

## SECONDARY ION MASS SPECTROMETRY (SIMS)

by

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### 1. INTRODUCTION

Phenomena involved in the interaction of charged particles, radiation and electric fields with solid surfaces are utilised in surface analytical methods such as SIMS, Ion Scattering Spectrometry (ISS), Auger Electron Spectroscopy (AES), Photon Appearance Potential Spectroscopy (PAPS), Electron Spectroscopy for Chemical Analysis (ESCA). The analysis includes the investigation of composition and structure of the surface.

In SIMS and ISS positive ions bombard the surface to be analysed and the ions resulting from the bombardment are analysed to investigate the surface. Energy analysis of elastically back scattered positive ions, is utilised in the ISS and mass analysis of sputtered positive and negative ions is utilised in the SIMS.

Fruitful application of a surface analysis method involves the selection of proper and optimum probe parameters and the discrimination of the desired resultant particles or radiation from the undesired ones before analysis and detection.

### 2. PRINCIPLE OF SIMS

The surface to be investigated is bombarded with primary ions in the energy range of a few keV in an ultra high vacuum (uhv) system. If the ions are not back-scattered, they penetrate to a certain depth into the solid and transfer their energy to the lattice atoms. Further impacts distribute the energy to an extended lattice zone. A fraction of this energy reaches the surface in a certain area around the points of incidence of the primary ions. Surface particles (atoms or molecules) receiving a sufficient amount of energy can leave the surface in a singular or cluster form in charged or uncharged state.

Some of the emitted surface particles are charged positively

or negatively and are known as secondary ions. The emission of secondary ions from a surface under ion bombardment was studied by Sloan<sup>1, 2</sup>, Herzog<sup>3</sup> in the past. Recent studies in this field have been made by Honig<sup>4</sup>, Leibl<sup>5</sup>, Castaing<sup>6</sup>, Werner<sup>7-9</sup>, Fogel<sup>10-13</sup> and Anderson<sup>14</sup>.

The details of various processes which cause the secondary ions are not yet fully understood. The most effective process is believed to be the so called chemical emission<sup>15,16</sup> which occurs when chemical bonds are broken. Dissociation of chemical compounds on the surface can give rise to an intense ionic emission. The destruction of covalent bonds and absorption bonds can also result into ionisation.

The secondary ions are separated according to their mass/charge ratio in a mass analyser and detected by a secondary electron multiplier. The mass spectrum of the positive and negative secondary ions gives information on the chemical composition of the top monolayer of the bombarded solid material. The nature of the surface is affected by the incident ions in a complicated manner. The original first monolayer can be altered by the ion bombardment which causes entrapment of ions, changes in crystalline structure and elemental composition, chemical processes, etc. The sputtering process eventually removes the original surface completely.

These effects are minimised by selecting a sufficiently low primary ion current density. This results into a sufficiently small probability of two ions hitting the same surface spot within a given time. The static process<sup>17-20</sup> of SIMS enables such analysis by using an extremely low primary ion current density ( $\sim 10^{-9}$  A/cm<sup>2</sup>) and a relatively large surface area (a few mm<sup>2</sup>). This extends the removal time for one monolayer to several hours. Assuming a sputtering yield of one sputtered particle per incident ion, only 1% of the surface monolayer is removed after 1000 sec with the primary ion current density of  $10^{-9}$  A/cm<sup>2</sup>. For many elements and components the detection limit is considerably below 1 ppm ( $10^{-6}$ ) of a monolayer.

In the past, high primary ion current densities have been

used. Because of the high sputtering rates, uhv conditions were not desired. The adsorption rate defined by the residual gas pressure was much less than the sputtering rate. The method was termed destructive due to this. This method can be used in conjunction with SIMS to obtain depth profiles of thin films for layer by layer analysis upto a thickness of a few 1000 Å. The method is known as dynamic process<sup>9</sup> of SIMS (BSIMS).

### 3. SPUTTERING CHARACTERISTICS

If  $j_p$  is the primary ion current density,  $A$  is the bombarded target area,  $\Theta$  is the relative coverage of the surface with the parent compound (structure),  $\gamma$  is the absolute secondary ion yield of the species,  $x$  is the overall transmission of the apparatus (detected fraction of the secondary ions emitted), then the secondary ion current  $I$ , registered by the ion collector is given by:

$$I = j_p A \Theta \gamma x \quad (1)$$

Sputtering of an individual monolayer can be described by the expression

$$\Theta(t) = \Theta(0) \exp(-t/\hat{t}) \quad (2)$$

where  $\Theta(t)$  is the relative coverage at time  $t$  and  $\hat{t}$  is the average lifetime of the uppermost monolayer given by:

$$\hat{t} = \frac{N_0}{nS} \quad (3)$$

In this expression  $N_0$  is the number of particles in a complete monolayer,  $n$  is the impingent rate of the primary ions ( $n = j_p/e_0$ ,  $e_0$  being the electronic charge on the ion) and  $S$  is the total sputtering yield (number of particle emitted from the surface by one incoming primary ion). It can be seen that for  $j_p = 1 \times 10^{-4} \text{ A/cm}^2$  and  $S = 5$ ,  $\hat{t}$  is in the range of some tenths of a second. Thus individual monolayers cannot be analysed thoroughly with such a high sputtering rate. It is therefore necessary to lower  $j_p$  by a few orders of magnitude to raise  $\hat{t}$  by equal orders of magnitude. In some cases  $j_p$  is lowered to  $1 \times 10^{-10} \text{ A/cm}^2$  to give  $\hat{t}$  in the range of some  $10^5$  sec. To compensate for the decrease in the

total number of emitted secondary ions due to lowering of  $j_p$ , the bombarded area is increased to  $0.1 \text{ cm}^2$ .

$\text{Ar}^+$  is chosen as the probe since it is a heavy inert gas ion with sufficient data<sup>22</sup> available on its sputtering characteristics. With energy of  $\text{Ar}^+$  between 500-3000 eV, S varies between 0.5 - 7.5 for different surface atoms and reaches almost saturation at about 3000 eV in many cases. In such cases S increases by about 50% when the angle of incidence of the primary ion beam changes to grazing angles from the normal incidence.

#### 4. INSTRUMENTATION

The apparatus consists of an ion source, target assembly, analyser and detector mounted in a uhv system.

**4.1 Ion Source:** A mass separated, singly charged, monoenergetic, parallel ion beam of uniform beam current density over the target is essential in view of the effects of the ion beam on the sputtering parameters discussed earlier. The desirable characteristics of the ion source are indicated below:

Production of singly charged  $\text{Ar}^+$  ions. This can be achieved by introducing high purity Ar gas and by maintaining the potential on the appropriate electrode (electron collector) slightly above the first ionisation potential for Ar. A quadrupole lens and a suitable magnetic field can be utilised to select the ions.

Energy of ions adjustable between 100 eV and 3000 eV. This is possible by employing proper methods of extraction and acceleration of ions emerging from ionisation chamber.

Ion current adjustable between  $10^{-11} \text{ A}$  and  $10^{-6} \text{ A}$ . This can be achieved by changing the pressure of Ar gas in the ionisation chamber.

The beam spot diameter adjustable between  $0.1 \text{ cm}^2$  and  $0.5 \text{ cm}^2$ .  
The beam current density  $j_p$  adjustable between  $10^{-10} \text{ A/cm}^2$  and

$10^{-5}$  A/cm<sup>2</sup>. This is necessary to obtain the secondary ion intensity in the measurable range of the detector ( $10^2$  to  $10^7$  cps, fsd), in view of a wide variation in secondary ion yields of the sputtered species ( $\gamma \cdot x$  varies between less than  $10^{-11}$  and  $1.2 \times 10^{-5}$ ). The adjustment of  $j_p$  is also necessary to take the depth profile measurements where high sputtering rate is desired.

Differential pumping of the ion source. This can be achieved by selecting the ion exit hole of a suitable conductance and by leaking the gas directly into the ionisation chamber of the ion source. With this arrangement it is possible to attain a pressure differential of 100 to 1000 between the ionisation chamber and the target region thus achieving higher sensitivities even at low pressures.

Huber<sup>20</sup> has described an electron impact type of ion source for use in the SIMS. This ion source is illustrated in Figure 1. It utilizes axial magnetic field for collimating the electrons. It also uses differential pumping through the ion exit hole. A quadrupole lens and a magnetic field ( $60^\circ$ , 10 cm path curvature) is utilised to select the primary ions.

4.2 Target Assembly, Analyser and Detector: A rotary feed-through that can allow sufficiently reproducible positioning of the target sample is essential. It should be possible to mount few individual samples at a time on such an insulated insert. The angle of incidence chosen for the primary beam is grazing ( $70^\circ$ ) relative to the target normal.

A mass spectrometer is essential to analyse the secondary ions from the solid surface. This could be a magnetic sector type or a double focussing combination of magnetic and electric fields or a quadrupole mass filter or a time of flight mass spectrometer. In the detection unit the mass selected secondary ions can finally be detected and registered. An open multiplier operating in the single ion counting mode can be used in order to get maximum sensitivity.

A specially modified quadrupole used by Benninghoven<sup>23</sup> consists of a focussing lens between the target and the analyser, the quadrupole

analyser itself, an electrostatic deflection system and the off-axis ion collector-cum-secondary electron multiplier. The field axis of the quadrupole is operated at higher potential to retard the incoming ions to spend sufficient time in the analyser field. Signal/Background ratio is improved by orders of magnitude due to the off-axis orientation of the multiplier. The background also includes scattered fast ions and neutrals. Switching arrangement for quadrupole is essential to measure both positive and negative ions.

The multiplier should be in a position to operate at voltages necessary for both positive and negative ions. The output pulses of the multiplier can be coupled through a capacitance to an amplifier/discriminator and further processed by a counting circuit. The different ranges of the detection circuit can be  $10^2$  to  $10^7$  cps (fsd). The detection unit should include rate meter and X-Y recorder.

The analyser can be combined with a programme unit that allows to scan only preselected parts of the spectrum.

**4.3 Ultra High Vacuum Systems:** An all-metal, bakeable, large-volume system capable of giving ultimate pressure of about  $5 \times 10^{-11}$  Torr is essential. Commercial systems employ titanium sublimation pumps with liquid nitrogen cooled walls in conjunction with an ion-pump/cryosorption pump system or a turbomolecular pump. High speed pumps are necessary as some samples cannot stand high temperature bakeout. A residual gas analyser and a Bayard-Alpert gauge is used to measure partial and residual pressures respectively. Isolation and leak valves for uhv application are essential.

## 5. APPLICATIONS

Figures 2a and 2b show the positive and negative secondary ion spectra<sup>24</sup> of the original outermost monolayer of a contaminated Mo foil. The spectra indicate the presence of the following details:

$H^+$  and  $H_2^+$  from hydrogen and hydrogen containing compounds,  
 $H_2O^+$  from water in contamination layer,  
 Ions of general composition  $C_m H_n^+$  (upto  $m = 14$ ),  
 $Mo^+$  and  $MoO^+$  from partially exposed oxide film,  
 $H^-$ ,  $OH^-$  and  $O^-$  from contamination film,

$\text{NO}_3^-$ ,  $\text{NO}_2^-$  from nitrate complexes,  
 $\text{MoO}_2^-$ ,  $\text{MoO}_3^-$  and  $\text{MoO}_4^-$  from typical molybdenum oxides,  
Hydrocarbon lines.

The spectra indicate the detectability of hydrogen and chemical compounds or their characteristic fragments. They also indicate the capability of distinguishing isotopes.

Figure 3 shows the effect<sup>25</sup> of oxygen exposure on a clean poly-crystalline Al surface. The spectra indicate changes in the intensity of negative secondary ions  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{AlO}^-$  and  $\text{AlO}_2^-$  with time from the surface. Saturation can be observed after about 1000 sec, corresponding to an oxygen dose of about 500 L, indicating that the surface is apparently covered with a closed oxide layer. Figure 4 shows the decrease in the secondary ion intensities with time during removal of the oxide layer by high current density ion bombardment. For one order of magnitude, the secondary ions  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{AlO}^-$  and  $\text{AlO}_2^-$  follow exactly an exponential time dependence. This is attributed to a structure of a thickness no more than one monolayer as can be observed from the expression (2) mentioned earlier. The secondary ions  $\text{AlO}^-$  and  $\text{AlO}_2^-$  exhibit the same time dependence, indicating that the same surface compound constitutes these two kinds of ions. This shows that with this method it is possible to study oxidation on surfaces.

Benninghoven<sup>26</sup> investigated a sample of Ag catalyst which had been used over a long period for the oxidation of ethylene. He utilised SIMS to study the chemical composition of the uppermost monolayers and changes in its composition as a result of ion bombardment, heating and surface diffusion processes.

SIMS can be utilised in research, development and quality control. Fields of application include surface reactions, surface technology, semiconductors, thin films, emission processes, chemistry, metallurgy, vacuum technology etc.

## 6. DISCUSSION

The other varieties<sup>27</sup> of the SIMS method include Dynamic SIMS

(DSIMS) Secondary Ion Imaging Mass Spectrometry (SIIMS) and Secondary Ion Microprobe Mass Spectrometry (SIMMS). DSIMS has been discussed earlier in this article.

In SIIMS, the sample is bombarded with a primary ion beam of about  $300 \mu\text{m}$  diameter. The instrument, tuned to one particular element, gives an image of the distribution of this element in the bombarded surface area through the ion optics of the mass spectrometer.

In SIMMS, the mass spectrometer is tuned to one particular mass. The primary beam of about  $1 \mu\text{m}$  diameter scans the surface across an area of approximately  $300 \times 300 \mu\text{m}^2$  and the output from the multiplier modulates the intensity of the beam in a cathode ray tube, the deflection of which is in synchronism with the primary beam deflection. Thus, the topographical distribution of a particular element is displayed.

The main features of SIMS (Static) as a method for surface investigation are:

- Information depth in monolayer range,
- Detection of elements and compounds,
- Detection of hydrogen and its compounds,
- Capability to distinguish isotopes,
- High sensitivity, the detection limits being less than  $10^{-6}$  of a monolayer or less than  $10^{-14}$  g for many elements and compounds,
- Capacity of quantitative analysis,
- Detection of changes in the concentration within the first monolayers (depth profile),
- Very small influence of the method on the surface composition. Only 1% monolayer is removed after 1000 sec.
- Difference in sensitivity for surface structures (elements, compounds), in certain cases this can be of more than three orders of magnitude. Ease of interpretation of the analysis.

Among the methods, SIMS gives the maximum sensitivity. The large difference in sensitivities for some structures is sometimes



disadvantageous compared to the small difference with AES and ESCA. Also, removal of 1% of monolayer after 1000 sec can be viewed as destructive nature of the method. It is important to note that SIMS and ISS are the only methods that can give information depth in monolayer range and can distinguish isotopes; such information is not possible with AES and ESCA. Detection of hydrogen and its compounds is also not possible with ISS, AES and ESCA.

In view of limitations of the different methods for surface analysis, a system incorporating combination of methods such as SIMS/AES, SIMS/ISS is often recommended for certain applications.

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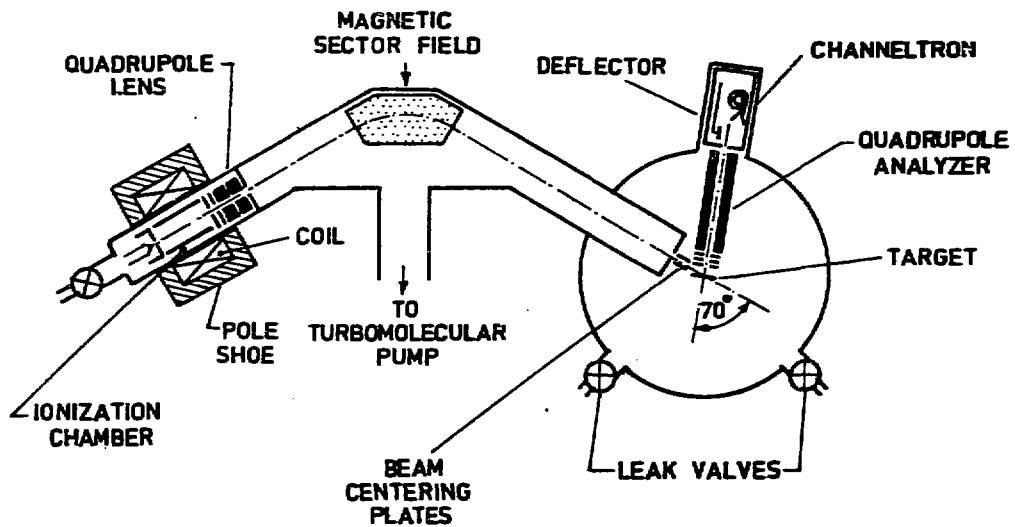


Fig.1: Schematic of SIMS system

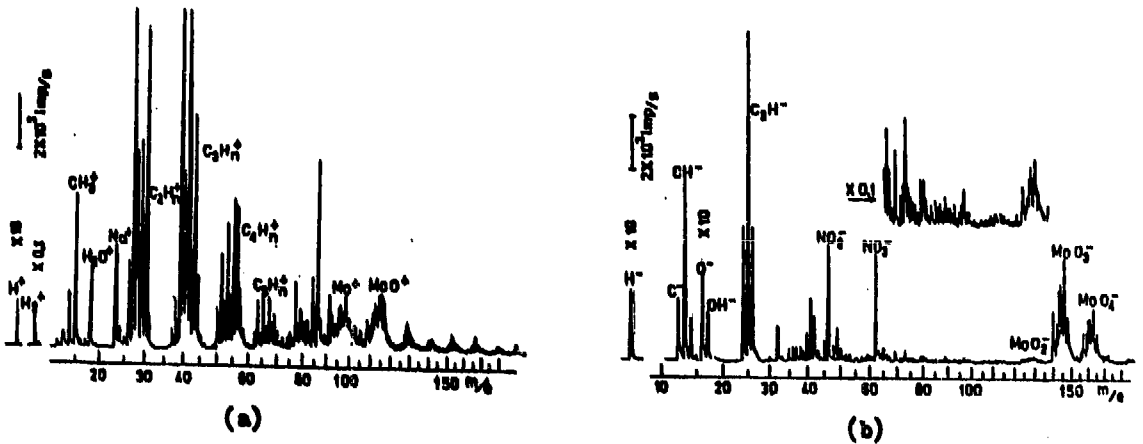


Fig.2: Positive(a) and negative(b) secondary ion spectra of a contaminated Mo foil taken at  $10^{-9}$  Torr with  $Ar^+$ , 3 KeV and  $1 \times 10^{-9}$  A/cm<sup>2</sup>.

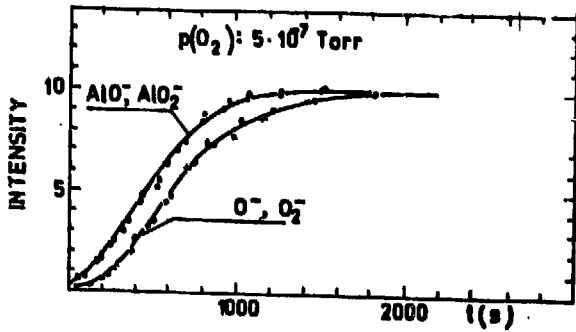


Fig.3: Negative secondary ion intensities showing increase during oxygen exposure of a clean Al surface.

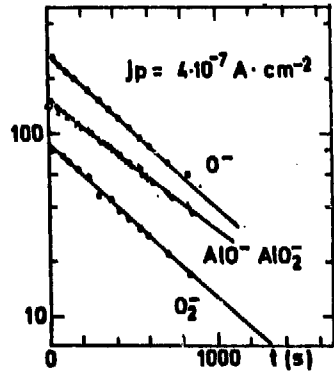


Fig.4: Negative secondary ion intensities showing decrease during sputtering of a monomolecular oxide layer on Al surface.