Time of Flight
Application Static/Dynamic	Dynamic (mostly)	Both	Static
Mass Resolution	1000->50,000	1000	1000 - 10000
Extraction Field	Strong 1000's V/mm	Weak 10's V/cm	Strong 1000's V/mm
Useful Yield (Maximum)	0.1	0.01	0.1
Main Applicat ons	Depth Profiling and Geological	General Purpose, Basic Phys.cs	Surface Analysis, Biological

See: Slodzian, Op Cit., K Wittmaack, Vacuum 32 (1982) 65-89, and Benninghoven, Rudenauer and Werner, Op Cit.

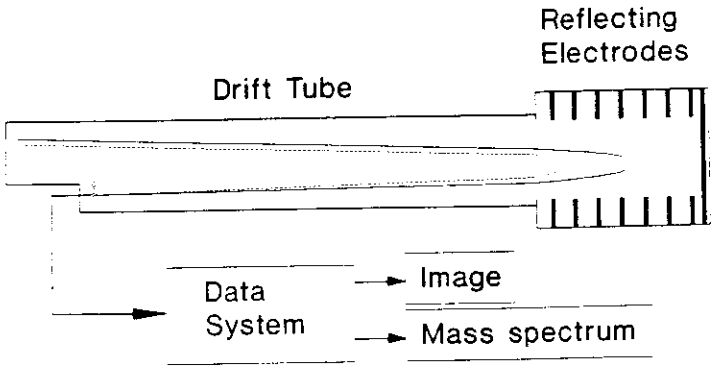
Secondary Ion Column (Transfer Optics) with Dynamic Emittance Matching

After: G Slodzian, Proc SIMS VI, John Wiley and Sons (1988) 3-12
See also: G Slodzian in Applied Charged Particle Optics, Advances in Electronics and Electron Physics Suppl. 13B, Academic Press (1980) 1-44 and H Liebl, Inst Phys Conf Ser No 38 (1978) 266-281

Ion Species used in SIMS

- Inert Gas - Argon, Xenon
  - *Static and Dynamic SIMS*
  - *Xenon used for high depth resolution*
  - *Duolasmatron, Penning or Electron Impact Source*
- Reactive Gas - Oxygen
  - *Dynamic SIMS*
  - *Use O_2^+ or O^- species*
  - *Enhances positive ion yields*
  - *Duoplasmatron or Penning Ion Sources*
- Reactive Gas - Caesium
  - *Dynamic SIMS*
  - *Enhances negative ion yields*
  - *Surface Ionisation Source*
- Liquid Metal - Gallium
  - *High resolution imaging*
  - *Liquid Metal ion Source*
- Others - CF_4^+, Cl^-, In, N_2^+ .....

Schematic Diagram of a Reflectron Time-of-Flight (TOF) Mass Spectrometer



See for example: E Niehuis, T Heller, H Field and A Benninghoven, Proc SIMS V, Springer Verlag (1986) 188-190

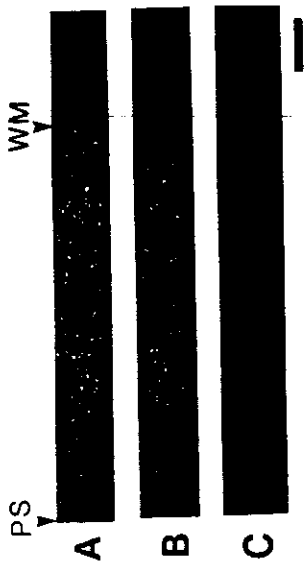
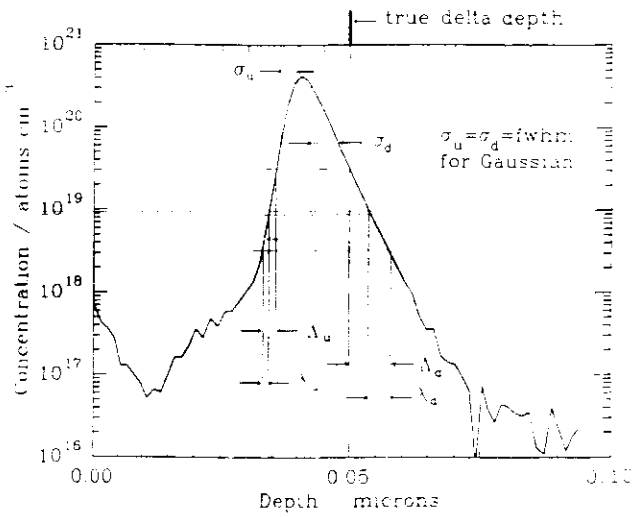
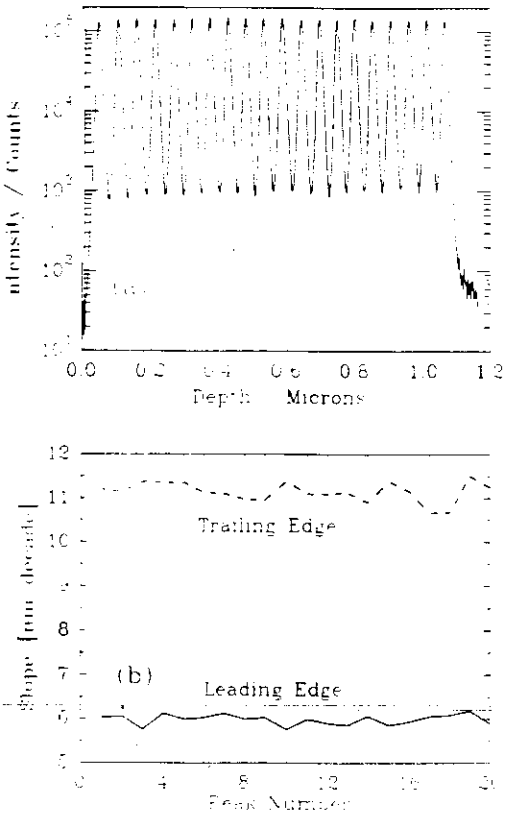
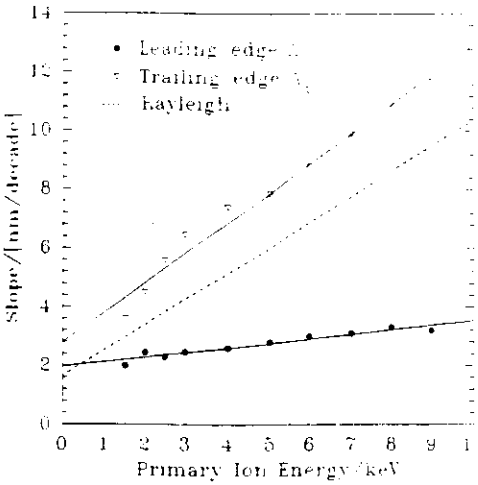


Fig 1 (A) The presence of numerous focal Al deposits, at a mass resolution of ~200, in the frontal cortex of a renal dialysis patient. (B) The almost identical distribution of Al at a mass resolution of ~1500. (C) Lack of focal Al deposits, at a mass resolution of ~200, in the frontal cortex of an age matched control patient PS, pial surface of cerebral cortex; WM, grey matter/white matter boundary. Scale bar represents 400μm.

FROM J. M. CANDY ET AL., PROC SIMS VII, J WILEY & SONS (1990) 323-326







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