

AD-A241 596

UNLIMITED

300052 (2)



Report No. 91015



Report No. 91015

ROYAL SIGNALS AND RADAR ESTABLISHMENT,  
MALVERN

DTIC  
ELECTE  
OCT 15 1991  
S D D

A REVIEW OF POSITIVE ION SENSITIVITIES  
FOR THE SIMS ANALYSIS OF CMT

Author: R Holland & G W Blackmore

This document has been approved  
for public release and sale; its  
distribution is unlimited.

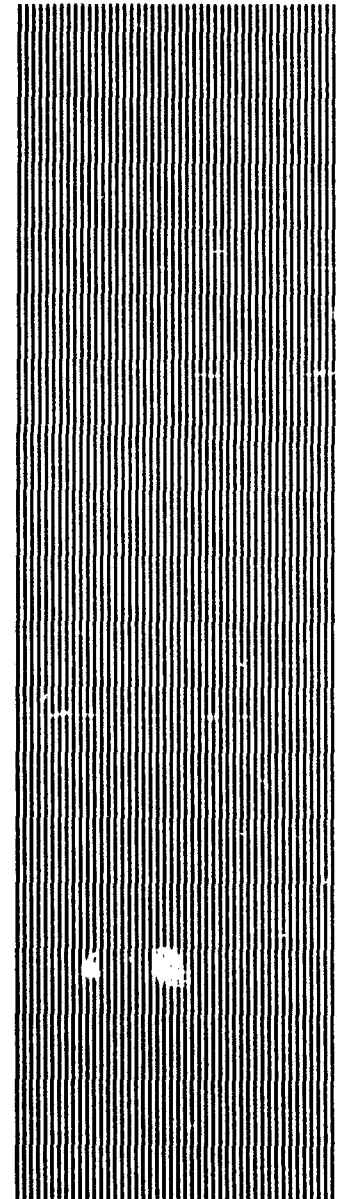
91-13150



PROCUREMENT EXECUTIVE, MINISTRY OF DEFENCE

RSRE

Malvern, Worcestershire.



May 1991

UNLIMITED

91 1011 027

CONDITIONS OF RELEASE

0106761

303252

.....

DRIC U

COPYRIGHT (c)  
1988  
CONTROLLER  
HMSO LONDON

.....

DRIC Y

Reports quoted are not necessarily available to members of the public or to commercial organisations.



INTENTIONALLY BLANK

## INTRODUCTION

The use of Secondary Ion Mass Spectrometry (SIMS) analysis has been an essential factor in the progress of the RSRE programme to develop infrared sensitive materials and devices based on high purity cadmium mercury telluride (CMT). SIMS identifies and counts the ionised particles sputtered from a surface bombarded by a focussed beam of ions of several keV energy. The resulting analysis can cover all elements with unrivalled sensitivity (down to  $10^{13}$  atoms/cm<sup>3</sup> in favourable cases) and can be highly localised, typically to less than a micron in width and/or depth. It is thus particularly suitable for the identification and location of dopants and impurities in epitaxial layers and device structures.

While the elemental composition of the sputtered material is representative of that of the parent material, SIMS can only detect the ionised components. The degree of ionisation varies widely between elements - eg between alkali metals and gold - by as much as 5 decades and is also dependent on the bulk chemistry of the parent surface, such as the matrix composition and its state of oxidation. Attempts to increase the degree of ionisation by the use of lasers or plasma discharge have had only limited success. Fortunately experience shows that under constant experimental conditions the degree of ionisation remains essentially constant over wide ranges of concentration, from parts per billion to a few percent, so that variations in the number of ions detected accurately reflect proportionate changes of composition with depth. In order to quantify such data, however, the analyst requires calibration factors for each element of interest in each matrix.

Singly charged monatomic and diatomic ions predominate in SIMS spectra. The degree of ionisation of most electropositive elements is greatly enhanced by surface oxidation, either by use of O<sub>2</sub><sup>+</sup> or O<sup>-</sup> primary ions or by back-flooding the sample chamber with oxygen at pressures up to 10<sup>-5</sup>Torr. Similarly the production of negative ions of electronegative elements is enhanced by caesium. The present report is concerned with the establishment and correlation of reliable calibrations for singly charged positive monatomic ions sputtered from CMT by oxygen primary ions. Particular attention is paid to metallic and metalloid elements with ionisation potentials in the range 5-10eV. For elements with higher ionisation potentials caesium primary ions are usually used.

During the past decade calibration factors have been measured in-house using doped crystals, ion implants and diffused radio-tracers. These can now be compared with data published by other workers and the predictions of theoretical models in order to establish the degree of confidence in their use, to identify those values which need further examination and to predict likely values for elements which may not have been measured previously.

The simplest correlation between positive secondary ion sensitivities in a given matrix is offered by the well-known inverse relationship between ionisation potential and the logarithm of the sensitivity. The theoretical basis for this relationship and the other factors which have been introduced to improve it are discussed later. Lapidès and co-workers<sup>1,2</sup> published sensitivity factors for 10 positive and 10 negative secondary ions from CMT. The values for 8 of the positive ions showed a reasonable correlation with

ionisation potentials while those for 2 elements, Mg and Be, departed from the trend line by a decade. Wilson<sup>3,4</sup> published values for 42 elements and showed a similar correlation, Mg and Be again lying off the line.

As the observed ion yield is dependent on instrumental factors which may vary between measurements, a suitable matrix isotope is usually chosen as an internal standard. The term 'Relative Sensitivity Factor' (RSF), now commonly used<sup>5</sup>, refers to the concentration of the impurity or dopant which would (assuming linear response) give the same number of secondary ions as the matrix element. Measurements based on particular isotopes should therefore be divided by the appropriate isotope fraction to give the total yield for the measured or matrix element. The term 'Relative Sensitivity Factor' is a misnomer as it varies inversely with the true sensitivity of the element. Nevertheless, it will be used here as it is coming into common usage<sup>5</sup>. The concentration  $c$  is given by:

$$c = \text{RSF} \cdot (I_M/I_N) \cdot (f_N/f_M)$$

where  $I_M$  and  $I_N$  are the secondary ion currents for isotopes M and N of the element and matrix and  $f_M$  and  $f_N$  are the respective isotope ratios.

## EXPERIMENTAL

SIMS measurements were made using the Cameca IMS-3f ion microscope formerly used at AMTE, Holton Heath, and now installed at RSRE. A beam of 8keV  $O_2^+$  primary ions was rastered over a  $500\mu\text{m}$  square area of the sample. The secondary ion optics were adjusted to measure the emission from a central circular area of  $60\mu\text{m}$  diameter. The  $^{125}\text{Te}$  isotope was chosen as a reference standard as it is free from molecular ion interferences.

Doubly charged ions of Cd and Te were found to interfere extensively with the measurement of singly charged ions with the same mass/charge ratio. This affected the transition elements Mn, Fe, Ni, Cu and Zn. Because of the low energy of the interfering ions, it was shown that this effect could be reduced by displacing the energy band-pass by 10eV<sup>6,7</sup>. The origin of this energy scale was arbitrarily taken from the energy at which the intensity of  $Al^+$  ions used to set up the instrument was a maximum. All measurements were made with a band-pass of 10eV centred on this displacement. The energy distributions of most of the elements of interest were found, in general, to parallel that for the  $Te^+$  ions used as a matrix reference (Fig 1). Consequently the choice of band-pass made little difference to the measured RSFs, apart from the removal of interferences. One exception is As, as discussed later.

Several doped crystals were prepared, the most satisfactory one being made by melting powdered CMT intimately mixed with finely powdered tellurides (specially made at BDH, Poole) of the range of elements of interest. The particles all passed through  $30\mu\text{m}$  mesh nylon sieves<sup>8</sup>. Where tellurides were unsuitable, appropriate alternative stable compounds such as cadmium salts were incorporated. The resulting crystal proved to be of remarkably uniform composition, whereas similarly prepared crystals of cadmium telluride were less satisfactory because of segregation of some dopants -

possibly because of lower solubilities. The dopant concentrations were measured by flameless atomic absorption and by ICP using standard solutions for calibration. Adjacent slices of the crystal were used for these analyses and for SIMS measurements. Not all dopants were measured but the agreement of the analyses with the amount of dopants used was so consistent that the few elements not measured were assumed to be present at the concentration used in crystal preparation.

Ion implants were also used to establish RSF values using the technique of Leta and Morrison<sup>9</sup> in which the integrated SIMS count, after subtracting the background, is compared with the total number of ions implanted. Applications of this technique were limited by the restricted availability of suitable implants. The range of implanted ions must be sufficient for them to be clearly distinguished from surface contamination, discrimination being especially difficult for fast diffusing ions<sup>10</sup>. Doubts were also entertained as to whether damage caused by the implantation would affect the results.

For Au and As, additional data was obtained by collaboration with studies at the University of Southampton in which profiles of the diffusion of radioactive tracers into CMT were measured using an etch technique<sup>11,12</sup>. Comparison of these profiles with those obtained by SIMS gave revised values for the RSFs.

## RESULTS

Between four and six measurements were made for each element and were generally found to be within a factor of 2 of the mean, readings markedly dissimilar to the mean being rejected. Where implants were available, the results were generally found to be in the same range. As the values for different elements ranged over 5 decades, an error factor of 2 was regarded as acceptable. The mean values are listed in Table 1, together with those published later by Lapidès et al and by Wilson. Fig 2 shows a plot of log (RSF) versus ionisation potential (in eV) and Fig 8 is the corresponding plot for Wilson's data. Of the 19 common elements, 16 showed differences on a log scale of 0.3 or less (ie a factor of 2). The points for the 3 elements which differed considerably are marked with circles in Figs 2 and 8 and the two values obtained on diffusion specimens are marked with crosses (x) and their values in Table 1 are enclosed in brackets.

## DISCUSSION

Most of RSRE's values for the RSFs listed in Table 1 were obtained in 1980 and the degree of agreement with those reported by other workers in 1984 and 1988 is remarkable in view of the very different methods employed. The results reported by Lapidès et al and by Wilson were all obtained from implants, whereas RSRE's results were nearly all based on doped crystals. Furthermore, it is most unlikely that the former workers used the somewhat arbitrary choice of energy band-pass used by RSRE. Their measurements were made by Evans Associates and the experimental conditions were not reported. Evans' usual practice had been to use a wide band-pass of some 120eV with an offset of some 30eV when mass interferences are suspected. The agreement is a fortunate consequence of the similarity between the energy distributions of the sputtered ions and that of  $\text{Te}^+$  used as a reference element. It suggests that these RSFs may be used with confidence and could also be used as a basis for any

generalised approach to establish a correlation between different elements. It also suggests that damage caused by ion implantation does not affect SIMS calibrations in this matrix.

The 3 elements for which Wilson's and RSRE's values differ widely are As, Sb and Cu. The number of measurements on which Wilson's values in Table 1 were based averaged 5 per element. Those for As<sup>+</sup> and Sb<sup>+</sup> were based on one each, although B<sup>+</sup> was based on 16 readings and In<sup>+</sup> on 13. It can be seen from Fig 1 that the energy distribution for As<sup>+</sup> differs in shape from that of the reference Te<sup>+</sup>, the maximum of the population curve being displaced to lower energy by some 10eV and the fall-off towards higher energies is steeper. Consequently, in view of the different energy windows used, agreement between the 2 laboratories could not be expected. The value based on diffusion profiles, involving many measurements using the maximum energy band-pass of the instrument, are probably the most reliable. The concentration of Sb in the RSRE doped sample was not measured directly but based on the amount added. The SIMS count was very low and the resulting RSF must be suspect. Doubt may also be cast on RSRE's value for Cu<sup>+</sup> as the interference from Te<sup>2+</sup> at mass 63 and 65 is only partially reduced by the voltage offset used<sup>13</sup>. Nor can one choose between Wilson's value and that of Lapides, which differed by a factor of 5.6. It was hoped that comparison with the RSFs of other elements using semi-empirical correlations, preferably supported by theoretical models of the ionisation mechanism, would help to resolve these anomalies.

There have been many attempts to formulate a general quantitative model for secondary ionisation. The most successful in terms of matching known data and predicting new values in a variety of matrices was the so-called Local Thermal Equilibrium (LTE) model proposed by Andersen and Hinthorne<sup>14</sup>. They suggested that the sputtering site could be likened to a plasma in which atoms, ions, electrons and molecular ions were in local equilibrium. They therefore used the Saha-Eggert equation, which successfully predicts ion intensities in flame and plasma spectra, to predict secondary ion concentrations. This takes the form:

$$Y = A.(B^1/B^0) . \exp(-E/kT)$$

where Y is the ion yield for a particular element, A is a constant for the matrix, B<sup>0</sup> and B<sup>1</sup> are the electronic partition functions of the unionised and ionised atoms of the element at temperature T, k is Boltzman's constant and E is the ionisation potential. A similar relation, with electron affinity replacing ionisation potential, applied to negative ions. These relations, extended to include oxide ions, formed the basis of a commercial computer programme called CARISMA for use with the ARL ion microprobe. Inter-laboratory exercises organised by NRL using standardised glasses and steels<sup>15</sup> showed considerable agreement usually within a factor of 2.

Unfortunately there was no physical basis for this model, despite its success. The 'temperature' T was unrealistically high, usually in the range 3000 to 10,000 degrees, and differed for positive and negative ion emissions. Morgan and Werner<sup>16,17</sup>, using an empirical approach and accepting these limitations, successfully used the relationship in simplified form, plotting log (Y.B<sup>0</sup>/B<sup>1</sup>) against E to find the best straight line. The slope gives the term kT, but the partition functions B are a function of T and an

iterative procedure is needed to find the best fit. B is defined as the sum:

$$\sum \exp(-e_i/kT)$$

over all electronic energy levels  $e_i$  and gives a weighting for the inclusion of electronically excited states. Values for B at temperature T can be calculated from published data<sup>18</sup>. Bearing in mind that RSF is reciprocally related to Y, Fig 3 shows a plot of  $\log [(RSF).B^1/B^0]$  using the mean  $\log (RSF)$  values of Table 1. The slope gives 5500°K for the value of T. Values of  $B^1/B^0$  at this temperature are listed in Table 2. Fig 3 shows only a slight improvement in linearity over Fig 1, the shift of Mg into the main family being offset by the loss of linearity among elements of lower ionisation potential and displacement of the point for Ca.

Morgan and Werner introduced the square root of the atomic weight thus:

$$Y = A.m^{-1/2} . (B^1/B^0) . \exp(-E/kT)$$

explaining that it was a composite factor taking into account the mass discrimination of the instrument transmission and detection as well as in ion formation, but mainly because it improved the fit. The fit was also improved by using the sum of ion and oxide ion yields. Use of the term  $m^{-1/2}$  did not improve the fit of the present data. Slodzian<sup>19</sup>, studying isotopic discrimination in SIMS, generalised the term to  $m^{-\alpha}$ , with  $\alpha$  lying usually in the range 0.5 to 2. There was no best value of  $\alpha$  to fit the present data and its use appears artificial.

The measurement by Rudat and Morrison<sup>20</sup> of correction factors to convert the signals from photo-multipliers into true ion currents is of more practical significance. The factors vary from element to element but are related more to the chemistry of the element than to its atomic mass. The data listed in Table 2 shows by what factor the true current is enhanced. The variation between these factors, however, is not sufficient to reduce the scatter of RSFs significantly (Fig 4).

Despite its many successes in predicting secondary ion sensitivities in a variety of matrices, Andersen and Hinthorne's LTE model is inconsistent with current ideas of the mechanism of sputtering. The incoming  $O_2^+$  ion is believed to initiate a collision cascade while penetrating several atomic layers and coming to rest as implanted atoms. Computer simulations show that the cascade, which dissipates in about  $10^{-14}$  second, causes some atoms to be ejected from the surface layer by impacts from within the solid<sup>21</sup>. This timescale is insufficient by several orders of magnitude for thermal equilibrium to be established. A primary current of  $1\mu A$  corresponds to  $6 \times 10^{12}$  impacts per second so that even if they all occurred at the same spot they would still be isolated events.

The surface region of the specimen must contain a high proportion of implanted oxygen which is progressively sputtered as it is exposed on the surface. To maintain equilibrium each sputtering event should, on average, involve the loss of 2 oxygen atoms. With a primary ion current of  $1\mu A$  on  $1/4mm^2$ , the rate of erosion of CMT found in the present work is  $5\mu m/hour$ , which corresponds to 1.6 matrix atoms per impact, in

addition to the 2 oxygen atoms. Changing the primary ion current would not affect this proportion provided the erosion rate remains proportional to the current. It also means that the oxygen concentration in the surface layers is 1.25 atoms per matrix atom. These oxygen atoms might well occupy the vacancies caused by the inevitable preferential loss of mercury as well as interstitial sites. Alternatively, allowing for the loss of mercury, there would be sufficient oxygen to convert all the remaining matrix atoms to oxides,  $\text{TeO}_2$  and  $\text{CdO}$ .

Any general theory of the ionisation of sputtered particles must account for the broad applicability of the Saha-Eggert relation, the variation between matrices and the enhancement of ion yields by oxygen. Morgan and Werner<sup>16</sup> pointed out that while the energy imparted to any one atom is random, the statistical effect should be the same for all elements provided the differences in cross-section can be discounted. The energy will be used partly to overcome the binding forces, partly as kinetic energy and partly as excitation energy distributed among the quantum levels. The probability of atoms acquiring excitation energy  $e_i$  can be shown by statistical mechanics (see Appendix A) to take the Boltzman form  $A \exp(-\beta e_i)$ , where  $\beta$  is analagous to  $1/kT$  and  $kT$  is a measure of the mean energy available. From this it follows that the ratio of ionised to neutral atoms is

$$B^1/B^0 \exp(-\beta E)$$

This approximates to the Saha-Eggert equation when the proportion of neutrals exceeds that of the ions.

This approach is grossly oversimplified. Apart from taking no account of the different binding energies, it appears to over-emphasise the role of neutral atoms rather than oxides and oxide ions. It is probably more applicable to metallic matrices than ionic lattices and is possibly more valid for the metal impurities than for alkali metals or alkaline earths. One would not expect to find neutral alkali metal atoms in such an oxidising environment. In recent years it has become customary to omit the partition functions and to plot  $\log(\text{RSF})$  directly against ionisation potential on an empirical basis<sup>22</sup>.

Strictly, as ionisation involves donating an electron to the surface,  $E$  should be replaced by  $(E-\phi)$ , where  $\phi$  is the work function. This would be included in the constant  $A$ . Deline et al<sup>23</sup> proposed that the matrix effect could be entirely accounted for by the effect of the work function. It is increased by oxygen coverage thus enhancing ionisation. Under oxygen bombardment the oxygen concentration in the surface layer will be greater the lower the sputter rate as discussed above. However, it is unlikely that the effect would be the same for all elements, eg one would expect a greater enhancement for iron and nickel than for gold.

The model outlined above is useful but is unlikely to reflect the true situation. Slodzian<sup>24</sup> suggested that oxygen chemically reacts with the impurity elements so that sputtering involves breaking oxide bonds. This 'bond-breaking' model is now widely accepted though it is difficult to quantify. Lang and Yu<sup>25,26,27</sup> have tried to estimate the probability that ions leaving the surface would be neutralised while traversing the

surface field but their calculations of the overlap of electron orbitals are not readily translated into practical RSFs.

It is evident that ionisation is a complex process and several mechanisms may be operative not only in different matrices but possibly for different elements in the same matrix. In ionic solids some ions may be ejected directly from the lattice. In other cases neutral atoms may be ejected in highly excited electronic states, possibly by promotion of electrons from inner orbitals. After a short lifetime an electron would then be ejected by an Auger process<sup>24</sup> outside the surface and the process would be independent of the work function. Alternatively, for elements which readily form oxides, short-lived oxide molecules with high degrees of rotational, vibrational and electronic excitation may also decompose outside the surface:



Examination of Fig 2 supports this idea that several mechanisms are operative. The spread covers two decades with the nobler elements Ag, Pt, Au and the non-metals B and Si forming the upper boundary of RSFs and the elements Mg and Be forming the lower boundary. This suggests that the latter elements are ionised by a different process than the former. Now that tables of RSFs are available for other semiconductors, it is interesting to compare them with those for CMT. Figs 5 to 8 show the plots for Si, GaAs, InP and CMT. In each case there is a general trend relating log RSF with E, the spread increasing towards higher values of E and with Mg and Be forming the lower boundary. Indeed Mg and Be appear to form a class by themselves.

It is tempting to suggest that the oxide decomposition mechanism applies to Mg and Be. Whereas an excited atom needs energy E to ionise, an oxide molecule or radical needs  $D + E - E_o$  where D is the heat of dissociation and  $E_o$  is the electron affinity of oxygen (1.46eV). If D is already acquired during the sputtering event (eg by bonding with a moving oxygen atom), the effective ionisation energy E is reduced by 1.46eV, which could account for the displacement of the points for Mg and Be on the graph from the main trend line. The high concentration of implanted oxygen would make oxygen atoms the most common particles in the cascade and their low mass would ensure they were the most mobile. It is possible that this type of mechanism could also apply even if the oxide molecule did not escape the surface - it could be formed transiently by oxygen atom impact, the  $O^-$  ion remaining in the surface. There is no obvious way of checking this theory.

If one discounts Mg and Be, it is evident that the spread of the plot for InP is much greater than that for Si and GaAs and more like that for CMT. This is illustrated by the spread of the points for Mn, Ni, Sn and Ag, all with similar ionisation potentials. The differences in log RSF between Mn and Ag are 0.75 and 0.72 decades in Si and GaAs but 1.17 and 1.95 decades in CMT and InP respectively. Furthermore, the vertical spread of elements tends to reflect their affinity for oxygen. The concentration of oxygen in the surface layers might well play an important role in determining this spread. Morgan and Werner showed that impurities in steels only fitted their modified Saha-Eggert relation if the oxygen enhancement was 'saturated', ie maximised by oxygen flooding. They had to reduce the  $O_2^+$  primary current to achieve this as too fast

an erosion rate prevented the effective adsorption of oxygen.

Wilson et al<sup>22</sup> give the relative sputter rates for Si, GaAs, InP and CMT in the ratios 1,2,3 and 5.6. As the concentration of implanted oxygen varies inversely as the sputter rate, these figures are consistent with the theory that in CMT, and possibly in InP, the concentration of implanted oxygen is insufficient to give optimum enhancement. It may be possible to correlate the deviation from linearity with relative affinities for oxygen. It would be interesting to test this theory by remeasuring the RSFs with a lower primary ion current and oxygen back-flooding though the results would be of more academic than practical interest as the resulting RSFs would only be applicable under such experimental conditions. If successful, however, it would lend weight to the above model and encourage further theoretical work on the effects of partial oxygenation which could result in a practical formula for RSFs.

## CONCLUSIONS

The general agreement, within a factor of 2, between the two groups of workers, despite widely differing techniques, shows that the scatter of points on the log (RSF) versus E plot for CMT is attributable not to the experimental error but to more fundamental aspects of the ionising process. Furthermore, the results do not fit the Saha-Eggert equation which works well for many other matrices, such as metals, glasses and ceramics.

Despite decades of basic studies there is still no universally accepted model of the ionisation process in sputtering and it is remarkable that although the LTC model is clearly unsound, it has given such good quantitative predictions. The cascade model of sputtering is well established. With simplifying assumptions, eg ignoring differences in binding energy, one can predict ionisation probabilities of similar form to the Saha-Eggert equation just as thermodynamic functions can be derived from Boltzman statistical mechanics.

The comparison of the semi-log plots for the semiconductors Si, GaAs, InP and CMT appears to show a progressive increase of spread from the trend lines, excluding the points for Mg and Be which appear to be in a class of their own and may well involve a different mechanism. The sputter rates for these matrices increase in the same order and, since the concentration of implanted oxygen varies inversely with the sputter rate, it suggests that the increasing spread may be associated with lower concentrations of ion-enhancing oxygen. If it proves possible to correlate these deviations from linearity with the affinity of the trace elements for oxygen, the prospect arises of deriving a semi-empirical relationship which would allow the quantitative prediction of RSFs for elements not yet measured as well as resolving the few discrepancies between the results of the two laboratories.

## REFERENCES

1. L E Lapides, G L Whiteman and R G Wilson, *Mat Res Soc Proc* 25 (1984) 657
2. L E Lapides, *Surf Interface Anal* 7 (1985) 211
3. R G Wilson, *J Appl Phys* 63 (1988) 5121

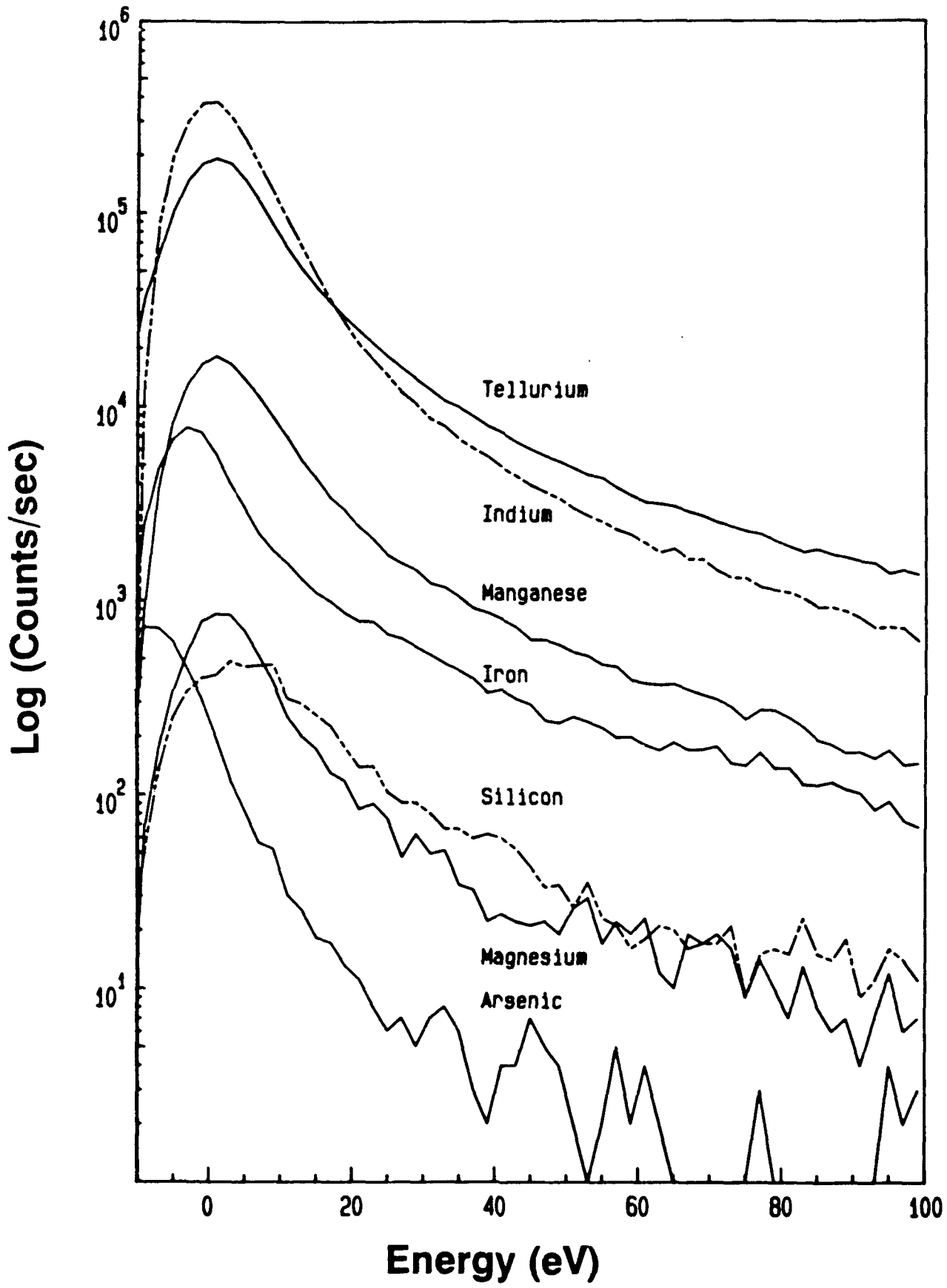
4. R G Wilson, *J Crystal Growth* **86** (1988) 735
5. R G Wilson F A Stevie and C W Magee, *Secondary Ion Mass Spectrometry*, J Wiley & Sons, Chichester, UK (1989)
6. R Holland and G W Blackmore, *Surf Interface Anal* **4** (1982) 174
7. R Holland and G W Blackmore, *Int J Mass Spectrom Ion Phys* **46** (1983) 527
8. G W Blackmore, S J Courtney, C D Dowding and G A Hicks, AMTE (Holton Heath, UK) Technical Memorandum 80113 (1980)
9. D P Leta and G H Morrison, *Int J Mass Spectrom Ion Phys* **27** (1978) 249
10. G W Blackmore, S J Courtney, M G Astles and N Shaw, *Surf Interface Anal* **15** (1990) 617
11. H D Palfrey, G W Blackmore and S J Courtney, *J Appl Phys* **58** (1985) 1404
12. J E Falconer, H D Palfrey and G W Blackmore, *J Crystal Growth* **100** (1990) 275
13. G W Blackmore, S J Courtney, R Holland, M G Astles, S J C Irvine, J S Gough and J B Mullin, SIMS VI, A Benningham et al eds, J Wiley & Sons, Chichester, UK (1987) 315
14. C A Andersen and J R Hinthorne, *Science* **175** (1972) 853
15. D E Newbury and K F J Heinrich, *Mikrochim Acta, Suppl* **8** (1979) 3
16. A E Morgan and H W Werner, *Anal Chem* **48** (1976) 699
17. A E Morgan and H W Werner, *Mikrochim Acta*, **11** (1978) 31
18. L de Galan, R Smith and J D Winefordner, *Spectrochim Acta, Part B* **23** (1963) 521
19. G Slodzian, SIMS III, A Benninghoven et al eds. (Springer Verlag, New York, 1982) 115
20. M A Rudat and G H Morrison, *Int J Mass Spectrom Ion Phys* **27** (1978) 249
21. D E Harrison, P W Kelly, B J Garrison and N Winograd, *Surf Sci* **76** (1978) 311
22. R G Wilson, S W Novak, S P Smith, S D Wilson and J C Norberg, SIMS VI, A Benningham et al eds, J Wiley & Sons, Chichester, UK (1987) 133
23. V R Deline, C A Evans and P Williams, *Appl Phys Lett* **33** (1978) 578
24. G Slodzian, *Surf Sci* **48** (1975) 161
25. N D Lang, *Phys Rev* **B27** (1983) 2019
26. M L Yu and N D Lang, *Nucl Instrum Methods Phys Res.* **B14** (1986) 403
27. M L Yu, *Nucl Instrum Methods Phys Res* **B15** (1986) 151

TABLE 1 COMPARISON OF MEASURED RSFs

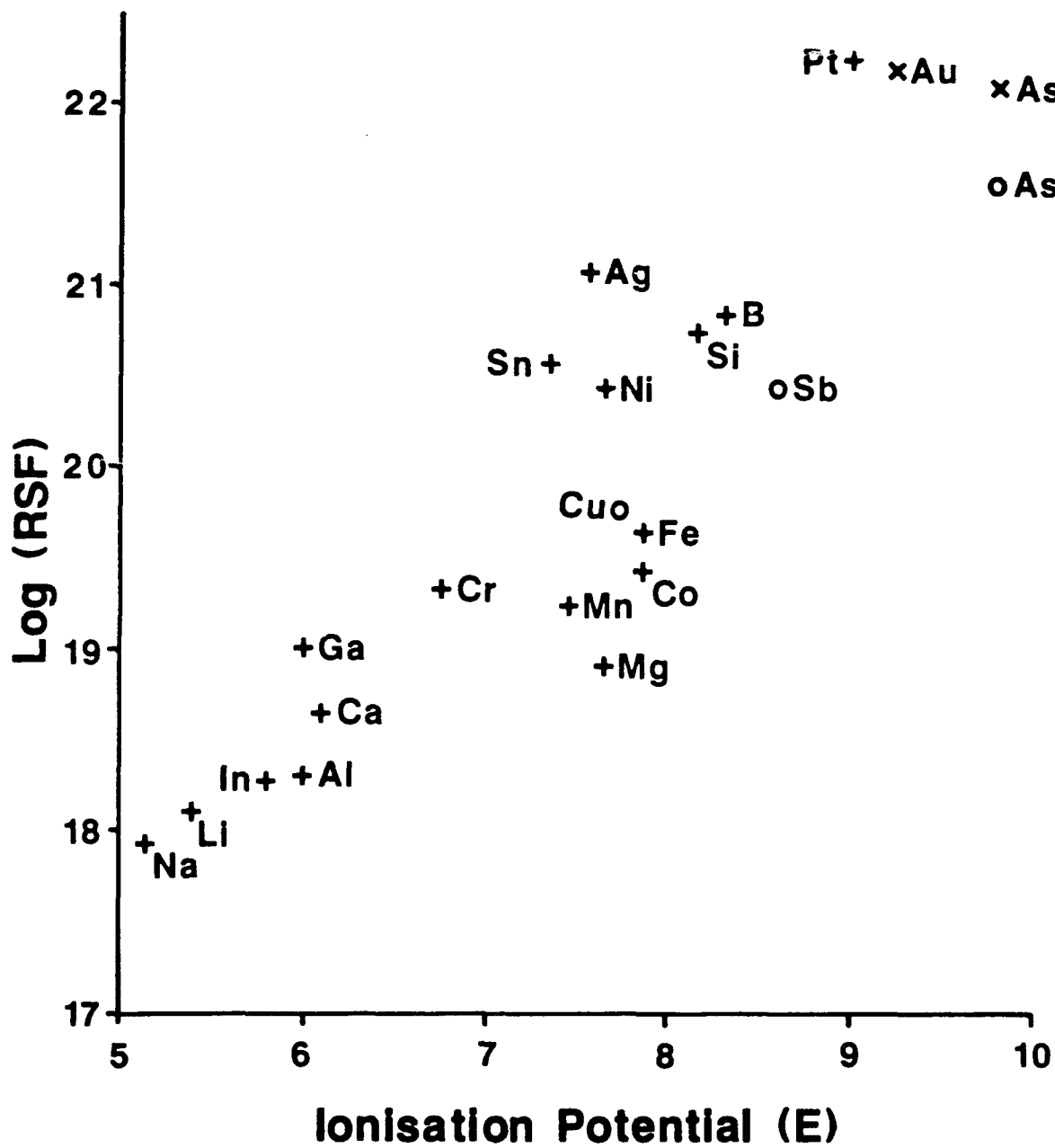
Element	RSF: RSRE	Wilson	Lapides	Log(Wilson) minus Log (RSRE)	Mean Log (RSF)
Ag	1.2e21	1.2e21		0.00	21.08
Al	2.0e18	4.0e18	4.0e18	0.30	18.45
B	6.8e20	9.8e20	5.6e20	0.16	20.91
Ca	4.5e18	3.3e20		-0.13	18.59
Co	2.7e19	4.9e19		0.26	19.56
Cr	2.1e19	1.6e19		-0.12	19.26
Fe	4.6e19	5.9e19		0.11	19.72
Ga	1.0e19	8.0e18	5.4e18	-0.10	18.95
In	1.9e18	1.8e18	1.3e18	-0.02	18.27
Li	1.3e18	8.0e17	1.3e18	-0.21	18.01
Mg	7.7e18	1.3e19	1.4e19	0.23	19.00
Mn	1.8e19	3.6e19		0.30	19.41
Na	8.6e17	4.4e17	4.0e17	-0.29	17.79
Ni	2.7e20	2.2e20		-0.09	20.39
Si	5.8e20	8.0e20	5.4e20	0.14	20.83
Sn	3.8e20	4.0e20		0.02	20.59
As	3.7e21 (1.2e22)	2.0e22		0.73	
Cu	6.0e19	2.0e21	3.6e20	1.52	
Sb	2.7e20	1.5e22		1.75	
Au	(1.5e21)				
Pt	1.8e22				
Be		3.6e20	3.6e20		
Tl		2.7e19			
Zn		1.5e22			

TABLE 2 FACTORS USED IN CORRELATION OF RSFs

Element	Ionisation Potential	$B^I/B^O(5500K)$	Detector Factor f	Mean log RSF
Ag	7.58	0.50	1.75	21.08
Al	5.99	0.17	1.85	18.45
B	8.30	0.17	3.00	20.91
Ca	6.11	1.82	2.69	18.59
Co	7.86	0.83	1.70	19.56
Cr	6.77	0.66	2.33	19.26
Fe	7.87	1.51	2.00	19.72
Ga	6.00	0.19	1.38	18.95
In	5.79	0.23	1.77	18.27
Li	5.39	0.47	1.67	18.01
Mg	7.65	1.95	1.68	19.00
Mn	7.44	0.87	2.10	19.41
Na	5.14	0.48	2.01	17.79
Ni	7.64	0.38	1.65	20.39
Si	8.15	0.72	2.18	20.83
Sn	7.34	0.60	1.80	20.59
As	9.81	1.35	1.90	-
Cu	7.73	0.43	1.48	-
Sb	8.64	0.74	1.95	-
Au	9.23	0.47	-	22.18
Pt	9.00	0.51	-	22.26



**Fig.1. Energy Distributions Of Elements In CMT**



**Fig 2 Log (RSF) vs E-RSRE data for CMT**

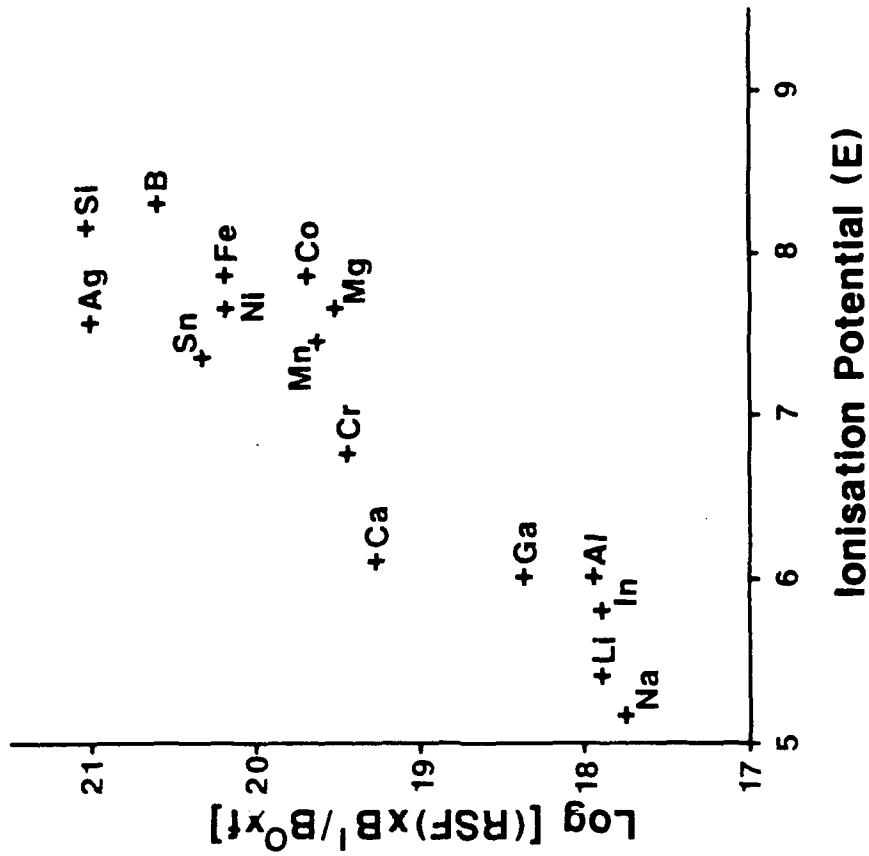


Fig 3 Plot of log (mean RSF) for CMT corrected for partition functions and detector factor

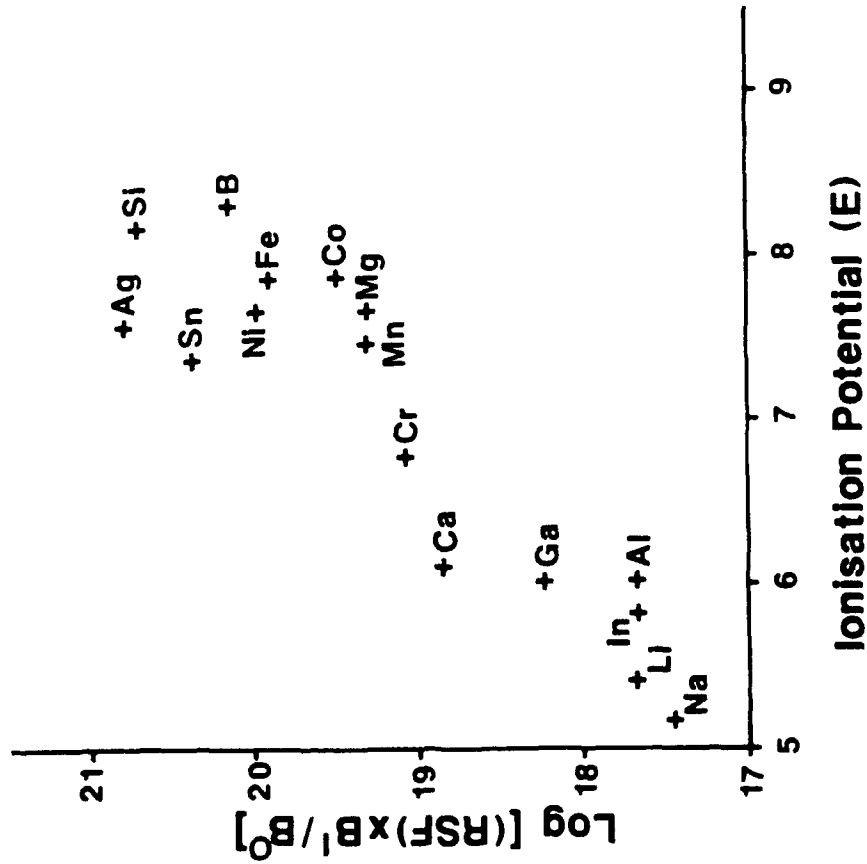


Fig 4 Plot of log (mean RSF) for CMT corrected for partition functions and detector factor

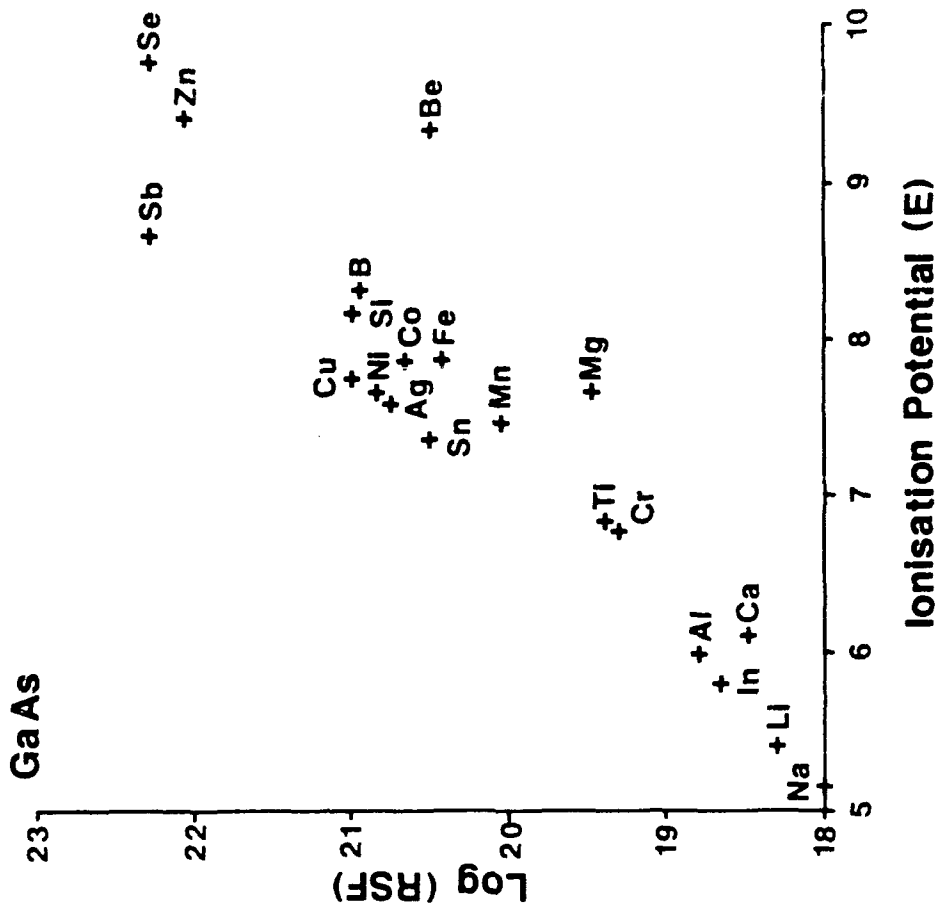


Fig 6 Log (RSF) vs E for elements in GaAs (referred to As<sup>+</sup>)

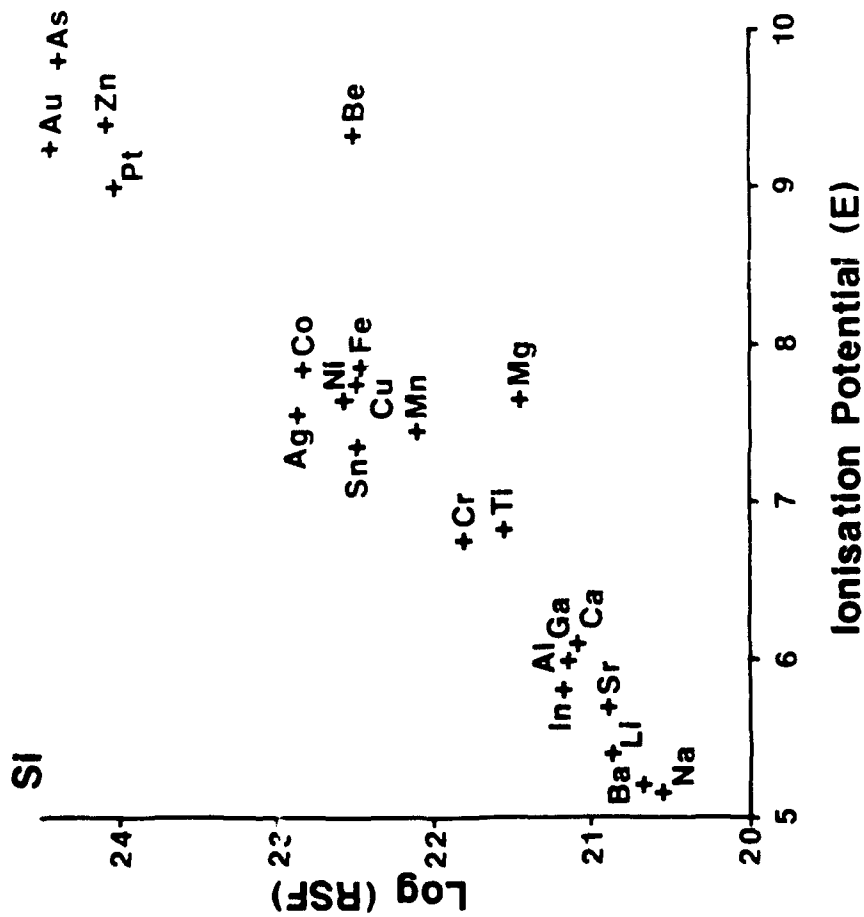


Fig 5 Log (RSF) vs E for elements in Si (referred to Si<sup>+</sup>)

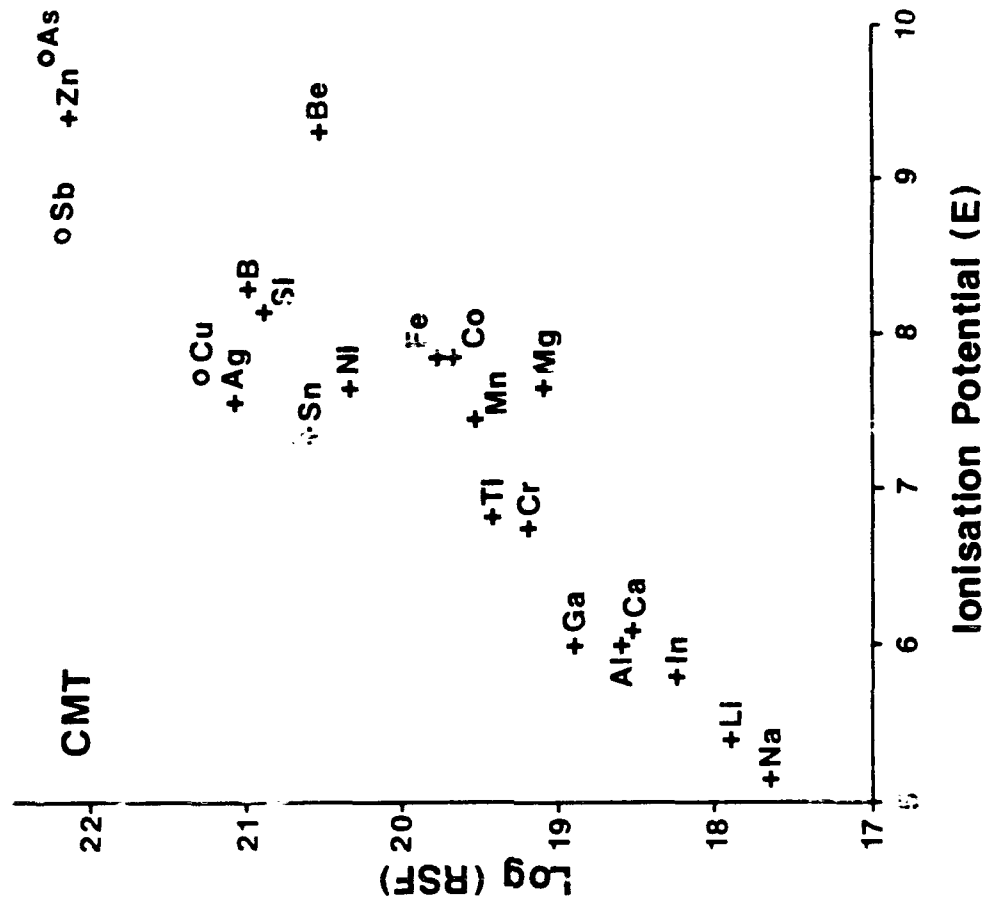


Fig 8 Log (RSF) vs E--Wilson data for CMT

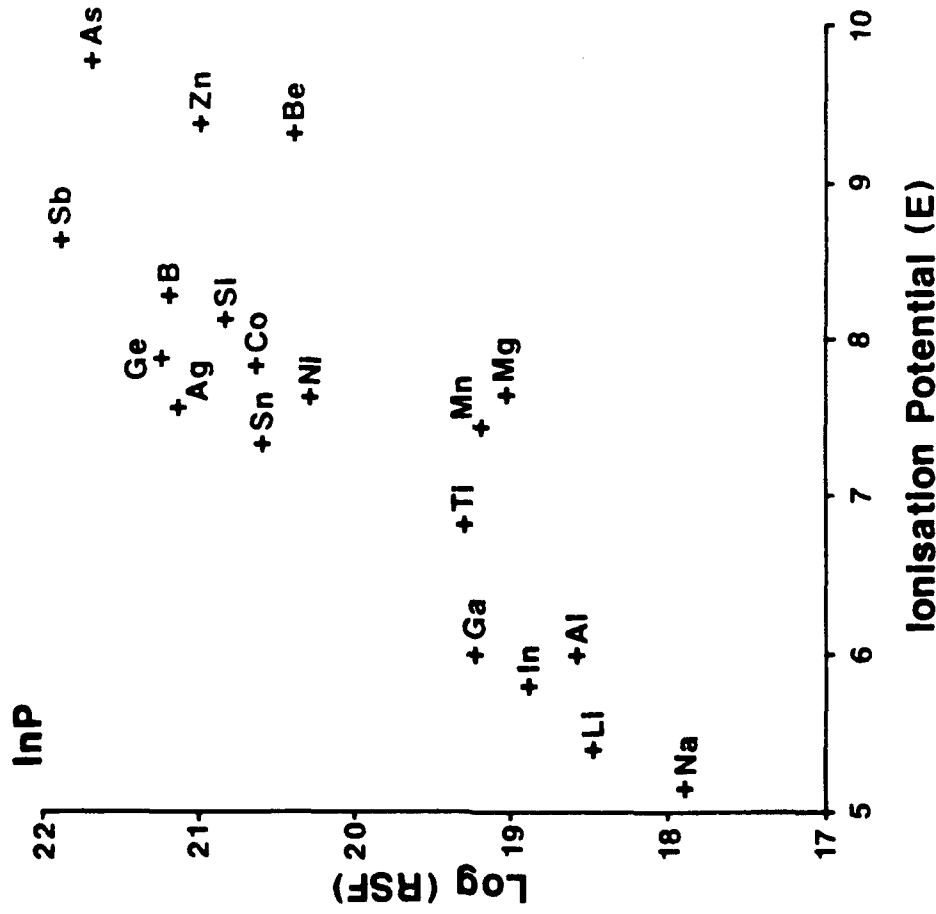


Fig 7 Log (RSF) vs E for elements in InP (referred to P<sup>+</sup>)

APPENDIX A

Though the excitation energy imported by cascade impacts may vary widely, Boltzmann's statistical approach may be used to predict the most likely population distribution between the quantum levels for each type of sputtered atom. The principal assumption is that despite the scatter of excitation energy the average energy is constant.

Consider a number of sputtered atoms  $N$ . Let the number excited to energy levels  $e_1, e_2 \dots e_m$  be  $n_1, n_2 \dots n_m$ .

The average energy  $E_A$  is given by

$$NE_A = n_1 e_1 + n_2 e_2 \dots + n_1 e_1 \dots + n_m e_m \quad (1)$$

$$\text{also } N = n_1 + n_2 + \dots + n_1 \dots + n_m \quad (2)$$

Let  $W$  the number of ways in which the  $N$  atoms may be distributed among the sets  $n_1, n_2$  etc to  $n_m$ . The number of possible combinations is:

$$W = \frac{N!}{n_1! \cdot n_2! \cdot \dots \cdot n_1! \cdot \dots \cdot n_m!}$$

$$\text{and } \ln W = \ln(N!) - \sum \ln(n_i!)$$

Boltzmann's assumption is that the most likely distribution,  $n_1, n_2, n_3$  etc is that for which  $W$  is a maximum, ie  $\delta \ln W = 0$  for all small changes  $\delta n_i$  in the variables  $n_i$ .

$$\text{Therefore } \sum \delta(\ln n_i!) = \delta \ln(N!) = 0 \quad (3)$$

since  $N$  is independent of such changes.

In Appendix B it is shown that the expression

$$n_i \ln n_i - n_i$$

is a good approximation for  $\ln(n_i!)$  especially for larger values of  $n_i$ .

Therefore  $\delta \ln (n_i!) = \ln n_i \cdot \delta n_i$

$$\text{and } \sum \delta (\ln n_i!) = \ln n_1 \cdot \delta n_1 + \ln n_2 \cdot \delta n_2 + \dots + \ln n_m \cdot \delta n_m \quad (4)$$

In general, if all the  $\delta n_i$  terms in an equation of the type

$$\sum f(n_i) \cdot \delta n_i = 0$$

are independent then the solution must be  $f(n_i) = 0$  for each  $n_i$ . In the present case however, the variables  $n_i$  are also subject to equations (1) and (2). Consequently there are  $(m-2)$  independent variables and the relations.

$$\delta n_1 + \delta n_2 + \delta n_3 + \dots + \delta n_m = 0 \quad (5)$$

$$\text{and } e_1 \delta n_1 + e_2 \delta n_2 + e_3 \delta n_3 + \dots + e_m \delta n_m = 0 \quad (6)$$

Multiplying (5) by a factor  $\alpha$  and (6) by  $\beta$  and adding both to (4) gives

$$\sum_{i=1}^{i=m} (\ln n_i + \alpha + \beta e_i) \cdot \delta n_i = 0 \quad (7)$$

by choosing  $\alpha$  and  $\beta$  to make

$$\ln n_1 + \alpha + \beta e_1 = 0$$

$$\text{and } \ln n_2 + \alpha + \beta e_2 = 0$$

equation (7) is reduced to the summation from  $i = 3$  to  $i = m$ , ie  $(m-2)$  independent variables. Consequently the generally solution is

$$\ln n_i + \alpha + \beta e_i = 0$$

for each of the sets  $n_i$ .

Therefore  $n_i = \exp(-\alpha - \beta e_i)$  which can be written as

$$n_i = A \exp(-\beta e_i)$$

This is the standard derivation of the Maxwell-Boltzmann distribution law, but with the assumption of thermal equilibrium replaced by the idea that the average excitation energy  $E_A$  is independent of  $N$ , the size of the sample. While it may accurately reflect the distribution of population between the energy levels of each individual sputtered element, the value of  $E_A$  and consequently  $\beta$ , and possible  $\alpha$ , may vary between elements because of the differences in finding energy. Similarly account must be taken of the kinetic energy imported to the particles by the cascade collisions but Fig 1 suggests that the kinetic energy distributions for different elements tend to be similar.

Let the energy levels of the neutral atoms be  $e_1, e_2 \dots$  etc and those of the ionised atoms, measured from the ground state of the ion, be  $e'_1, e'_2 \dots$  etc.

The partition functions  $B^0$  and  $B'$ , listed in Table 2, are defined as

$$B^0 = \sum_i \exp(-\beta e_i) \text{ and } B' = \sum_i \exp(-\beta e'_i)$$

the summations being taken over the energy levels of the atom and ion respectively.

Then the ratio of ions to atoms is:

$$\begin{aligned} & \sum \exp[-\beta(E + e'_i)] / \sum \exp(-\beta e_i) \\ & = B' / B^0 \exp(-\beta E) \end{aligned}$$

INTENTIONALLY BLANK

APPENDIX B

Sterling's approximation to factorial n is

$$n! = \sqrt{2\pi n} (n/e)^n$$

The following table shows how good this approximation is even for small numbers:

n	Factorial n	Sterling
3	6	5.8
5	120	118.0
7	5040	4980.4
10	3.63e6	3.60e6
25	1.55e25	1.55e25
100	9.33e157	9.32e157

Taking logarithms,  $\ln(n!) = \frac{1}{2}\ln(2\pi n) + n \ln(n) - n$

As n increases the first term becomes less significant, so that:

$$\ln(n!) \approx n \ln(n) - n$$

as shown in the following table:

n	$\ln(n!)$	$n \ln n - n$
10	15.10	13.03
25	58.00	55.47
50	148.5	145.6
100	363.7	350.5
300	1415	1411

INTENTIONALLY BLANK

**REPORT DOCUMENTATION PAGE**

DRIC Reference Number (if known) .....

Overall security classification of sheet ..... UNCLASSIFIED .....  
 (As far as possible this sheet should contain only unclassified information. If it is necessary to enter classified information, the field concerned must be marked to indicate the classification eg (R), (C) or (S).)

Originators Reference/Report No. REPORT 91015		Month MAY	Year 1991
Originators Name and Location RSRE, St Andrews Road Malvern, Worcs WR14 3PS			
Monitoring Agency Name and Location			
Title A REVIEW OF POSITIVE ION SENSITIVITIES FOR THE SIMS ANALYSIS OF CMT			
Report Security Classification UNCLASSIFIED		Title Classification (U, R, C or S) U	
Foreign Language Title (in the case of translations)			
Conference Details			
Agency Reference		Contract Number and Period	
Project Number		Other References	
Authors HOLLAND, R; BLACKMORE, G W			Pagination and Ref 29
Abstract  Measurement of the relative intensities of positive ion emission from CMT under SIMS analysis provides calibration factors for the high sensitivity analysis of impurities. The Relative Sensitivity Factor (RSF) values found by RSRE, mainly from uniformly doped samples, compared well with those obtained later by other workers using implants. Theoretical models for sputtered ion emission are reviewed in detail and their applicability to the CMT data is considered, particularly in relation to plots of log (RSF) against ionisation potential. It is suggested that more than one mechanism is likely to be operative. Comparison with the results for other semiconductors suggests that the observed spread from a linear relationship might be attributable to a low implanted oxygen concentration resulting from a high sputter rate.			
			Abstract Classification (U,R,C or S) U
Descriptors			
Distribution Statement (Enter any limitations on the distribution of the document) UNLIMITED			

INTENTIONALLY BLANK