

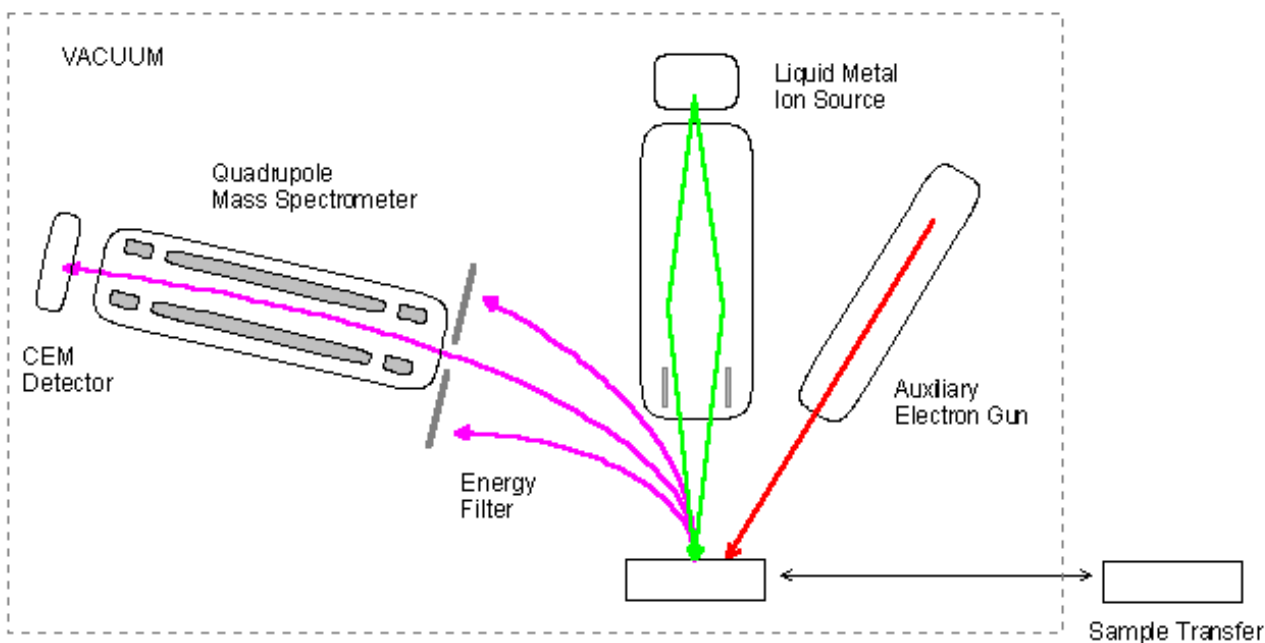


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## B Instrumental Requirements for SIMS

As an example of SIMS instrumentation, a schematic of the MiniSIMS instrument is shown below (this corresponds closely to the main screen display of the MiniSIMS control software).



The following Sections describe each of the major components in more detail.

### **B.1 The Vacuum System**

### **B.2 The Ion Gun**

#### **B.2.1 Liquid Metal Ion Source**

#### **B.2.2 Ion Beam Rastering**

### **B.3 The Quadrupole Mass Spectrometer**

### **B.4 The Detector**

### **B.5 The Electron Gun & Charge Compensation System**

## **B.1 The Vacuum System**

There are two reasons why a vacuum system is required. In a SIMS analysis, charged particles have to travel distances of up to 20 cm without being scattered through collisions with ambient molecules. To achieve this requirement the gas pressure in the instrument has to be reduced such that the mean free path between such gas molecule collisions is at least of the same order of magnitude, and this condition is met at  $\sim 10^{-5}$  mbar.

However, since SIMS is a highly surface sensitive technique, there is a further requirement to limit the adsorption of molecules on to the sample surface from within the chamber. Here the concept of sticking coefficient is important. For a very reactive surface (e.g. a clean oxidisable metal) and a very active gas (e.g. oxygen) each collision of the gas molecule with the surface would lead to adsorption - which would be a sticking coefficient of unity. In such circumstances a complete monolayer of adsorbed molecules would form in 1 second at a pressure of  $\sim 10^{-6}$  mbar. This represents a worse case scenario, and in general sticking coefficients are less than unity. For samples that have been exposed to normal environments, and are therefore likely to have adsorbed molecules (e.g. hydrocarbons) already on the surface, sticking coefficients will be well below unity.

The base pressure of the MiniSIMS is around  $5 \times 10^{-7}$  mbar and normal operating pressures are around  $1 \times 10^{-6}$  mbar. This is a reasonable compromise between the ideal situation of an operating pressure of  $10^{-8}$ - $10^{-9}$  mbar (which would require large pumping systems and regular instrument bakeout to remove water vapour) and an inexpensive, compact, high sample throughput design.

It should be remembered that in the vacuum system there is an equilibrium between molecules in the gas phase and those adsorbed on the internal surfaces of the vacuum chamber. Population of the surface sites of the chamber walls with molecules from a highly outgassing (volatile) sample can lead to memory effects (i.e. a later sample may show evidence of these molecules on its surface) and outgassing samples should not be loaded into the instrument.

The MiniSIMS has a two-stage pumping system, namely a turbomolecular pump backed by a diaphragm pump. These pumps are highly compact devices and they also have the advantage that they are essentially oil-free, hence they are not themselves a possible source of contaminating molecules within the vacuum system.

Pressure monitoring is performed by two gauges. A thermocouple gauge on the backing pump senses the variation in thermal conductivity of the gas in the system and can measure pressures down to  $<10^{-1}$  mbar. A gauge on the main vacuum chamber senses the number density of molecules in the system by ionization and can measure pressures down to  $\sim 10^{-8}$  mbar.

There is a large ballast volume called a reservoir incorporated in the backing vacuum. This smooths out any transient rises in pressure that occur during sample loading, and also allows the diaphragm pump to be turned off for extended periods if required.

To provide a rapid pump-down time for high throughput of samples, the volume of gas introduced during sample introduction has been kept to a minimum (about 1-2 cm<sup>3</sup>). This is why the sample loading system dimensions have been kept small. This volume is pumped continuously as the sample is automatically transferred into the instrument, and normally analysis can begin as soon as the sample reaches the analysis position.

If the sample has volatile components then a sustained pressure rise will be seen in the main chamber; should the pressure exceed the threshold pressure of  $3 \times 10^{-6}$  mbar then analysis cannot be initiated to prevent damage to the instrument. As well as the delay there is also the danger of introducing memory effects (see above), and so the operator should avoid volatile samples.

## **B.2 The Ion Gun**

The ion gun creates the high energy primary beam of ions that are used to bombard the sample surface. It essentially consists of a source of ions and lenses to focus the beam of ions and direct it at the sample. The ion source is the most interesting part of the ion gun and will be described in greatest detail.

### **B.2.1 Liquid Metal Ion Source**

Several types of ion source are used in SIMS depending on the type of analysis. The liquid metal ion source is unrivaled in its ability to provide a finely focused beam without having to sacrifice current density and so it is the obvious choice for the MiniSIMS.

In the source, a tungsten needle with a tip radius of 10 μm dips into a reservoir of liquid metal. The liquid metal wets the tip and is drawn up over the tip surface by capillary action. An extractor electrode with a central aperture is placed a short distance from the tip and a high voltage is applied between the needle and the extractor. The combination of surface tension and electrostatic forces acting on the liquid metal film leads to the formation of a conical protrusion at the tip of the needle (known as a Taylor cone) and this has an even higher radius of curvature.

Once the field strength across the tip-extractor gap exceeds  $\sim 10^8$  Vcm<sup>-1</sup> then field emission of positive ions occurs from the tip of the Taylor cone. In an analogous term to light sources, the liquid metal ion source is said to very “bright” because a relatively intense beam of ions is originating from what is essentially a point source. The high voltage (~6 kV) is applied to the needle and the ions therefore acquire the high energy (~6 keV) required for the primary ion beam in a SIMS analysis. The ion emission from the source is stabilized by variation of the voltage difference.

There will be gradual build up of contamination on the liquid metal film from the residual gases in the vacuum system (from the samples introduced) and the formation of irregularities on the exposed needle (probably mainly due to metal oxide nucleation - the relatively high partial pressure of water in the vacuum system is a major contributor to this behaviour). The source is designed to be easily replaced and tip failure takes place long before the reservoir of liquid metal is exhausted.

After formation the ions are focused to the small spot needed for chemical microscopy and are directed at the sample (see below). There are two preset options for the beam intensity at the sample, “Lo” and “Hi”. “Lo” corresponds a low beam current of about 3 nA and this setting is used for analysis. “Hi” corresponds to a higher emission current, and this setting is primarily used for short periods (less than 1 minute) to clean the ion source. The ion beam current at the sample is monitored and displayed on the main software control screen.

The liquid metal used in the ion source of the MiniSIMS is gallium. The melting point is ~30 °C and the metal is liquid under normal laboratory conditions. However, to ensure full wetting of the needle, the reservoir and needle are fitted with a heater to maintain a temperature of 70 °C.

Gallium has two isotopes:  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  with relative abundances of 60% and 40% respectively.  $\text{Ga}^+$  appears in positive ion SIMS spectra as a characteristic doublet at  $m/z = 69$  &  $71$  with the appropriate 3:2 intensity ratio. At very low primary ion dose, little or no  $\text{Ga}^+$  is detected, and any  $\text{Ga}^+$  seen is from reflected primary ions. At higher doses the intensity increases as implanted gallium builds up in the surface and near surface layers, and the  $\text{Ga}_2^+$  triplet around  $m/z = 140$  may also be seen. In the negative ion spectra peaks due to  $\text{GaO}^-$  appear at  $m/z = 85$  &  $87$ , indicating the reactivity of implanted Ga to residual gases in the vacuum system.

## **B.2.2 Ion Beam Rastering**

The primary ions are focused to produce a spot diameter at the sample of 5  $\mu\text{m}$ . However there is a rather broader component to the beam (which may have up to ~10% of the total intensity) with ~10  $\mu\text{m}$  diameter. This produces a low intensity ‘halo’ around features discernible at the highest spatial resolution. The ion beam can be raster scanned line-by-line (as in a TV picture) over a region of maximum size about 4.5 mm x 4.5 mm (lowest magnification). The zoom feature allows smaller areas to be raster scanned (down to 0.45 mm or 450  $\mu\text{m}$  square) to give higher magnification.

The number of pixels in the image frame is fixed at 200 x 200 so at maximum magnification the pixel size is ~ 2  $\mu\text{m}$ . This is smaller than the ion beam diameter so the beam spot overlaps several pixels. At 2 mm x 2 mm the spot and pixel dimensions are comparable. Higher magnification is appropriate for microanalysis when defining regions for acquiring spectra,

where the primary beam diameter sets the ultimate limit of minimum attainable size.

### **B.3 The Quadrupole Mass Spectrometer**

The quadrupole mass filter consists of four electrically conducting parallel rods. Opposite rods are connected to the same potential  $P$ , which has both a dc component and an RF component. For each pair of rods the sign of this potential at any given time  $t$  is opposite, and is given by

$$P(t) = +/- [U + V\cos(2\pi ft)]$$

where  $U$  is the dc voltage and  $V$  is the peak amplitude of the RF frequency with frequency  $f$ .

Secondary ions are injected into the assembly parallel to the rods and undergo transverse motion leading to oscillatory trajectories which in general result in collision with the rods. For any set value of  $U$ ,  $V$  and  $f$  however, an ion of a certain  $m/z$  will have a stable trajectory through the assembly and will emerge at the far end of the rods. Thus the quadrupole can be used as a filter to pass ions of only a certain  $m/z$  value; by sequentially changing the values of  $U$ ,  $V$  and  $f$ , ions of each different mass of interest can be allowed to pass through the filter in turn.

There are several ways in which these parameters can be systematically varied to scan a mass range, characterized by different interrelationships between mass resolution and transmission (these were defined in Section A). In the MiniSIMS the mass filter is operated at constant  $f$ , and  $U$  and  $V$  are simultaneously increased whilst maintaining a fixed ratio  $U/V$ . The parameters are set to give  $\Delta m_b \sim 1$  across the mass range (i.e. separation and filtration of adjacent unit mass peaks), which results in transmission falling with mass.

Large diameter rods increase transmission, and the higher the frequency  $f$  the shorter the rods can be. Transmission is also significantly degraded by the large fringing fields at the ends of the rods, leading to trapping and reflection of low velocity ions. This problem can be largely overcome by placing additional short rods before and after the main rods (termed a segmented rod configuration). The quadrupole mass filter used in the MiniSIMS uses this segmented arrangement with 6 mm diameter rods. In order to achieve a reasonable mass range with a relatively short filter it is advantageous to scan from  $m/z = 2$  and sacrifice the detection of H at  $m/z = 1$ . Thus the available mass range is 2 to 300 daltons for singly charged secondary ions (normally optimized for the  $m/z = 3$  to 300 range).

A quadrupole cannot filter out secondary ions that leave the sample surface with high kinetic energies. The secondary ions leaving the sample are therefore sent through an energy filter before injection into the quadrupole. In the MiniSIMS this is achieved by electrostatic deflection of the ions through a simple spherical sector field. This allows the selection of mean energy and a narrow energy spread (from the total secondary ion energy distribution), which is compatible with the acceptance characteristics of the quadrupole filter. In particular,

the high-energy tail in the distribution of atomic species is rejected and the collection of the lower energy polyatomic (or cluster) ions, which have a narrow energy distribution, is optimized. Because the trajectories of the secondary ions curve during energy filtration, the largely neutral component of the sputtered flux is prevented from entering the mass filter.

The field of view or acceptance area of the ion optics that collect the secondary ions from the sample is scanned in tandem with the primary beam position, an arrangement known as dynamic emittance matching. This therefore allows large areas to be imaged with uniform intensity.

## **B.4 The Detector**

Following mass filtering, the secondary ions of selected  $m/z$  need to be detected. This is achieved by conversion of secondary ion pulses into amplified electron pulses using a channel electron multiplier (usually abbreviated to channeltron). This consists of a collection cone, about 1 cm in diameter, to which is attached a coiled hollow tube (channel) of semi-conducting glass (total length  $\sim 6$  cm). Secondary ions are accelerated into the cone by a potential of 1 kV and a voltage of 1.5 - 3.5 kV is maintained across the length of the coiled tube.

When the ions impact inside the cone, electrons are generated; these in turn strike the inner walls of the tube and produce a high yield of yet more electrons. The coiled shape of the channeltron means that the electron shower cascades down the tube leading to an exponential increase (multiplying) in the number of electrons. Overall the device acts to amplify the initial pulse, and the effective gain of this amplifier is  $\sim 10^8$ .

The channeltron efficiency is a function of the voltage across the coil and there is a threshold voltage beyond which the amplification gain shows no further increase. The aim is to operate at just over the “knee” of this plateau, and this optimum operating voltage gradually increases with usage. The detector performance is checked at the MiniSIMS routine service, and the channeltron voltage is adjusted to maintain optimum efficiency over its lifetime.

The channeltron is operated in ac mode and each amplified pulse is detected by an electronic circuit. As the quadrupole is digitally scanned over the mass range, the detected pulses are accumulated by the system computer into individual channels. In this way the secondary ion intensity at each  $m/z$  value is recorded and a mass spectrum is built up. Each pulse is called a “count”, and the vertical axis of a mass spectrum is displayed as the number of counts detected per second (cps).

If there are no secondary ions entering the channeltron, there is a very low random noise level of  $< 1$  pulse per second (known as the dark count rate). After each pulse passes down the tube there is a short recovery period before another electron shower can be initiated; this effect limits the maximum count rate to approximately  $10^6$  pulses per second. This so called saturation effect means that very intense peaks in the mass spectrum will have flat or concave

tops and the spectrum will be distorted.

Channeltrons age over time and are normally replaced once every 2-5 years. This aging process is dramatically accelerated if the channeltron is used continuously at high count rates, and noticeable degradation will occur within a few hours. A replacement is expensive (around £1000) and under no circumstances should sustained high count rates be measured – such conditions will also result in misleading data due to the saturation effect described above.

## **B.5 The Electron Gun and Charge Compensation System**

Under primary ion bombardment by  $\text{Ga}^+$ , an insulating sample will charge positively because there is no effective path to dissipate the incoming charge. This effect will suppress negative secondary ion emission altogether. It will also increase the energy of the positive secondary ions, which prevents their transmission by the energy filter (see above) that is used to filter the ions prior to analysis in the quadrupole.

In either event the effect is the same. Peaks in the mass spectrum do not move or even particularly alter their shape. They simply decrease in intensity so that the mass spectrum is very weak or (usually) non-existent.

To neutralise the charging effect and stabilise the surface potential at its correct value (close to ground), it is necessary to flood the surface with negatively charged particles during analysis. Electrons are used for this purpose, and so the MiniSIMS has the option to be fitted with an auxiliary electron gun.

The electron gun consists of a heated filament at a high negative potential. Electrons are accelerated to the sample through a series of apertures, a lens and a set of XY plates to position the beam.

The charge compensation system of the MiniSIMS is based on a design developed at NPL in Teddington by Gilmore and Seah (see further reading). The electron gun is producing an intense primary beam of high energy electrons. If these were directed at the sample itself, the user would need to adjust precisely the electron flux to balance the incoming primary ion charge density. This would therefore depend on the rate of any charge dissipation by the sample, and the correct value would need to be found for every new type of sample and further adjusted for every change in ion beam raster area and speed. This would be a very difficult task.

Instead, the high energy electron beam is directed at a point beside the sample. At the point of impact, low energy secondary electrons are generated and these are automatically attracted to neutralise any areas of the sample that are beginning to charge positively under the primary ion beam. Once the charge is neutralized the attraction of secondary electrons stops, and so the sample is not overcompensated to a negative potential.

The ease of use is improved still further by oscillating the sample potential so that even with slight residual charge the secondary ions will have the correct energy to be transmitted through the energy filter at least part of each oscillation cycle.

In operation, the sample surface is surrounded by a metal cover with a raised lip. This helps to define the potential of the surface of the sample showing through the square hole in the cover. The high energy electron beam is focused into the angle at the bottom of the raised lip, which maximises secondary electron emission across the sample surface.

The result of this sophisticated charge compensation system is that the process is self-regulating and only minimal adjustment of the electron beam intensity by the user is necessary. However, the system has its limits and it cannot uniformly neutralize the full analysis area. The self-regulating system also cannot cope with the severe sample charging induced by the high current density of a fully focused primary ion beam. For this reason, the primary ion beam is slightly defocused from its optimum value during the analysis of insulators. Although the spatial resolution is not as high, the reduced current density allows positive secondary ion analysis with a focused beam. Spatially resolved negative secondary ion analysis may also be possible if the sample is not too highly insulating.

#### Further reading

For a detailed treatment of all aspects of static and dynamic SIMS see:

*Practical Surface Analysis Second Edition, Vol. 2: Ion and Neutral Spectroscopy*  
Eds. D. Briggs and M.P. Seah, Wiley, Chichester (1996)

For further details of the principles used for the charge compensation system:-

I.S. Gilmore & M.P. Seah, *Surface and Interface Analysis* 23 (1995) 191



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## **C Samples Suitable for SIMS Analysis**

### **C.1 Types of Sample**

### **C.2 Sample Handling and Preparation**

### **C.3 Sample Mounting**

#### **C.1 Types of Sample**

Samples for analysis in the MiniSIMS must be solids (see below for the analysis of liquids in special circumstances).

Samples must be vacuum compatible i.e. they must not contain volatile solvents etc. that will degrade the vacuum in the instrument.

Samples that are electrically conducting (or very weakly insulating) across the surface to be analysed will in general give better results than insulating samples. Insulators cannot be analysed unless the MiniSIMS is fitted with the optional auxiliary electron gun.

For best results, samples should be flat with surface roughness of less than 0.5 mm.

#### **C.2 Sample Handling and Preparation**

The critical point to remember is that SIMS is extremely surface sensitive. Whilst this is the reason why the MiniSIMS can provide unique information relating to surface behaviour, the corollary is that surface contamination during handling and preparation will seriously affect, if not render meaningless, the analytical result.

Therefore, all possible care must be taken to ensure that surface contamination does not happen - starting with the education of sample providers. Samples should not be stored or transported in plastic containers, especially plastic bags, because these contain migratory molecules (additives). Even the polyethylene caps of glass bottles should be avoided. Loose wrapping in two layers of non-patterned domestic aluminium foil (dull side inside) is

recommended. Where appropriate new glass vials with cork stoppers are an alternative. Plain paper envelopes are also usually free of contaminating material. Samples should of course never be directly labeled on the surface of interest.

Taking care with sample handling during loading does result in more consistent instrumental performance over the long-term. In particular:-

Sample stubs should be frequently cleaned using acetone or similar solvents, ideally before each use.

The sample “parking” tray in the sample hatch should similarly be cleaned regularly (e.g. once per week). The tray can be simply lifted out to make this task easier.

Discarded samples should not be allowed to accumulate in the sample parking tray.

Although not essential for a non-UHV instrument, wearing gloves when handling the sample stubs prevents the build up of contamination. Plastic gloves should be both powder and silicone free. If using cotton gloves, take care that no loose fibres are trapped on the sharp edges of the neutralization covers.

When handling the samples themselves, it is essential to avoid contact of the surface with skin. Tweezers should always be used, taking care to avoid making contact with any areas of the surface that will eventually be analyzed.

Thin metal samples can be cut with strong scissors or snips. For material thicker than ~ 0.5 mm a hacksaw will probably be required. Care must be taken to minimize the sticking of particles to the surface, but some is inevitable. This stray material can usually be removed by use of a puff duster (designed to clean camera lenses) or jet of gas from a compressed source. Aerosols are best avoided since many contain halide-based propellants which could leave residues on the surface.

Some semiconductor wafers or devices will fracture easily along the crystal planes, and if the wafer is complete the crystal orientation is often indicated by flats on the outer circumference. Other wafers may be cut to size by scribing straight lines on the sample and pressing gently along the direction of the scribe mark over a slightly raised edge (e.g. a metal rule or glass microscope slide). This operation can be carried out on the reverse side because fine particles are formed during cutting and these can be difficult to remove. However the side of interest will then be in contact with another surface and may become contaminated.

Liquid samples can be attempted by smearing a thin film on to a clean sample stub. The aim is to produce a monolayer thickness, because thicker films will give no greater signal intensity and are likely to be susceptible to charging. The volatile content should be removed (see below) before loading, so only non-volatile components of the original liquid will remain for analysis.

Powdered samples are best avoided! Loose powder samples will fly about when the sample region is pumped out during sample transfer. Particles could penetrate the vacuum seals of the transfer mechanism or enter the pumps and cause permanent damage. Differential charging may also occur when the charged particle beam strikes the surface, leading to electrostatic repulsion between grains. Internal contamination of the secondary ion optics by powders will lead to a severe decrease in secondary ion collection efficiency. Internal cleaning of the instrument to rectify the problem is not covered under normal warranty and service contracts.

If powders must be analysed, and they cannot be compressed into a pellet, then it is essential to form a firmly compressed, uniform layer of powdered material with as flat a surface as possible. This is best achieved by putting the powder on to double sided conductive tape and pressing using a clean glass coverslide. Alternatively, for conducting materials, the powder can be mounted in indium foil; the “sandwich” method is recommended. Place a piece of foil about 10 mm x 5 mm on a flat surface and cover half the surface with the powder. Fold the foil to form a sandwich and press firmly on the outside. Gently peel open the sandwich and cut to size for mounting.

In either case, any loose powder should be removed by:-

- Firmly tapping the edge of the stub on a hard surface to dislodge loose powder
- Wiping any excess off the rim of the sample (outside the central analysis area)
- Brushing the powder surface lightly with a clean tissue
- Blowing with an airjet (compressed gas or lens cleaning bulb)

The above sequence may need to be repeated several times to ensure that all remaining particles of powder are firmly held on the tape or indium foil in a single layer.

### **C.3 Sample Mounting**

Wearing disposable gloves is not essential for this stage but it is recommended to avoid contamination from the skin's natural oils.

For the standard sample stub size, the surface of the sample when mounted on the stub should be 5 mm above the base of the sample platen. For the upgraded sample transfer, these standard stubs are mounted in an adapter of 2 mm thickness. The equivalent height value for stubs designed for use without the adapter is therefore 7 mm.

At lower heights than this, the analysis performance will be progressively degraded. Higher than this, there is a danger of the sample catching and jamming in the instrument (although the arched shape of the sample entry point means that thicker samples of small diameter can be

loaded with extreme care). For conducting samples, little difference in performance will be seen provided that the sample surface is within 2 mm of the correct height. For insulating samples the height is much more critical.

With conducting samples it is essential to provide good electrical contact between the sample surface and the sample stub. It is also necessary to ensure that the sample cannot be blown off the stub when the air is evacuated during sample transfer.

The sample can be secured in a number of ways, e.g. by the use of adhesive tape, conductive silver paint, molten indium or a metal clip. Prior to mounting a sample, the stub should be cleaned using a lint-free tissue soaked in acetone.

The sample can be fixed to the stub using a brand of double-sided adhesive tape which is low in volatiles and which does not involve a silicone release agent (often used to impregnate the backing paper). The minimum sized piece of tape should be used to avoid contaminating the vacuum unnecessarily. "Conducting" tape should be treated with scepticism unless it has been proved to work! Instead a thin strip of aluminium foil placed under and at right angles to the tape can be folded back over the top of tape before the sample is placed in position; this makes good electrical contact between the stub and the back of the sample.

For a conductive coating on an insulating substrate, the back of the sample is electrically isolated from the surface of interest. Placing a neutralization cover over the sample is one way to make a conductive path from the surface of a sample to the sample stub. Alternatively a very small drop of conductive paint (see below) can be used to make an electrical contact between the edge of the sample surface and the stub.

Conductive silver paint is also a means of bonding the back of a sample to the stub because it remains viscous long enough for the sample to be manoeuvred. Unfortunately, as the paint dries it loses volatile solvents. It cannot, therefore, be introduced into the instrument until this process is complete and often this can be inhibited because the paint is trapped in an irregularity in the underside of the sample. Drying off in a low temperature oven for 5-10 minutes is helpful (a glassware drying cabinet, at about 50 °C, is ideal). In general the other methods of sample mounting are to be preferred, but if silver paint is used the amount should be kept to the absolute minimum.

Indium metal can also be used as a bonding agent. A small quantity can be melted on the stub, the sample rapidly brought into contact and the metal allowed to re-freeze.

If the sample surface to be analysed is insulating there is no advantage to having a conductive path from the sample surface to the sample stub. In many ways this makes sample mounting less complicated and the sample can simply be stuck down using vacuum compatible double-sided tape.

Samples with a volatile content (and especially those involving organics rather than water)

should not be loaded directly and allowed to outgas in the sample chamber. This type of sample includes samples that have been freshly mounted using silver conductive paint. Heating and cooling of the sample prior to loading is advisable whenever possible. All such samples should then be allowed to outgas fully in the low vacuum region during loading.