Quantitative Microanalysis Using
The Hyperbolic Field Analyser

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Abstract

In this thesis, a new instrument for Auger spectroscopy, the Hyperbolic Field Analyser has been developed from a working prototype to a fully characterised device for quantitative microanalysis. The HFA is a parallel acquisition electron energy spectrometer enabling very rapid analysis. This is a valuable feature when examining delicate surfaces or mapping large areas.

The speed of the HFA was exploited in the investigation of the electron stimulated desorption of HCl from InP(110). Electron energy spectra were recorded during desorption, showing the time evolution of the Cl and substrate peaks. To explain these, sample absorption current imaging was used to determine the adsorbate distribution, which showed evidence of surface diffusion. Values were obtained for the desorption and diffusion parameters; desorption constant, \( k = (3.75 \pm 0.3) \times 10^{-4} \, \text{A}^{-1}\text{m}^2\text{s}^{-1} \), and the diffusion coefficient \( D < 7.0 \times 10^{-14} \, \text{m}^2\text{s}^{-1} \).

Development of the commercial prototype of the HFA has taken place at Shimadzu Research Laboratory (Europe) Ltd. (SRL) who part funded this work. This was tested and used to investigate various materials, relevant to semiconductor processing. A study into the detection of differences between Ti and TiN showed that the ratio of the \( \sim 380 \, \text{eV} \) Ti/TiN peak to the 416 eV peak, taken in the differential spectrum, could resolve the two. Reliability of the detector was improved, allowing the first spectrum-images to be acquired.

In the final stages, another HFA was built, learning from previous versions to produce a longer, narrower device capable of fitting through a 2½” port. This device allows useful detection ranges down to \( \sim 20 - 500 \, \text{eV} \) and is currently fitted to the MULSAM system, to provide rapid spectrum-imaging capabilities.
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Declaration

I declare that the work presented in this thesis, except contributions acknowledged explicitly in the text or by references, is based on my own research. No part of this work has previously been submitted for any award or qualification.

The following publications have arisen from this work:


Introduction

The surface of a material determines how it will interact chemically with its near environment, be that atmosphere or another material. It can also play an important role in its optical, electronic and magnetic properties. To investigate the surface, it must be probed in some way, so that the results of the probing are unique to the material. This interaction can provide information about the arrangement of atoms on the surface through methods such as scanning tunnelling microscopy\cite{(1)} and atomic force microscopy\cite{(2)} or low-energy electron diffraction (LEED)\cite{(3),(4)} and their elemental composition using such methods as secondary ion mass spectrometry (SIMS), energy-dispersive x-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The relative merits of these methods are covered in general references such as Prutton\cite{(5)} or Briggs and Seah\cite{(6)}.

Today, the proliferation of surface analysis techniques into industry is widespread which, with advances in technology, places increasing demands on the tools used. In the semiconductor industry, for example, there is pressure for ever-more powerful processors, for faster computers. The elements of integrated circuits are being forced smaller, to allow a greater component density. The prime analysis tool for defect analysis at present is EDX, which uses an electron beam to interact with the sample and usually a lithium doped silicon detector to monitor the energy of the X-rays emitted during this interaction. This technique is fast due to the parallel acquisition of X-ray energies, but is limited by a spatial and depth resolution of \(~1 \mu m\). Current photo-lithography techniques produce structures with dimensions of \(~0.13 \mu m\), with next generation devices likely to be better than 60 nm. As the device size decreases, the critical defect size decreases, scaling as approximately 0.3 times that of the device.\cite{References} These defects can include foreign material on the surface,
i.e. point defects, or by a surface or interface having an unexpected composition. This drives the need for analysis techniques with better spatial resolution.

**The emerging importance of Auger electron spectroscopy**

Auger electrons can be generated by bombardment of the sample with either X-rays (hence, Auger features are present on XPS spectra) or a beam of electrons. The latter has the advantage that the beam can be manipulated with electron lenses enabling deflection and focussing.

Electron columns are now available with various electron sources, including thermionic emitters, consisting of a tungsten or LaB$_6$ filament and field-emitters. The latter utilises (for Schottky field emitters) a sharpened tungsten/zirconium tip mounted on a filament wire, situated in a strong electrostatic field. This arrangement provides an electron source with an extremely high brightness, generating a probe of very small size (~10 - 100 nm diameter). Although the probe penetrates deeply (of the order of microns) into the sample, the Auger electrons, with energies up to 2 keV, are subject to strong inelastic scattering, resulting in the electrons being emitted from only the top few atomic layers. This makes the technique as surface sensitive as XPS, though with better lateral resolution. It is also virtually non-destructive, except for materials sensitive to electron beam radiation damage.[8]

The combination of surface sensitivity and spatial resolution make Auger spectroscopy a promising tool for analysis in the semiconductor industry. Manufacturers now produce systems designed for defect analysis on semiconductor wafers primarily using this technique, for example the Physical Electronics SMART-Tool, which uses a combination of a Schottky field-emission electron source and cylindrical mirror analyser. Another example is an instrument built for Intel Corporation by FEI Company. It is designed to perform defect analysis using Auger electron spectroscopy on 300 mm wafers. Due to the high value of such wafers, and the non-destructive nature of AES, this instrument is designed to move a wafer from the fabrication line, analyse defects and return it for completion. The
problem is that unlike EDX detectors the electron spectrometers in these instruments are serial acquisition devices. The long analysis time that this imposes is one of the main obstacles to more widespread use of AES.

**Parallel acquisition**

Electron spectrometers used to analyse the energy of electrons, are commercially available from many manufacturers. They include the *retarding field analyser* (RFA) which is a high pass filter commonly used as a Auger facility on a LEED system, and analysers based on dispersion, such as the *cylindrical mirror analyser* (CMA). This is popular for Auger work due to its second-order focussing ability, which greatly increases the level of signal that can be acquired. Again, these are described in detail in Briggs and Seah.\(^6\) Also used for Auger work is the *concentric hemispherical analyser* or CHA, which is equally suitable to both XPS and AES. Most CHAs are designed for high resolution and are large and costly devices, with mean hemisphere radii of up to 150 mm. A common feature of most dispersion analysers is that focussing properties depend on electron energy. At each energy channel in the spectrum, a finite time is spent acquiring the signal and, for a typical energy spectrum of over 2000 eV energy range, total acquisition time can be of the order of minutes.

Although acceptable for a single high-resolution spectrum, the duration of acquisition can become a hindrance if time-varying effects are being investigated and the whole spectrum is repeatedly required. This can be detrimental to the measurement undertaken; changes to the sample can occur through exposure to the electron beam,\(^8\) mechanical vibration can move the area of interest, etc. Scanning Auger microscopy also becomes very time-consuming, especially elemental mapping. To reduce the acquisition time, usually only a few energies of interest are selected, necessitating prior knowledge of the surface composition. To reduce the acquisition time, a new energy analyser has been developed which can collect the whole spectrum in parallel, the Hyperbolic Field Analyser (HFA).
Motivation for this research

At York, the Surface Physics Group, under Professor Martin Prutton, has had an active interest in Auger spectroscopy since 1970. This has led to the development of the Multi-Spectral Analytical Microscope (MULSAM), which is capable of conducting scanning Auger microscopy. The principle behind MULSAM is to collect as many signals as possible resulting from an electron beam probing the surface, of which the Auger spectrum is the most important, but also the slowest to acquire. This work represents the continuation of the development of the Hyperbolic Field Analyser and its uses, culminating in its inclusion in MULSAM.

In the process of this work, valuable experience has been gained with the industrial partner, Shimadzu Research Laboratories (Europe) Ltd., who permitted the chance to experience working in an industrial research and development environment.
Chapter 1

Auger Spectroscopy

1.1 The Auger process

The process in which an electron is emitted from an atom by adsorbing the energy liberated when another electron falls to a lower energy level was initially observed independently in the 1920’s by Lise Meitner$^{[16]}$ and Pierre Auger,$^{[17]}$ This radiationless atomic relaxation became known as the Auger process, however, it was not until the commercial availability of ultra-high vacuum systems in the 1960’s that the technique became used for surface analysis.

As an analysis technique, Auger electron spectroscopy can determine the elemental composition of a surface by energy analysis of the emitted electrons. The process is initiated by the removal of an inner shell electron by incident electron bombardment or by an X-ray photon (hence, Auger features are also visible in spectra obtained using XPS). An electron from a less tightly bound shell then fills the vacancy, with the energy liberated used to eject a third electron into the vacuum. The energy of this liberated electron, the Auger electron, is therefore dependent on the energy levels (and therefore the atom) from which it originated, as shown in Figure 1.1. The energy of the Auger electron is independent of the primary (exciting) electron energy, so this is usually set to between about 5 and 15 keV to allow both small spot size and high Auger emission cross section.

The Auger process is one of only two methods of decay for core ionised atoms. The other is through the emission of an X-ray photon, with the probability of X-ray emission (the fluorescence yield) increasing with atomic number, and the probability of Auger emission decreasing. Auger emission is the more dominant
1. Auger Spectroscopy

relaxation method at low Z (at Z < 20 the Auger relaxation accounts for more than 90% of transitions).

![Diagram of atomic transitions](image)

Figure 1.1 Schematic of the atomic transitions that result in either the emission of (a) an X-ray photon (of energy $h\nu = E_K - E_{L_1}$) or (b) an Auger electron emission. Adapted from Briggs and Seah.\cite{6}

X-ray notation is conventionally used to describe Auger transitions. The energy of the Auger electron can be approximately represented in this case by

$$E_{KL_{2,3}} \approx E_K - E_{L_i} - E^*_{L_{2,3}}.$$

In this equation $E_K - E_{L_1}$ represents the energy liberated by the electron transition between the two levels and $E^*_{L_{2,3}}$ is the binding energy (starred as it represents the binding energy with a core hole present) of the Auger electron to be overcome. A more complete description can be found in, for example, Briggs and Seah.\cite{6}
1.2 Quantitative Auger spectroscopy.

Auger electron spectroscopy is often used in a qualitative manner to investigate the surface composition of a sample. However, the electron spectrum can also yield quantitative information about the surface composition, which can be used to perform quantitative AES mapping,\cite{18} and depth profiling.\cite{19}

1.2.1 Information extraction

One of the difficulties in using AES is that the signal due to Auger electrons is low in relation to the total electron yield (Figure 1.2). Secondary electrons and primary electrons suffering inelastic collisions contribute to a large background (from 0 eV to around half the primary beam energy). Plotting the differential energy spectrum, \( d(N(E))/dE \) (where \( N \) is the signal, proportional to the number of electrons detected), causes the Auger features to become represented by a positive and negative peak excursion, corresponding to the gradient of the \( N(E) \) peak. Historically it was common to measure derivative spectra (that being more suited to some electron energy analysers). It is now routine to acquire the \( N(E) \) spectrum and, if desired, apply post acquisition differentiation, although there is a penalty of reduced signal to noise when doing so.

![Figure 1.2 A generalised electron energy spectrum from zero energy to the primary beam energy (elastic peak position).](image)
1. Auger Spectroscopy

Absolute measures of peak intensities, with the spectrum being plotted as \( N(E) \) against energy, can be obtained either from a measure of the peak height, or more accurately, the integrated area under the peak. However, the effect of the secondary electron cascade background must be taken into account.

Measuring the intensity of the spectrum at two points with a higher energy than a feature of interest enables an estimation of the background to be linearly extrapolated. This method is rapid to apply, though does not always accurately represent the background curve. It has been determined\(^{[20-22]}\) that the function \( AE^{-m} \) is a good fit to the secondary electron cascade, where \( A \) and \( m \) are adjusted for best fit. This function can be applied using a non-linear least square fitting method,\(^{[23]}\) providing the analyser’s transfer function has been correctly calibrated.

Auger electrons ejected from atoms within the sample may undergo inelastic collisions with other atoms before leaving the surface, causing the Auger signal to have a spread of energies on the low-energy side. Techniques for removing this ‘inelastic tail’ have been devised,\(^{[24-26]}\) with a more comprehensive technique developed by Tougaard.\(^{[27]}\)

1.2.2 Quantification of bulk and overlayers

The magnitude of an Auger electron signal is dependent on the amount of a particular element within the electron beam interaction region. This Auger current, \( I_i \), can be expressed symbolically as\(^{[5]}\)

\[
I_i = N\Omega I_0 \tau r (1 - \omega) \Phi \sec \phi / 4\pi ,
\]

where \( N \) is the atomic density; \( \Omega \), the solid angle of acceptance of the analyser; \( I_0 \), the incident electron beam current and \( \tau \), the escape depth of the Auger electrons. The Auger back scattering factor is \( r \), the ionisation cross section caused by incident electrons is \( \Phi \), the Auger yield is \( (1 - \omega) \), where \( \omega \) is the X-ray fluorescence yield. The angle of the analyser with respect to the surface normal is \( \phi \).
Equation 1.2 provides a direct method of obtaining the absolute surface chemical composition of a sample. In practise however, this is not usually applied directly as parameters such as the ionisation cross section and the escape depth are often not accurately known.

Using relative quantities provides a simpler method of obtaining quantitative information about a sample (assuming all elements are homogeneously distributed). Comparing the measured Auger signal from a sample, $I_i$, with that of a pure elemental standard, $I_i^0$ will yield the atomic concentration, $X_i$, of that element within the sample, thus:

$$X_i = \frac{I_i}{I_i^0}. \quad (1.3)$$

This can also be applied to compound samples.\[6\] Here, the atomic concentration is given by

$$X_j = \frac{I_i/I_i^0}{\sum_j I_j/I_j^0}, \quad (1.4)$$

where $j$ represents all elements present on the surface. This can also be expressed in terms of inverse relative sensitivity factors, $\alpha_i$ (which depend on incident energy and can be found in tabulated form\[28\]), such that

$$X_i = \frac{\alpha_i I_i}{\sum_j \alpha_j I_j}. \quad (1.5)$$

In Chapter 5 Auger spectroscopy is used to determine if an adsorbate is present on the surface of a material. The intensity of an Auger peak emitted from the substrate, $I$, will be attenuated, depending on the layer thickness, $C$, such that,\[6\]

$$I_{measured} = I_{clean} \exp\left(\frac{-C}{\lambda \cos \theta}\right). \quad (1.6)$$
The term $\theta$ represents the angle of the analyser to the surface normal and $\lambda$, the electron mean free path. As this adsorbate thickness changes, the intensity of the recorded Auger signal will change, leading to an estimation of the change in overlayer thickness, $\Delta C$, of

$$\Delta C = \lambda \cos \theta \ln \left( \frac{I_{\text{final}}}{I_{\text{initial}}} \right).$$

(1.7)

The method of Chang$^{[29]}$ can be used to relate adsorbate coverage to the intensity of the adsorbate Auger peak. In this case, the atomic concentration of an overlayer of element $i$, is related to the depth of the layer, $C_i$, by

$$X_i = 1 - \exp \left( -\frac{C_i}{\lambda \cos \theta} \right).$$

(1.8)

The depth of the overlayer of element $i$ is therefore given by

$$C_i = -\lambda \cos \theta \ln \left( 1 - \frac{\alpha_i I_i}{\sum_j \alpha_j I_j} \right).$$

(1.9)

These equations provide a first approximation to quantitative analysis, though neglect certain factors known collectively as matrix effects. This is a term for the effects such as the Auger back scattering factor, $r$; the mean free path of the electrons, $\lambda$; and the density, $\rho$, being dependent on the sample composition. To account for this, a matrix correction term, $F$, can be applied which generates a refined atomic concentration of

$$X_i = \frac{I_i / I_i^0}{\sum_j F_{ij} I_j / I_j^0},$$

(1.10)

with

$$F_{ij} = \frac{r_{ji} (E_j) \lambda_i (E_i) \lambda_j (E_j) a_j^3}{r_{ji} (E_j) \lambda_i (E_i) \lambda_j (E_j) a_j^3}.$$
Here, $E$ represents the Auger electron energy and $a$ is the atomic size. The subscript $M$ refers to properties of the matrix of elements comprising the sample. The correction factor is evaluated for element $i$ over all other elements $j$ in turn.

1.3 Multi-dimensional Auger measurements

Whilst the electron energy spectrum, yields information about the elemental surface structure at a given point, on a sample surface, it may be sometimes desirable to have information about a range of points, across a defect or interface for example. The AES process can be extended to two-dimensions, giving rise to the technique, similar in operating principle to SEM, of scanning Auger microscopy (SAM). This uses a scanned electron beam to map the surface of a sample, however, instead of using a secondary electron detector, an electron spectrometer is used, enabling the energy of the emitted electrons to be investigated. This process is very slow, due to the acquisition time of the analyser used and if a large image is required, the total acquisition time can be impractically long. To overcome this, a few energies are usually selected to be investigated, usually the relevant peak and some points nearby to obtain a measure of the background. This does however require some prior knowledge of the surface composition.

Using SAM to collect the complete electron energy spectrum spanning most Auger energy features is known as spectrum-imaging. The HFA, being a fast parallel acquisition Auger spectrometer was designed with this purpose in mind. Being able to acquire the entire spectrum at every point removes the need for prior knowledge about the surface composition and enables the detection of unexpected surface contaminants. The increased amount of data acquired also allows the shape of the Auger features and the background to be more accurately characterised. This increased data volume recorded cannot be visualised directly and must be appropriately processed. Lines or slices through the data sometimes reveal the interesting effects (see Figure 1.3). Processing and visualisation software has been developed at York for this purpose.\cite{30,31}
Figure 1.3 Information collected during a spectrum-image consists of a ‘cube’ of data, with each colour representing the intensity of the signal at that point. Inspecting data within the cube is difficult, requiring rapid modern computing power and data mining tools, such as Hercules.\[31\]
Chapter 2
The HFA Systems

The work in this thesis was carried out using two experimental systems, the York MULSAM and another smaller system, initially constructed to test the HFA. A goal was to unify these two systems by incorporating a HFA into the MULSAM apparatus.

2.1 Development of the HFA

The aim of decreasing electron-energy analyser acquisition time can be achieved by two approaches – increasing the solid angle of collection or increasing the range of energy channels that are simultaneously acquired. Whilst the first method has many benefits, in the extreme case a larger area around the sample is occupied, which can cause difficulties in locating other detectors and manipulating the sample itself. At York, the second approach is taken.

Modifications to some current serial acquisition devices permit a modest increase in the number of simultaneously acquired measurements; for example the adaptation of a conventional CHA by replacing the exit slit with a position sensitive detector\cite{10,32} providing parallel acquisition over a small energy band (~10% of the middle pass energy). Other devices also exist to gather a larger energy band, such as the double-pass parallel plate analyser\cite{33} that can gather an energy span of ~50% of the middle pass energy.

The new approach taken at York was an attempt to capture the whole electron energy spectrum in one go. This began with the development of the Concentric Cone Spectrometer (CCS),\cite{34} an electrostatic deflection device consisting of two concentric
cone segments, with the sample located at the common centre. An electron probe was mounted on the rotational axis of the cones, with electrons detected on an annulus behind the sample.

The best performance from the CCS was the parallel acquisition of a spectrum ranging from 500 eV to 1400 eV, with a mean resolution of ~7 eV. The problem was traced to a mistake in the theory of the device which failed to take into account the change in energy of the electrons as they passed from the field-free region around the sample into the analyser itself. This point was addressed with the development of another analyser, known as the Wedge-Field Analyser, the optimised version of which became the HFA.

The HFA is a compact lens-less device which uses an electrostatic field to focus electrons onto a linear position sensitive detector. Various aspects of the theoretical principles are given in the references above, but are brought together for the first time in the following summary.

### 2.1.1 Energy analysis with a hyperbolic field

The field used is one quadrant of a two-dimensional quadrupole (or hyperbolic) field. In many mass spectrometers, a quadrupole field is used in a different orientation, though one mass spectrometer has been found in the literature\[35\] which operates in the same manner as the HFA.

Figure 2.1 shows how the field is used. It is low near the origin and increases linearly in both $x$ and $y$ directions (equation 2.1).
Figure 2.1 The equipotentials in a hyperbolic field. The planes at $x = 0, y = 0$ are grounded and the electrode has a potential $V_1$. The field has a characteristic size $b$, with the electrons entering at angle $\alpha$.

\[ V = \frac{V_1}{b^2} xy. \] (2.1)

For electrons entering the field at $x_0$, their position at any subsequent time $t$, whilst still in the field, is described by

\[ x = \frac{x_0}{2} (\cos \tau + \cosh \tau) + \sqrt{\frac{E}{2V_1}} \{ \cos(\alpha - \frac{\pi}{4}) \sin \tau - \sin(\alpha - \frac{\pi}{4}) \sinh \tau \} \] (2.2)

and

\[ y = \frac{x_0}{2} (\cos \tau - \cosh \tau) + \sqrt{\frac{E}{2V_1}} \{ \cos(\alpha - \frac{\pi}{4}) \sin \tau + \sin(\alpha - \frac{\pi}{4}) \sinh \tau \}, \] (2.3)

where

\[ \tau = \sqrt{\frac{2eV_1}{m} t} \] (2.4)

and $b = \frac{\sqrt{2}}{\sqrt{5}}$ to simplify the scaling. For $\alpha < 45^\circ$, once inside the field, the electrons are deflected towards the $x$-axis. The detector in the HFA is situated along this
plane. The electrons will cross this plane at a distance $x_f$, and putting $y = 0$, equations 2.2 and 2.3 can be simplified to

\[ x_f = x_0 \cos \tau + P_A \sin \tau \]
\[ = x_0 \cosh \tau + P_B \sinh \tau . \]  
(2.5)

where

\[ P_A = \sqrt{\frac{2E}{V_1}} \cos \left( \frac{\tau}{2} - \alpha \right) \quad \text{and} \quad P_B = \sqrt{\frac{2E}{V_1}} \sin \left( \frac{\tau}{2} - \alpha \right) . \]  
(2.6)

To aid further analysis, this equation can then be rearranged to a form containing only $x_f$ and known variables,

\[ \tau = \sin^{-1} \left( \frac{x_f}{\left( x_0^2 + P_A^2 \right)^{1/2}} \right) - \sin^{-1} \left( \frac{x_0}{\left( x_0^2 + P_A^2 \right)^{1/2}} \right) \]
\[ = \cosh^{-1} \left( \frac{x_f}{\left( x_0^2 - P_B^2 \right)^{1/2}} \right) - \ln \left( \frac{x_0}{\left( x_0^2 - P_B^2 \right)^{1/2}} \right) . \]  
(2.7)

The condition for focussing of a diverging source of electrons onto the detector plane is

\[ \frac{\partial x_f}{\partial \alpha} = 0 . \]  
(2.8)

The simplest case is when $x_0 = 0$. A similar case is the focussing of a parallel beam:

\[ \frac{\partial x_f}{\partial x_0} = 0 . \]  
(2.9)

This is covered by Jacka et al.\cite{11} and yields the solutions shown in Table 2.1. Importantly, the launch angle is independent of the energy of the electrons.
Table 2.1 Solutions obtained for the first order focussing of electrons originating from a point source or as a parallel beam.

<table>
<thead>
<tr>
<th></th>
<th>Point to Point</th>
<th>Parallel to Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value of $\tau$</td>
<td>1.7145</td>
<td>$\frac{\pi}{2}$</td>
</tr>
<tr>
<td>Launch angle, $\alpha$</td>
<td>20.219°</td>
<td>23.4867°</td>
</tr>
<tr>
<td>Dispersion function</td>
<td>$x_f = 1.3134 \sqrt{\frac{E}{V_1}}$</td>
<td>$x_f = 1.2970 \sqrt{\frac{E}{V_1}}$</td>
</tr>
</tbody>
</table>

For a practical design (without using an input lens), a field free region is desired between the sample and the entrance to the analyser. For a point source at some distance from the entrance, there is no single value of $\alpha$ that will produce energy independent focussing. However, the focussing can closely approximate this by making $x_0 > 0$. The source position is related to $x_0$ by

$$x_0 = x_s - y_s \cot \alpha.$$  \hspace{1cm} (2.10)

Three methods have been used to determine the focussing conditions in this more complex situation.

- A finite difference model was used to ray trace the electron trajectories by calculating the position from the equations of motion, incrementing the value of $\tau$ by a small value each loop.\cite{15}

- Walker et al.\cite{13} used variational methods and considered small changes in the launch angle from which an approximation to the dispersion is generated. This is only valid for small values of $x_0$.

- In the present work, the equation 2.7 was solved simultaneously with its derivative (the first order focussing condition (equation 2.8)),\cite{14} using MathCAD.\cite{36}

With correct settings for $\alpha$, a given geometry with a non-zero $x_0$ can focus electrons, to first-order, nearly independent of energy. In addition it has been found that the
2. The HFA Systems

The hyperbolic field can also be used to focus electrons to second order for a specific energy (contradicting the claim made by Read[37]). If equation 2.7 is twice differentiated and solved (again using MathCAD) for the second order focussing condition,

\[
\frac{\partial x_f}{\partial \alpha} = \frac{\partial^2 x}{\partial \alpha^2} = 0 ,
\]

then for given values of \(x_s, y_s, \alpha\) and \(E/V_1\), the position of second order focussing can be obtained.[14] This feature has been incorporated into the latest HFA (Chapter 7).

2.1.2 The HFA device

This section describes the HFA used to acquire all results obtained at York. During the course of this work, another HFA device was constructed, with certain improvements, being slightly longer than the first, but sharing many common design features (such as a resistive chain providing the field boundaries). This is described in the final chapter, and the reader may wish to refer to it following this section.

The original Hyperbolic Field Analyser was mounted from an 8” port, perpendicular to the axis of the electron gun. It is a compact device, measuring just 100 mm in length, and is manufactured from non-magnetic materials, such as stainless steel and titanium. The analyser has two main sections, the focussing field region and the electron detector, shown in Figure 2.2.

The hyperbolic field was approximated inside the device by the curved electrode, as well as further electrodes on the top and sloping faces (Figure 2.2). The effect of the finite width on the field was reduced by using longer electrodes mounted on the sides. The detector is comprised of a micro-channel plate (MCP) and phosphor screen to convert the electron signal to a light signal, which is then measured using a linear photo-diode array (PDA) with 1024 channels, each measuring...
2.5 × 0.05 mm. This is made by Hamamatsu (S3901-1024F), and has a total active length of 51 mm in the dispersion direction.

Figure 2.2 Schematic of the HFA, showing how the electrons, under the influence of the field, come to focus on the detector.

Under normal operating conditions, the energy range that could be measured simultaneously was approximately 74 to 2600 eV (with a potential of -3 kV applied to the hyperbolic electrode). By changing the field strength higher or lower energy ranges could be acquired, but always with $E_{\text{max}}/E_{\text{min}} \sim 34$.

Designed for rapid acquisition, the HFA was able to acquire this energy range in fewer than 50 ms, with an energy resolution, $\Delta E/E$, of approximately $1/500$. The quality of this spectrum was dependent on the probe current and the sample under investigation. Previous investigations with the HFA have shown\textsuperscript{[15]} that the signal to noise ratio for the 916 eV LMM Auger peak of copper (using a 5 keV incident beam) can be approximately expressed as $3(\text{It})^{\frac{1}{2}}$, where $I$ is the incident current in nanoamperes and $t$ is the acquisition time in seconds. In the present work, further investigations of the signal to noise ratio were conducted and comparisons made with other analysers (Chapter 6).

2.2 The HFA test system

The first experiments with the original HFA were done in a test chamber built for the purpose. This system was made from a commercially available stainless steel...
six-way cross with 8” ports (Figure 2.3). It enabled all equipment to be connected with the centre of the chamber at the analysis position.

Figure 2.3 A photograph of the HFA test system.

The operating pressure of the system was around $10^{-9}$ mbar. This was achieved with a 250 ls$^{-1}$ turbo molecular pump, with magnetic bearings to reduce vibration. Several samples could be stored within the vacuum chamber in a sample tray located close to the manipulator. Samples could be introduced through a 2¾” port to which a portable vacuum system, known as the ‘transfer-trolley’ could be attached.

Sample cleaning was performed by an argon ion gun. This had a non-focussed diverging beam and gave an effective sputtering area of approximately 1 cm$^2$. 
The electron source was a single-lens, 0.5 - 10 keV gun, with a Schottky field emission tip that produced a finely focused spot of the order of 100 nm. The probe current was fixed, with a current limiting aperture mounted within the column and was usually of the order of 4 nA. The electron beam could be scanned over the surface by means of potentials applied to an octupole lens mounted on the electron exit of the column. These were generated within a scan box, which also had provision for astigmatism correction. A mu-metal shield surrounding the gun helped reduce stray AC fields.

Figure 2.4 A schematic plan of the HFA system. The signals collected by the acquisition cards are from the HFA (1), the sample absorption current (3), and from the secondary electron detector (4). The residual gas analyser (2), was connected to the serial port of the acquisition PC.

The sample was electrically isolated from ground by a non-conductive spacer mounted in the manipulator shaft. The sample was then grounded through a pico-ammeter enabling the current flow to be measured. A fast current amplifier replaced the pico-ammeter when sample current imaging was conducted.
The secondary electron detector fitted to the system was of an Everhart and Thornley type, consisting of an in vacuum mounted scintillator and externally mounted photo-multiplier tube. A grid mounted in front of the scintillator attracts secondary electrons of low energy. The raster used to steer the electron beam was also connected to the scanning inputs of a monitor, with the secondary electron signal (0 – 1 V) used to modulate the intensity. This provided real time sub-micron imaging of the sample surface.

To enable computer-based measurements of the secondary electron and sample absorption signals, the outputs of the two detectors were connected to a National Instruments SC-2040 sample and hold board. This enabled both signal levels to be recorded at the same time, giving spatially correlated images. The signals were then measured by the 12-bit analogue to digital converters (ADCs) present on a National Instruments PCI-MIO-16E-4 board, installed in the acquisition PC. This PC was also interfaced to the electron-gun scan unit by means of digital to analogue converters (DACs) on a National Instruments AT-AO-10 ten-channel output board. The signal connections can be seen in Figure 2.4 and Figure 2.5. (This material, though not very stimulating for most readers, is included for the benefit of those who will continue this work).

Figure 2.5 The computer controlled hardware connections on the HFA test system.
2.3 The MULSAM system

A complete description of the MULSAM apparatus (shown in Figure 2.6, and schematically in Figure 2.7) has previously been published,[10] though a basic description will be presented. In essence, MULSAM is a scanning Auger microscope, with additional detectors providing complementary information about the surface under investigation.[9] Collecting all the information at one time not only provides spatially registered data, but also minimises the amount of time the sample is exposed to the electron beam. This reduces sample drift and the damage caused by the electron beam.

Figure 2.6 A photograph of the MULSAM system.

The main electron source in the system is provided by a field emission electron gun, NanoFEG.[39] This is an electrostatic two-lens field emission electron column and is
able to provide an electron beam with a variable energy from 100 eV to 15 keV. At 5 keV it can deliver a probe current of ~5 nA with a beam diameter approaching 50 nm. Sample cleaning within the vacuum system is provided by a differentially pumped, Xenon ion gun, enabling controlled cleaning or ion bevelling.

The detectors in MULSAM are:

- A multi-channel concentric hemispherical analyser to record electron energy spectra, with a channeltron electron multiplier mounted on the straight through position to monitor high-energy electrons.
2. The HFA Systems

- A low energy-loss detector, able to measure electrons with energies near the primary beam energy.\[40\]

- The sample absorption current measured to ground.

- A secondary electron detector.

- A Si(Li) X-ray detector to provide energy dispersive X-ray spectra.\[41\]

- A four-quadrant back scattered electron detector.\[42\]

Those detectors used in this work are described in more detail below.

2.3.1 The low loss detector

The low loss detector is a high-pass filter that measures electrons having lost less than a set amount of energy, which is usually of the order of a few hundred electron volts. Such losses give rise to a measured signal that originates from within the top few nanometres of the surface, comparable to the information depth observed using Auger spectroscopy.\[40\] The main contrast mechanism is due to atomic number, and because it is a high pass filter there is sufficient signal for rapid imaging.

The detector consists of a grounded tube with a grid at the entrance, to preserve the field free region around the sample. Another grid is electrically isolated inside and is held at a potential of \((E_P - E_L)\) volts, where \(E_P\) is the energy of the primary beam, and \(E_L\) is the desired maximum electron energy loss. The transmitted electrons are collected by a channeltron electron multiplier and amplified by a charge sensitive amplifier.
2. The HFA Systems

2.3.2 The CHA

The electron energy spectrum is measured in MULSAM using the multi-channel CHA.\textsuperscript{[10,43]} The analyser detector consists of a 15-channel detector mounted symmetrically about the optical axis on the output plane. When the pass energy of the hemispheres is 126 eV, the energy spread at the output plane is 15 eV (giving 1 eV per channel of the detector and hence 1 eV resolution).

![Figure 2.8 Schematic of the multi-channel CHA in the MULSAM system. Adapted from Prutton.\textsuperscript{[10]}](image)

2.3.3 Changes to the MULSAM layout

The initial layout of the MULSAM system was altered slightly during work, becoming as shown in Figure 2.9, to allow the addition of a HFA. The SAMFEG 20 keV electron gun was removed and replaced by the NanoFEG column in the differentially pumped gun chamber. Other detector positions were altered slightly,
where necessary, to maintain line of sight to the sample. The new HFA, when completed, was mounted from a 4” port, perpendicular to the electron beam.

Figure 2.9 Schematic of the changes to the MULSAM system. Changes include moving of the NanoFEG gun to the differentially pumped gun chamber (1), moving the low-loss detector and SEM detectors to maintain line of sight (2)(4), and moving the ion gun (5) to accommodate the HFA2 (3).
Chapter 3
HFA System Acquisition Software

3.1 Introduction

The decreasing cost and increasing power of readily available computers, and the increasing complexity of modern scientific instrumentation, has led to the role of the computer changing from data acquisition to complete control of the instrumentation. In modern scientific instrumentation the development of the software is almost as important as the hardware. Many instruments require the simultaneous acquisition of many different signals, from a variety of detectors, which can generate very large quantities of data. Computer control is often a necessity, for example when spectrum-imaging, to ensure all data is stored, and in a manner suitable for future processing. The software must be able to acquire data simply and efficiently, in a manner suitable for the analyst (rather than a software engineer), providing an abstraction layer between the inner workings of the computer and measurement being undertaken. It was the aim of the HFA acquisition code to provide such a solution.

Initially, computer control software was written for the HFA system computer that allowed the digitisation of SEM images to be analysed or stored as required (Figure 3.1). It became apparent that this software could be enhanced with the addition of procedures for recording sample absorption current images and to control the HFA itself. Software had previously been written for control of the HFA,[15] though this was designed for preliminary testing of the HFA. It was desirable to have a robust, single program capable of recording both SEM and SAC images, as well as providing a simple ‘point and click’ method of rapidly acquiring Auger spectra.
The ultimate aim is to incorporate this into the MULSAM system for providing spectrum-imaging.

![Figure 3.1 Screenshot of a program designed to record secondary electron and sample absorption current images.](image)

The HFA control program, which became known as Semaphore, was written in the C programming language for an IBM compatible PC using the National Instruments LabWindows/CVI development environment. This package comprises of an integrated C compiler and collection of library functions designed to aid in the interfacing of a computer to National Instruments hardware. It also provides utilities to aid in the construction of programs for the Microsoft Windows operating system.
3.2 Semaphore operating principles

3.2.1 Beam manipulation

The program operates by manipulating the electron beam via a scan box and recording the results from the various detectors, digitised by the control computer. The scan box can operate in two modes, the normal stand alone and in a remote mode. During normal operation, the control box generates the appropriate voltages to deflect the electron beam in response to settings altered on the front panel. If remote operation is used input signals are supplied externally and are scaled and processed by the scan box to produce the desired deflection. When running in manual mode, the scan is generated in the scan box and starts as a fixed amplitude waveform. The signal is then attenuated by an amount related to the magnification. The modified signal is then offset by a DC voltage, adjusted by the shift controls, before being amplified and distributed accordingly to the eight pole deflector.

Computer control of the scan box is achieved by replacing the source signals in the various stages of the scan creation (Figure 3.2). A memory array is loaded with appropriate values to generate a scan of the desired resolution, providing a buffer for the waveform transfer. This is then used by the AT-AO-10 analogue output card to produce the two waveforms, for horizontal and vertical scanning. These waveforms, each with amplitude ±5 V, are connected to the scan box where they become the initial (fixed amplitude) scanning waveform.

The magnification setting of the scan box can be manually adjusted by a rotary encoder on the front panel. This generates a 4-bit number that is used to control the scaling of the initial raster. For computer control, this signal is substituted by a 4-bit TTL level signal supplied by the computer, in this case using the 8-bit digital output port on the AT-AO-10. This simply supplies the appropriate binary value representing the requested magnification.
3. HFA System Acquisition Software

Figure 3.2 Flowchart of the main signal paths within the scan control box showing the main processes; scan generation, scan magnitude modification, DC offset mixing and distribution.

The final stage, the application of a fixed offset to the scanned region, is supplied as two DC voltages (maximum ± 6V) from the computer. These replace the setting from the shift controls and provide movement of the scanned region in the X and Y directions. The scan box then provides the appropriate scaling and distribution of the final signals.

3.2.2 SEM/SAC image acquisition

The voltage outputs from the secondary electron detector and the sample absorption current amplifier can be connected to a monitor for simple imaging, or can be measured by the computer for storage. Using Semaphore, digital acquisition of these images can be conducted at different sampling resolutions (i.e. the number of point measurements taken of the visible area), from $128^2$ to $1024^2$. A wave table is stored on disk for each of these as the array size ranges from 256 kB to 16 MB. The tables contain the pre-calculated values required to load into the output buffer of the AT-AO-10 output card. When the computer acquires an image, the values in the table are stepped through, producing the fixed amplitude raster. The rate at which these values are stepped through, and hence the image acquisition
frequency, is controlled by a continuous TTL level pulse train, generated by a 24-bit counter present on the PCI-MIO-16E-4.

### 3.2.3 Acquiring Auger spectra

The role of the software in acquiring Auger spectra is to position the electron beam and operate the photodiode array. The internal timing within the PDA is controlled from an external low noise driver/amplifier circuit (the C4070). This in turn is controlled by two user supplied pulse trains - the master clock pulses and the master start pulses. The master clock pulses (Figure 3.3a) provide the basis for the timing signals between the C4070 and the PDA, while the master start pulses (Figure 3.3b) control the exposure time. For testing purposes, the pulses can be supplied from a Hamamatsu C4091 pulse generating board.

![Figure 3.3 Timing signals for the C4070 controlling the PDA. The only pulses to be supplied are the master start pulses and the master clock pulses, with the others being generated by the C4070.](image-url)
During spectrum acquisition, pulse trains are generated by 24-bit counters present on the PCI-MIO-16XE-10 card, with timings corresponding to the requested exposure time and PDA read time. The output video signal from the C4070 is a rectangular waveform with an amplitude proportional to the charge accumulation (exposure) of each photocell (Figure 3.3g). This signal is measured using the 16-bit ADC on the PCI-MIO-16XE-10 card. The master start pulse output is also used to inform the ADC to begin conversion from the next update pulse (this being the TRIG signal (Figure 3.3f) available from the C4070).

An Auger spectrum can be acquired from a single point or, by rastering the electron beam, be averaged over a small region. This can be advantageous, as the effect of small-scale impurities and topographic effects on the Auger spectrum will be reduced.

3.2.4 Multidimensional Auger data acquisition

The parallel acquisition nature of the HFA enables this device to detect the entire energy spectrum of a sample in a very short time frame. Thus for a given analysis time, more information can be acquired (i.e. a larger energy window), which presents the problem of how to display the data. When acquiring multiple energy spectra, such as line-scans or a series of spectra acquired at the same point over a period of time, images are used to display the data (Figure 3.4). The intensity of a signal is proportional to the either the brightness or colour of a pixel in the image, with the energy scale represented on one axis, and the time or position represented on the other. Spectral information can be extracted from these images; taking a cross section through the image at a given time or position yields an energy spectrum, and a cross section at constant energy shows the time evolution or spatial distribution of a given peak.

A spectrum-image is an extension of the spectrum line-scan providing information about a surface by acquiring spectra in a regular array over that surface. This data is acquired in a similar manner to that of line-scans, but produces a much larger
3. HFA System Acquisition Software

volume of data due to an area being inspected rather than a linear section. Further
details will be given in the following section.

![Figure 3.4 Examples of multidimensional Auger data. A line-scan (A) is the result of taking regularly displaced multiple Auger spectra. The image shown shows a line-scan across a bevelled Cu (764, 836, 916 eV) and Co (646, 708, 771 eV) multi-layer structure. A time-scan (B) is multiple Auger spectra taken at a single point over time, in this case, showing desorption of chlorine from the surface of InP (Chapter 5). In both cases, horizontal cross sections through the image give conventional energy spectra.]

3.3 The User Interface – main controls

The main user interface was constructed using the tools present within the LabWindows environment and as such is a ‘dialogue’ based window. This enables a simple, clear interface design to be implemented, which displays most controls permanently on the screen with as little hidden as possible. The main interface panel can be seen in Figure 3.5. This panel allows the most frequently altered controls to be adjusted and the results of acquisition to be seen. The main display
3. HFA System Acquisition Software

window is also an active control with different functionality depending on the type of acquisition occurring. Between sessions, most variables are stored within an ASCII text file, along with less frequently altered values, such as directory locations, the available palettes.

![Image 1] Figure 3.5 The main user interface for the acquisition software. The main image shows a SAC image of a bevel through a copper-cobalt multi-layer structure.

3.3.1 Image Acquisition controls

The program is designed so the user first acquires SEM/SAC images of the sample surface, then conducts an Auger investigation using these as a guide to the sample surface. The first image is acquired using the ‘Initial Image’ button. This causes SEM/SAC images to be acquired with the beam shifts centred and the magnification set to the lowest level. This represents an outer bound on the inspection area. To acquire further images, the interactive display is normally used,
in conjunction with the magnification setting. The image can be refreshed by selecting the ‘Take Image’ button.

Normally the image in the main window represents the intensity distribution for a single scan of the surface. However, it can be often useful to acquire more images and average the result to reduce the effects of random noise, especially if the secondary electron yield is low. This can be achieved by means of the ‘fast/average’ toggle within the image acquisition controls.

The image displayed in the main window can be saved using option in the ‘Current View’ controls. If this is SEM/SAC image or the 2D Auger spectra, this can be in the form of Hercules files or SAMProc files (details of these are discussed below). The images can also be saved in a standard 8-bit Microsoft Windows uncompressed bitmap (.bmp) format (an example is shown in Figure 3.6). These bitmaps are useful only as a quick reference to the images obtained, as data is acquired at 12 or 16-bit and information is therefore lost in the conversion to an 8-bit image. Extra information is appended to SEM/SAC bitmaps, including the beam energy used and a length scale bar. The bitmap is also stored using the palette in use at the time of saving.

![Figure 3.6 Example of saved SAC image (silver paint on TiN), from the acquisition software.](image)

Figure 3.6 Example of saved SAC image (silver paint on TiN), from the acquisition software.
When analogue images of the sample surface are displayed on the SEM monitor, the beam continually scans the sample surface. Under computer control, this is not always desirable as the electron beam may affect the surface under inspection, therefore the beam is only scanned during image acquisitions. At other times the beam is ‘parked’ at a user-defined position, usually at maximum beam deflection.

### 3.3.2 Spectrum Acquisition controls

The type of Auger investigation (single spectrum, line-scan, etc.) can be selected using the spectrum acquisition controls. This determines how the beam steering controls are affected during Auger acquisition, and changes the functionality of main window. The currently acquiring electron energy spectrum is displayed in the ‘Auger spectrum’ window. If the spectrum is comprised of multiple acquisitions, the graph display during acquisition represents the current average of the individual acquisitions until the final spectrum is generated.

If the time-scan or line-scan options are selected, then as the spectra are acquired, the 2D-spectra window is updated. When Auger acquisition is complete, the currently displayed spectrum can be enlarged with the ‘zoom’ button. This displays the spectrum in a new larger window in which selecting a point causes a cursor to locate the closest point on the spectrum and display information about the intensity at this energy.

### 3.3.3 The Main Display window

The functionality of the main window changes depending on the type of information being displayed. If an Auger data window is selected, either spectrum display or the 2D spectra view, then the main window becomes a display device. However, if a SEM or SAC image is being displayed, the window becomes interactive.
Provision for beam displacement is incorporated into the main image window. When a SEM/SAC image is displayed, clicking on any point on the main display window will cause a displacement in the centre position of the electron beam. A new image is then acquired about this point. This can be done at any magnification with the displacement scaled accordingly. An image acquired at the minimum magnification represents the outer limit of beam shift.

A scale-bar is superimposed over SEM/SAC images. This was calibrated by measuring the visible area of a mesh with a known spacing at various magnifications and beam energies. From these measurements, the length of the bar is linearly related to the beam energy. The scale-bar represents a length dependant on the magnification setting, corresponding to 1 mm at 10x, 500 μm at 20x, etc. This method provides a method of measuring distance, providing the geometry of the system is the same, especially the distance from the electron beam to the sample. It is usual practise to acquire SEM/SAC images at the HFA analysis position, which, due to the relatively small field of view of the HFA, is kept constant.

The interactive nature of the main display window enables a ‘point and click’ method of acquiring Auger spectra. If an average, rather than a single point, Auger spectrum is acquired, then the area under inspection is that represented by the SEM/SAC image in the main window.

The window functions similarly when the desired Auger data is a spectrum-image. In this case, the image displayed represents the outer bounds of the spectrum-image array. The magnification of the individual elements is calculated by a routine in the program, which allows the element to have as low magnification as possible without overlap. During acquisition, the location of the elements is overlaid on the SEM and SAC images, with the currently acquiring element highlighted.

If the Auger investigation is a line-scan, the role of the main display window changes. If a SEM/SAC image is displayed, then clicking on the window sets the end position of the line-scan. Selecting another point on the image then sets a new
end position with the previous click now indicating the line-scan start position. This provides a rapid way to set a line-scan across a feature of interest. Between the two points, the desired number of spectra will be acquired, with the magnification of the elements again calculated to be the lowest possible without overlap. The proposed line-scan is then overlaid on the SEM/SAC image. If single point spectra are required, then the beam is not scanned over these line-scan elements during acquisition.

3.3.4 Auto saving

An individual energy spectrum can be stored to disk using the save button when the spectrum is displayed in the main window. However, with larger amounts of data, the auto saving function is used. The panel is accessed through the ‘Autosave’ button. The filename used to save the data is generated from user input and has a three digit number automatically appended. This number increases with each file saved, to prevent data being overwritten. Estimated time to completion of the current data acquisition is displayed, which is particularly useful when recording spectrum-images as acquisition time increases greatly when increasing the dimensions.

3.3.5 File formats

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Spectrum</th>
<th>Image</th>
<th>Herc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASCII</td>
<td>SP</td>
<td>Herc</td>
</tr>
<tr>
<td></td>
<td>.xls</td>
<td>.rhs</td>
<td>.hrs</td>
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<td></td>
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<td>Herc</td>
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<td></td>
<td>Bitmap</td>
<td>.bmp</td>
<td>.hrsi</td>
</tr>
<tr>
<td>Auger spectrum</td>
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<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Auger time-scan</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Auger line-scan</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Spectrum-image</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>SEM/SAC image</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 3.1 Storage possibilities for data acquired by Semaphore.
The data obtained by Semaphore is stored in different ways depending on the data measured and the file format selected. The data can be stored as a simple text based file, in the SAMProc format, or in the Hercules file format (Table 3.1). SAMProc and Hercules are software packages developed and used at York, to aid in the visualisation and processing of Auger data.

The ASCII file format is useful for rapid viewing of the data and can be imported into most analysis programs. When the ASCII format is selected, Auger spectra are saved as a simple list of energy (or photodiode channel) and intensity value. This is preceded by a simple header containing information about the conditions for experiment. Auger line-scans are saved in a similar manner with the spectra for each point along the line stored sequentially.

SAMProc is a text-based spectrum processing package written at York. It is used to both visualise and process data obtained at York, handling single dimension data, such as individual spectra, and two-dimensional data such as line-scans and images. The file format consists of a header containing fixed width fields and an encoded data block. This data is stored such that only the differences between values are stored (run-length encoding) decreasing the file size. The values are then stored such that they correspond to an ASCII character between 33 ('!') and 126 ('~'), with a new line occurring between encoded values every 73 to 79 characters. This ensures the data can be read into a text editor if information in the header is required on a machine without the SAMProc program installed.

The Hercules format is the native format of new spectrum processing software being developed at York. This program builds on SAMProc, and runs under Microsoft Windows. The main feature of this software is that it can handle three-dimensional data, such as spectrum-imaging. The file format consists of a header followed by an encoded data block and uses different compression routines depending on whether the data is in the form of floating point or integer values. The data output from the HFA is of an integer nature and is compressed in the same manner as that for the SAMProc format.
3.3.6 Transfer function correction

Multiplicative and additive calibration factors can be applied to the spectrum received from the HFA during acquisition. These are stored as spectra (that can be loaded prior to acquisition) corresponding to either a scaling factor, or a value to be subtracted, for each photodiode element. In addition a dispersion function can be applied so that the x-axis corresponds to energy rather than photodiode channel. Details of how these analyser calibration functions can be found in Chapter 4.

The PDA is generally a very reliable device. However, during use it was sometime noted that a single photodiode channel would become defective. This would be manifest in the signal from a single channel becoming saturated. This often made rapid inspection difficult, due to the auto scaling of both spectrum axis and image intensities within the program. To remove the erroneous data generated by the damaged channel, the saturated value was substituted with the interpolated value from the two neighbouring channels. Providing this correction is not located very close to an Auger peak on the energy spectrum, this procedure does not affect the validity of the measurement. This procedure is accessed from the veto channel settings.

3.3.7 The user displays

The currently acquired data is displayed in windows located below the main display window. These windows are updated if new data is acquired and are present to provide a thumbnail of the most recently acquired data. One of these views will always be missing, corresponding to the information being displayed in the main display window. The user can select which information is displayed by simply selecting the small window of interest. The target area window is updated only when the ‘initial image’ button is selected, providing a small view of the entire surface at lowest magnification. A cross hair is superimposed representing the position on the surface of the current SEM/SAC image.
3.4 Future improvements

At present many of the arrays, such as that used to generate the scan arrays and the acquired images are stored on hard disk and read into memory when required. This was done deliberately to reduce the memory footprint of the program when running. When recording line-scans or spectrum-images, the currently acquiring spectrum is also cached to disk, ensuring that in the event of computer failure, as much data as possible will be saved. This does have the effect of slowing the program slightly however. Therefore, with the ever-decreasing cost of memory, it would be a better compromise to maintain more of the data in memory and only immediately store the data acquired from the detectors.

The HFA has been designed with the intention of providing another supplementary detection method to the MULSAM instrument. Therefore, it will eventually become necessary to integrate the control functions for the HFA with the currently existing software for the other detectors, or vice versa. This will not be a trivial task as there are several hardware and software compatibility issues to be dealt with.
Chapter 4
HFA Calibration Methods

4.1 Introduction

The output obtained from the HFA is a set of signals, related to the electron energy spectrum leaving the surface of a material, but also a function of the properties of the HFA itself. It is the purpose of calibration to determine the nature of this relationship.

Seah and Smith\cite{46} have previously reported on the thorough characterisation of an electron spectrometer. They determined that the various contributions to the observed output signal, \( I(E) \), could be expressed by

\[
I(E) = I_0 
\]

\[
Q(E) \ n_i(E) ,
\]

(4.1)

where \( n_i(E) \) is the absolute spectral intensity emitted from a sample \( i \), per incident electron. The primary beam current is \( I_0 \) and \( Q(E) \) represents the effect of the measuring process as a whole on the output spectrum. These effects can be divided into four main terms,\cite{47}

\[
Q(E) = H(E) T(E) D(E) F(E) .
\]

(4.2)

\( H(E) \) represents an efficiency term caused by design tolerances, electron scattering, and stray magnetic fields. It can be thought of as representing the uncertainty in \( T(E) \) which represents the electron transmission of the analyser. \( D(E) \) is the efficiency of the detection system and \( F(E) \) is the efficiency of acquisition electronics.
Seah and Smith were then able to isolate each component and investigate its effect on the final spectrum, enabling the creation of a calibration spectrum which, when applied to their spectrometer, provided a direct measure of $n(E)$.

Direct calibration of a parallel acquisition device is more complicated, due to the increased number of detectors (for example, there are 1024 individual channels in the current HFA detector), each with a different relationship to the true energy spectrum.

Calibrating the measured signal from the HFA to the ‘true’ electron energy spectrum can be divided into two tasks. The first (and simpler) is to determine the relationship between the energy of the detected electrons and the position along the detector at which they are recorded (the dispersion relationship). Secondly, it must be established how the signal recorded by any one channel relates to the number of electrons that leave the sample surface at the corresponding energy (the intensity relationship).

The main points affecting the intensity relationship can be divided into two main categories, additive factors, and multiplicative factors. The former are introduced through the semiconductor based PDA detector (and associated electronics) used to measure the electron signal, and the latter represents all other factors influencing the intensity of the recorded signal. These can be seen in Table 4.1. It is not necessary to calculate a correction term for each of these factors as, providing experimental conditions remain unaltered, a single gain factor can represent the composite effect on the recorded spectrum. There can also be a further contribution due to internal scattering of high-energy electrons.
### 4. HFA Calibration Methods

<table>
<thead>
<tr>
<th>Factor</th>
<th>Influenced by</th>
<th>Related to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probability that electrons enter HFA.</td>
<td>Solid angle of collection.</td>
<td>$T(E)$</td>
</tr>
<tr>
<td>Probability of an electron landing on the detector.</td>
<td>Solid angle of collection as seen by the position sensitive detector.</td>
<td>$T(E)$</td>
</tr>
<tr>
<td>Residual internal scattering</td>
<td>Electron energy</td>
<td>$H(E)$</td>
</tr>
<tr>
<td>Gain of the MCP.</td>
<td>Electron energy</td>
<td>$D(E)$</td>
</tr>
<tr>
<td>Conversion efficiency of the phosphor screen.</td>
<td>Electron position (and electron energy)</td>
<td>$D(E)$</td>
</tr>
<tr>
<td>Gain variation of the individual elements of the PDA.</td>
<td>Electron position</td>
<td>$D(E)F(E)$</td>
</tr>
</tbody>
</table>

Table 4.1 Factors affecting the intensity of the recorded energy spectrum.

The calibration is therefore confined to a single multiplicative correction spectrum and a single additive correction spectrum to be applied to the recorded spectrum. The work of Hunt and Williams\cite{48} is of particular relevance in the determination of these factors as they consider the acquisition of parallel spectra using a similar detection system to that of the HFA, for a parallel acquisition electron-energy loss spectroscopy instrument.

#### 4.2 Dispersion calibration

Electrons entering the analysing field of the HFA are focussed onto the zero-volt focal plane. In order to optimise the focussing for a narrowly diverging beam, electrons enter the field at a distance $x_0$ from the origin (Chapter 2). The energy dispersion of electrons along the focal plane depends on this value. If electrons were to enter at the origin of the field, $x_0 = 0$, then the dispersion distance, $x_f$, would be proportional to the electron momentum ($x_f \propto \sqrt{E}$). As $x_0$ increases, the relationship between $x_f$ and energy changes until as $x_0 \to \infty$, the analysing field becomes uniform, similar to that used in a parallel plate analyser. In this extreme, the dispersion becomes linear with energy, i.e. $x_f \propto E$. This change in the
The recorded electron spectrum is spread over 1024 discrete channels, corresponding to the individual elements of the PDA, which are linearly distributed over 51 mm. The relationship between energy channel \((i)\), and therefore distance, can be approximated with the function of the form

\[
E(i) = ai^2 + bi + c ,
\]

(4.3)

which fits well to both SIMION models and measured features of known energy. The coefficients \(a\), \(b\), and \(c\), are obtained by recording (for at least three different energies) the photodiode channel position of the elastic peak. This should preferably be done over a large energy range to improve the fit at the high and low energy ends.
4. HFA Calibration Methods

4.3 Additive factor adjustment

A reverse-biased photodiode has a very high resistance, which is reduced as light falls on the semiconductor junction region, so the signal is related to the current flowing across this region. When no light is incident on the junction however, a small leakage current still flows, known as dark current. The dark current signal is temperature dependent and becomes increasingly important if the signal level is small. The measured dark current also includes offset effects introduced by the acquisition hardware (such as output signal clamp levels, ADC offsets, etc.).

Removal of these effects has been discussed previously by Hunt and Williams.[48] Here, the dark current spectrum, $D_{S_i}$, was considered to be a repeatable term, $D_{C}$, caused by the leakage current and acquisition offsets, and a dark current noise term $D_{N}$. The noise is a random factor and therefore different for each spectrum acquired. Thus, the acquired spectrum may be expressed as

$$R_S = GS + D_{S_i}, \quad (4.4)$$

where

$$D_{S_i} = D_C + D_{N_i}, \quad (4.5)$$

$R_S$ is the acquired raw spectrum, $G$ is the gain function, or multiplicative correction term (equivalent to $Q(E)$ in equation 4.1) and $S$ represents the true energy spectrum.

Subtracting the dark current spectrum from the raw spectrum can be performed, providing the spectra were acquired with common acquisition times. This removes the repeatable term, but increases the noise (if Poisson statistics are assumed) by a factor $\sqrt{2}$, thus

$$R_S - D_{S_i} = GS + D_{S_i} - D_{S_i}$$

$$= GS + D_{N_1} - D_{N_2}$$

$$\Rightarrow \quad \left| D_{N_{1,2}} \right|^2 = \left| D_{N_1} \right|^2 + \left| D_{N_2} \right|^2. \quad (4.6)$$

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The noise factor can be reduced asymptotically to 1 by increasing the number of dark current spectra acquired, \( n \), and combining them with appropriate scaling such that,

\[
D_S = D_c + \frac{1}{n} \sum_{i=1}^{n} D_{N_i},
\]

where

\[
\lim_{n \to \infty} \sum_{i=1}^{n} D_{N_i} = 0 \text{ and therefore } \lim_{n \to \infty} (R_S - D_S) = GS + D_{N_i}.
\]

Therefore by averaging the dark current spectrum over numerous acquisitions (Figure 4.2), it can be removed from the raw spectrum without appreciably increasing the dark noise.

![Figure 4.2 Dark current measurements (spectrum acquisition time 100 s) made at varying temperatures. Normal operation is at room temperature. The photodiode saturates at 65535. To make the most of the dynamic range, the spectral intensities are generally tens of thousands, so the few hundred counts of dark current is a small effect.](image)
4.4 Detector calibration with standards

At first glance, a raw spectrum acquired from the HFA looks ‘noisy’ regardless of acquisition time, e.g. Figure 4.3. This is caused by the detector effects, most notably the difference in gain of the individual photodiode elements. The small scale inter-channel variations could be measured by looking at spectra from several different metal samples.

Samples of copper, gold, molybdenum, silver, and stainless steel were arranged side by side on a sample plate. The samples were of similar thickness, ensuring that the sample-analyser distance did not require altering between measurements. Following the bake-out of the vacuum system, the samples were Argon ion cleaned to produce a clean surface. Electron energy spectra were then acquired using the HFA, with 5 keV beam energy and a probe current of 3.2 nA. To reduce random noise, 200 one-second acquisitions were combined, giving a total acquisition time of 200 s.

A running average (20 point) was taken of each spectrum leaving only large-scale changes and the ratio taken with the original. This produced a spectrum comprising of mainly the small-scale inter-channel variance, with features caused by the Auger peaks. The Auger features were removed from the spectrum and the process repeated for the other samples, before averaging to provide the correction spectra.

This method of calibration only corrects for the small-scale variances caused mainly by the differing gain between photodiode elements. Other factors influencing the intensity of the signal, such as internal scattering are not affected by this method as changes occur over a broad energy range. However, it does enhance Auger peaks with low intensities. Figure 4.3 shows the effect of applying this correction method to an energy spectrum of silver. While the main transmission at 349 eV can be seen on both the corrected and the uncorrected spectrum, the lower intensity transition at 289 eV only becomes visible with the correction spectrum applied.
4.5 HFA and CHA comparative calibration

The CHA in the MULSAM instrument used at York is a well characterised device, especially in regard to the internal scattering, providing spectra without influence from the analyser. The spectrum acquired from this device can be assumed to be very close to the actual energy spectrum of electrons leaving the sample and therefore be used to characterise the instrumental factors affecting spectra acquired from a different spectrometer.

The electron-energy spectrum of beryllium is generally featureless, consisting of a single Auger feature, the 98 eV KLL transition. Assuming experimental parameters remain constant, the spectrum acquired using the MULSAM CHA (and therefore the ‘correct’ spectrum) can be related to the beryllium spectrum acquired using the HFA by means of equation 4.4. The correction term being
4. HFA Calibration Methods

\[ G = \frac{R_{Be,HFA} - D_S}{S_{Be,MULSAM}}. \]  \hspace{1cm} (4.10)

The same sample of beryllium was used to acquire the spectra from both the HFA system and the MULSAM system. In the MULSAM system, the sample was cleaned with 5 keV Xe bombardment for 30 minutes. The resulting spectrum can be seen in Figure 4.4.

![Figure 4.4 CHA spectrum of Be. Beam energy 5 keV, probe current 4 nA, with 2 sec accumulation per eV.](image)

The sample was then transferred under vacuum (~10^{-7} mbar) to the HFA system, by means of the transfer trolley and cleaned further. It was then inspected (Figure 4.5) using the HFA under the same conditions as with the CHA.

In the constant absolute resolution mode, the CHA present on the MULSAM system measures the number of counts for a given energy. The voltages are adjusted between measurements such that the energy scale linearly increases; in the case of the calibration the step size was 1 eV. The HFA requires a calibration factor for each
of the 1024 detectors present in the PDA. Since the energy spread of the electrons is non-linear with respect to the detector, the spectrum acquired with the CHA was fitted to a ‘channel-number’ abscissa, using a standard interpolation technique.[50]

Figure 4.5 Electron energy spectrum of Be acquired by the HFA. Beam energy 5 keV, probe current 4 nA, with a total acquisition time of 100 sec.

To compensate for the greater carbon signal in the spectrum acquired with the CHA (Figure 4.4), a Gaussian curve was fitted to the carbon Auger signal and subtracted from the CHA data. This was also done to correct for the difference in Auger peak heights of the Be peak between the two spectra. The ratio of the two spectra was then taken, giving the calibration function for the HFA, Figure 4.6. The remaining spectrum is then believed to represent the effects of the analyser on the measured signal at that beam energy.
A difference in the experimental conditions is the entrance angle of the analysers and the angle of the probe to the sample surface. In the case of the HFA system, the geometry is such that the electron probe is at normal incidence, and the analyser is at an angle of 24° to the sample (66° to the sample normal). At the time of measurements, the geometry of the MULSAM system had the angle of incidence and the analyser entrance angle at 32° to the sample normal.

The effect of angle on the Auger spectrum acquired from a sample has been extensively covered in the literature.\textsuperscript{[51]} It has been shown that neither the angle of emission nor the angle of incidence (between 0° and 32°) affect the shape of background curve.

Figure 4.7 shows a spectrum to which these calibration methods have been applied. Note that it is from a material which was not used in establishing the calibration functions, yet the final result resembles that from MULSAM.
Figure 4.7 Applying a comparative calibration to the raw HFA spectrum of Ti (A) removes many of the analyser induced artefacts present in the spectrum, resulting in a spectrum (B) that more closely matches that obtained from the MULSAM CHA (C). There are different levels of contaminants seen on the surface of these samples.
4.6 Depth calibration

The angle at which the electrons enter the HFA greatly affects the energy resolution of the acquired spectra, as the focal plane is coincident with the detector plane over a limited range of angles, as can be seen in Figure 4.8.

Figure 4.8 At the correct sample-analyser distance, the electrons leave the sample and enter the analyser with an appropriate angle that permits focussing onto the detector plane (b). If the sample is too close (and the entrance angle too shallow) the electrons post-focus (a), and if too distant, pre-focussing occurs.
4. HFA Calibration Methods

It is therefore important that the sample–analyser geometry is close to the ideal case, to both optimise resolution and improve reproducibility of spectra. This can be achieved by reducing the beam energy so that an elastic peak can be observed in the output spectrum (there is a depth calibrate function in the acquisition software for this). The potential across the MCP and on the phosphor screen must also be reduced due to the high intensity, localised electron exposure. The sample is then moved perpendicular to the focal plane of the analyser (i.e. towards and away from the electron gun), with changes to the elastic peak shape and intensity noted. The analysis position is achieved when the elastic peak is sharpest and has greatest amplitude. This can be repeated at other energies.
Chapter 5

Electron Stimulated Desorption From InP

5.1 Introduction

The parallel acquisition capabilities of the HFA enable the analyst to observe time dependant effects, and even the presence of elements that could be missed by conventional serial acquisition devices. One such effect was noticed during the initial testing of the HFA: the electron stimulated desorption of chlorinated molecules adsorbed on the surface of InP (110). This proved the value of the HFA since the adsorbate was completely unexpected. This work has been expanded upon to obtain quantitative information about the rate and nature of the desorption effect. Auger spectroscopy was conducted with the HFA to monitor the changes caused by the desorption, in particular the decay profile of the chlorine Auger signal. In addition, sample absorption current imaging showed contrast in regions subject to electron bombardment. This technique was used to gather information about the local spatial distribution of the chlorine on the surface, to determine the role, not only desorption, but also surface diffusion. The experiments were also repeated on GaAs samples.

This study could be considered as a test case for establishing methods of analysis, which might be applicable to industrial processes, such as semiconductor device manufacturing. With the size of microelectronic devices continually reducing, the effect of low levels of adsorbed contaminants becomes more significant.

The example of halogen compounds is relevant because of their use in semiconductor processing. Here, they are used in dry etching where a substrate is exposed to ion beams, plasmas, or reactive gases to create the pattern. In the case of
gallium arsenide, core-level photoelectron spectroscopy reveals that this etching occurs incrementally as follows,[52] though the reaction paths for GaCl₃ and AsCl₃ production may interact.[53]

\[
\begin{align*}
\text{GaAs} + 2\text{Cl} & \rightarrow \text{GaCl} + \text{AsCl}_2, \quad (5.1) \\
\text{GaCl} + \text{Cl} & \rightarrow \text{GaCl}_2, \quad (5.2a) \\
\text{AsCl} + \text{Cl} & \rightarrow \text{AsCl}_2, \quad (5.2b) \\
\text{GaCl}_2 + \text{Cl} & \rightarrow \text{GaCl}_3, \quad (5.3a) \\
\text{AsCl}_2 + \text{Cl} & \rightarrow \text{AsCl}_3, \quad (5.3b)
\end{align*}
\]

As well as residual chlorine, there is the possibility of the other halogen-containing reaction products remaining adsorbed to the surface. These can be detected in sub-monolayer quantities using AES, though this is made more difficult if the process of detection disrupts the surface through mechanisms such as electron stimulated desorption (ESD).[8] The surface must therefore be investigated with sufficient speed to ensure the adsorbate is still present to be measured. With conventional electron energy analysers, such as the CHA, it is possible to monitor the presence of desorbing species providing a suitable energy window is chosen. If the window is too large, for example the entire energy spectrum, then the species may be missed due to the short desorption time.

### 5.2 Experimental setup

The HFA system was set up as described in Chapter 2. The semiconductor samples were mounted in a copper block on a modified sample plate, slotted to take the sections of wafers and additionally secured using a high conductivity silver paint (Figure 5.1). This enabled two wafer slivers, with the (100) face transverse to the analysis plane to be investigated. The surface under investigation was obtained by cleaving of the wafer in vacuum. This was done using a wobble-stick when the pressure was below \(10^{-9}\) mbar (to ensure surface cleanliness). Being a III-V semiconductor, the wafer fractured along the natural cleavage plane revealing the clean, flat, glassy (110) surface.[54]
Experiments were conducted with a fixed primary beam energy of 5 keV and a probe current of approximately 3 nA. The beam was parked far from the area of interest on the sample between experiments. During the experiments, the beam was repeatedly scanned over a given area of the surface, producing a controlled irradiated region with higher edge definition than that produced by a defocused static electron beam. This area was defined by the magnification setting for the electron gun, giving irradiated dimensions ranging from $3 \times 3 \mu m$ to $80 \times 80 \mu m$, with corresponding electron probe intensities of between 300 and 0.5 Am$^{-2}$. To the authors knowledge, this is the first study of desorption with such well defined (spatially) and controllable irradiation.

Auger spectra were acquired using the HFA with a spectrum acquisition time of 1, 5 or 10 seconds, depending on the intensity of the electron flux. This ensured the decay of the chlorine peak could be monitored, with spectra continually acquired until the chlorine peak had decayed appreciably, as in Figure 5.2. The beam was then left scanning on the sample surface for an extended period (15 – 30 minutes) to obtain a spectrum representative of the steady state, with a negligible chlorine Auger peak.
Figure 5.2 Example raw HFA electron energy spectra obtained from the (110) surface of InP with no prior electron beam irradiation, (A), and after 250 s of bombardment, (B). Each full spectrum (1024 energy channels) was acquired in 5 s. The spectra are offset in the y-axis for display.

5.3 Residual gas analysis

A residual gas analyser (VG Gas Smart IQ+) was used during desorption in an attempt to further identify the adsorbate. Before irradiating the sample, the gas spectrum contained no chlorine peaks. Atomic masses 35, 36, 37 and 38 were observed and measured during irradiation of the sample, but no other features associated with chlorine were detected (such as 70). The magnitudes of these peaks were found to have decaying amplitudes, indicating that desorption was occurring. The partial pressure of each was less than $10^{-13}$ mbar and as such was close to the minimum detectable pressure of $5 \times 10^{-14}$ mbar. This, combined with the low initial concentration of surface chlorine, resulted in a relatively noisy RGA signal, but with clearly visible features.
For measurement purposes, an area of the sample was chosen, over which the silver paint overlapped. When exposed to the electron beam, the signal from the RGA showed the same desorbing character as that encountered nearer the centre of the sample, though with an amplitude an order of magnitude greater. This is possibly due to the vastly increased surface area of the rough silver paint and perhaps a weaker bonding mechanism for the adsorbate. Figure 5.3 shows the time evolving RGA signal from this region. The experiment was repeated three times, each time moving to an undisturbed region.

To ensure total desorption had occurred, the area of the electron beam scan was reduced near the end of a run (thereby increasing the current density). The relative quantities of desorbed species were measured by integrating the area beneath the decay curve, with the final points averaged to provide a background level. Elemental chlorine has two isotopes being masses 35 and 37, found in the ratio 75% : 25%. Accounting for this and the cracking patterns of HCl, the detected quantities were consistent with the presence of HCl and Cl in the approximate ratio 2:1.
5.4 Analysis

5.4.1 Chlorine origin

A possible origin of the chlorinated contaminants is thought to be impurities within the copper mounting block. When the electron beam was irradiating the silver paint used to secure the samples within the copper block, chlorinated molecules were liberated. The solvent used to dilute the silver paint (iso-butyl methyl ketone) contains no chlorine and hence cannot be the source. However, it is possible that a reaction between this solvent and the copper block leads to a concentration of the chlorine impurities on the surface of the silver paint. Practical considerations, such as charging, gave unreliable electron energy spectra, therefore this region could not be investigated.

5.4.2 Auger investigation

The acquired Auger signal information was displayed as a 2D image with time on the ordinate axis, energy on the abscissa (Figure 5.4c). To highlight time varying features, each energy channel in the Auger image was divided by the corresponding channel in the final steady-state spectrum as can be seen in Figure 5.4b.

The decay of the 176 eV chlorine peak was seen by taking cross-sections through the Auger images at constant energy (Figure 5.4a). This was conducted on the raw spectra obtained from the HFA without correcting for transfer function, as only relative changes in peak height for specific energies were being considered. The peak height was taken to be the height of the peak, with a simple linear background removed. This linear background was fit either side of the peak rather than extrapolating from the high energy side. This seemed reasonable as the peak position and shape did not significantly change.
Figure 5.4 Spectra obtained from the surface of InP(110) such as (D) were compiled into time versus energy images as can be seen in (C). To highlight the time varying nature of the spectra, each channel was divided by its final steady state giving the image seen in (B). Taking cross sections of this image at a given energy, showed the time-evolving Auger features, (A), in this case normalised by the initial value.
It can be seen that as the chlorine peak decayed, there is an increase in the signal intensity of the 404 eV indium peak and 115 eV phosphorus peak corresponding to the bulk components becoming exposed. From this, information about the location of the adsorbate could be inferred. Using the equation 1.9, and the value of 24° for the entrance angle of the HFA, the overlayer thickness can be described by

\[ \Delta C = \frac{\lambda}{2.46} \ln \left( \frac{I_{\text{final}}}{I_{\text{initial}}} \right) . \]  

(5.4)

where the intensities refer to the bulk components and that chlorine is completely desorbed. The mean free path is calculated from the approximate relationship:

\[ \lambda = 0.2 \sqrt{E} , \]  

(5.5)

Using this relation, the attenuation in the 115 eV phosphorus signal corresponds to an adsorbate overlayer of thickness 0.46±0.05 monolayers and for the 404 eV indium signal, 0.36±0.04 monolayers. This suggests that the chlorine is preferentially located on the phosphorus atoms. If the surface chlorine is assumed to be Cl atoms and forms HCl during or following desorption, then the location is consistent with the behaviour of Cl on GaAs as determined by photoelectron spectroscopy.\[^{55}\]

The weak point to this argument is the model used for the mean free path, \(\lambda\), which is independent of overlayer composition. Some other models\[^{56}\] have a sample dependant term but keep the energy to the power 0.5 (for the range \(E > \sim 100 \text{ eV}\)), in this case the absolute values of the overlayer thickness will change, but the ratio of the two, and hence the site preference will remain unaltered. However, if the power term is sample dependant as suggested by Wagner et al.\[^{57}\] this would affect the ratio somewhat.
5.4.3 Decay schemes

The measured intensity of the Auger peak height was related to the monolayer coverage, using the method of Chang. In this, the measured intensity of all three Auger peaks \( I_j \), combined with a knowledge of the bulk composition and relative sensitivity factors can be related using the expression

\[
C = \frac{-\lambda}{2.46} \ln \left( 1 - \frac{\alpha_{Cl} I_{Cl}}{\sum_j \alpha_j I_j} \right). \tag{5.6}
\]

The inverse relative sensitivity factors for the bulk components, \( \alpha_j \), are taken as 1.05 and 2.22 for indium and phosphorus, 5.88 and 8.33 for gallium and arsenic, and \( \alpha_{Cl} = 1.0 \) for chlorine, and can be obtained from standard sources. This relation showed that the adsorbate concentration remained well below a monolayer before electron stimulation.

Figure 5.5 Decay of the 176 eV Cl (LMM) Auger signal. The decay was modelled in different ways, by a single exponential decay curve (A), the sum of two exponential decay curves (B) and a numerically modelled exponential decay moderated by a diffusion term (C). The fits are discussed in the main text.
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The Auger images were acquired at different areas on the sample each time and for a range of electron beam intensities. If the decay of the 176 eV chlorine Auger peak is plotted as a graph of coverage verses dose (Cm\(^2\)) then all data obtained can be displayed. This has been done for Figure 5.5, along with curves describing three proposed models of the decay.

5.4.3.1 Model A: Single-site desorption

In the simplest model, the adsorbate – surface – electron interactions are considered to be independent of the coverage with the rate of adsorbate change described by the rate equation,

\[
\frac{dC}{dt} = -kC ,
\]

which gives an exponential decay of the chlorine Auger peak, with a time constant of \(k\).

\[
C = A \exp (-kt) .
\]

The best fit to the data give a value of \(k = 3.75 \times 10^{-4} \text{ A}^{-1} \text{m}^{2} \text{s}^{-1}\), although this clearly fails at high doses. One possible explanation for this is that the energy required to remove the adsorbate was dependent on the thickness of the overlayer, however, in similar systems,\(^{[59]}\) this effect manifests as a transition occurring when the adsorbate coverage reaches 1 monolayer. In this work however, the adsorbate coverage was always sub-monolayer so this explanation is unlikely to be correct. Other possibilities are that the adsorbate-surface interaction is non-uniform, or the adsorbate coverage is not influenced solely by the desorption process, but is moderated by surface diffusion effects.
5.4.3.2 Model B: Two-site desorption

The zinc-blende (110) surface consists of an equal number of the two atom components, so it is logical to assume two adsorption sites corresponding to the different surface atoms. This is consistent with the results from section 5.4.2. If two adsorption sites exist with no exchange of adsorbate between them, i.e. no diffusion, the amount of adsorbate present as a function of time would take the form of the sum of two exponential decay curves i.e.,

\[ C = A \exp(-k_1 t) + B \exp(-k_2 t). \]  

(5.9)

The best fit of this model to the data gives a second time constant of \(1.0 \times 10^{-5} \text{ A}^{-1} \text{m}^2 \text{s}^{-1}\) and the initial population of the sites being in the ratio of nearly 10:1. This model is a better fit to the decay curves, but is almost identical to a further model discussed next. In addition, it does not fit well to the slight preference of one adsorption site to the other seen earlier.

5.4.3.3 Model C: Desorption and diffusion

It is possible that the effects of surface diffusion, combined with electron stimulated desorption are responsible for the rate of decay observed. Auger spectra taken immediately after cleaving showed the presence of both indium and phosphorus peaks, but not of chlorine peaks. The chlorine was not deliberately deposited on the surface in a beam and residual gas analysis showed it was not present within the vacuum system before irradiation. After some minutes, the presence of the 176 eV chlorine peak was noticed. Therefore, it is likely that the initial presence of chlorine on the cleaved surface is transported through surface diffusion. If this is the case, then it may be possible to investigate the effect of chlorine peak build up, onto the (110) surface. However, due to the nature of the source of the chlorine being unknown and the complex geometry around the sample this was not attempted. By allowing the chlorine coverage on the surface to reach equilibrium, each investigation can be regarded as an isolated event, without causing interference to adjacent measurements.
A surface diffusion moderated decay scheme was investigated by constructing a relative difference computer model of the effects at the surface, a screenshot of which can be seen in Figure 5.6. The model represented one quarter of the two-dimensional sample area, the remainder being considered symmetrical to this. A 20 × 20 array was used internally to represent the irradiation area, with the remainder of the sample area having significantly greater dimensions (150 × 150). This was to ensure no errors were introduced from boundary conditions. The model was written using LabWindows/CVI giving an output of the decay curve together with a coverage profile taken through the irradiated area.

The diffusion was modelled according to Fick’s law. For the region of the sample not under electron beam exposure, the change in local adsorbate coverage ($\Delta C_{x,y}$)...
after each time step is determined from the average of the gradients in both the x and y directions, thus:

\[
\Delta C_{x,y} = -\frac{D\Delta t}{4(\Delta x)^2} \left( C_{x-1, y} + C_{x+1, y} + C_{x, y-1} + C_{x, y+1} \right).
\] (5.10)

Here \( D \) represents the diffusion coefficient, \( \Delta t \) the time step used and \( \Delta x \) the physical size represented by an array point in the model.

The area subject to electron beam irradiation had an additional term \( \Delta C'_{x,y} \), proportional to the amount of adsorbate present, removed in each time step to simulate the electron stimulated desorption;

\[
\Delta C'_{x,y} = -\left( \frac{kJ\Delta t}{A} \right) C_{x,y}.
\] (5.11)

In this equation, \( k \) is the desorption parameter, \( J \) the sample absorption current and \( A \) is the irradiation area.

The average local concentration of adsorbate from this model can be seen as curve C. This best fit has a diffusion coefficient of \( D = (7.0 \pm 1.4) \times 10^{-14} \text{ m}^2\text{s}^{-1} \). The two proposed models B and C gave decay curves that were very similar and could not be distinguished by the experimental AES data.

### 5.4.4 Sample current imaging

To investigate whether surface diffusion was actually taking place, information about the adsorbate coverage profile was used. In the absence of surface diffusion, a cross-section of adsorbate concentration across the irradiated area would be a square sided, flat bottomed well (Figure 5.7). If diffusion is occurring however, this is modified, due to the mobile adsorbate. Sample absorption current images provided information about this.
It was noticed that during electron irradiation (and therefore desorption), the sample absorption current decreased (by as much as \(~10\%\)) with the removal of the adsorbate. The reverse effect was also noticed within the secondary electron signal, but to a lesser degree. The contrast is unlikely to be caused by dissociation of the surface, caused by localised electron beam heating, as this leads to an indium rich surface\[^{[60]}\] whereas the Auger analysis shows an increased phosphorus signal after exposure. In addition, the heating effect of the electron beam would be dependent on the focus of the electron beam. Moderately defocusing the electron beam significantly reduces the local heating effects, but was found to have no effect on the desorption process or sample absorption current image profile. It could be concluded therefore that the change in signal is directly related to the change in adsorbate coverage.

The small spot size of the electron beam made it possible to conduct measurements over the boundary region between the irradiated and non-irradiated regions to determine whether surface diffusion was occurring. After conducting Auger analysis on a region of the sample, a single larger area scan was taken (by decreasing the magnification by a factor 2) to give both sample absorption and secondary electron images (Figure 5.8). Since this final scan could be taken in a much shorter time, little desorption occurred.
Figure 5.8 The method by which secondary electron and sample absorption current images were generated (A) and recorded (B). The contrast was always less in the secondary electron images (C) compared to those obtained using the sample adsorption current (D).

In the sample absorption current images the inner darker region corresponds to the area under electron bombardment during the monitoring of the desorption rate. It can be seen that the boundary between the irradiated and non-irradiated region is not sharp. This region is also much broader than the electron beam spot size, indicating that diffusion is taking place.

Cross sections taken through the sample absorption current images represent the adsorbate distribution. For increased accuracy, multiple cross-sections were taken and compiled into an average profile. This could then be compared with the predicted cross-sections generated from models B and C (Figure 5.9). It can be seen that the case where no diffusion occurs is not applicable to the experimental data.
However, the best fit from the model representing uniform desorption and diffusion is not an exact fit either, suggesting that a single effect may not be taking place, but that both diffusion and non-uniform adsorption site effects are present.

Figure 5.9 The sample absorption current profile, representing the adsorbate concentration across the sample surface. The area on the left shows the area under electron beam bombardment. The red line represents the case with no surface diffusion (model B) and the green, that of diffusion (model C).

The curves generated by the two models bracket the experimental data and can be used to provide some measure of the desorption and diffusion parameters. The main desorption constant is similar for each model, at $k = (3.75 \pm 0.3) \times 10^{-4}$ A$^{-1}$ m$^2$s$^{-1}$. The surface diffusion predicted by the model C is greater than the experimental data. At least this provides an upper bounds of $D = 7.0 \times 10^{-14}$ m$^2$s$^{-1}$.

These results contrast with those obtained by Mokler et al[61] who reported no diffusion of chlorine present on the surface of GaAs (100). Their probe current was 15 µA, much greater than the present study. They inspected the surface using a rastered electron beam, and created a chlorine depletion by stopping the raster and leaving the spot on the surface until the chlorine peak was removed. The beam was then turned back on to measure the Auger signal at intervals and monitoring the
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chlorine Auger peak at intervals. It is also reported that quantities of chlorine remain (up to 25%). It is possible that the relatively large spot size used for these experiments is masking the effects of diffusion as it has been observed in this work that the diffusion occurs over short distances of >~5\( \mu \)m.

There is difficulty in further quantifying the individual roles of desorption and diffusion with the current data as the parameter space rapidly becomes prohibitively large. For example models considering surface diffusion occurring with multiple adsorbate sites, as proposed by Chvoj et al.\(^{[62]}\) could be modified to include the effects of desorption, however it would not be possible for a unique solution to be found without more precise data.

5.4.5 Origin of SAC contrast

The sample absorption current is the incident probe current minus the sum of the ejected electron spectrum. Attempts were made to discover the location in the energy spectrum that was responsible for the decreasing SAC current noticed during desorption experiments. This might provide an even more sensitive measure of adsorbate coverage. The detectors present in the MULSAM system enabled the low energy range (from ~20 eV to 2.5 keV) to be investigated using the CHA, and the high energy range (4 keV to 5 keV) using the low loss detector.

The low loss detector, used to investigate change in the region close to the elastic peak, was primarily designed as an imaging tool. To permit the acquisition of a low loss spectrum, manual adjustment of the loss energy was required for each point. Spectra of this kind were acquired as soon as the electron beam was moved to a fresh area of the sample, and after an appreciable length of time, allowing the chlorine to be desorbed, an example is shown in Figure 5.10.

The low loss spectra are characteristic of those obtained for both GaAs and InP. It can be seen that the recorded difference in loss spectra before and after is low. This indicates that the contrast seen on the SAC images is not primarily caused by
changes within the back-scattered electron yield. It is possible, that the method of spectrum acquisition is too crude to permit changes in back-scattered electron yield to be monitored since in the time required, some chlorine will be depleted from the ‘Cl present’ data.

Figure 5.10 Low electron-energy loss spectra of GaAs taken before (blue) and after (red) chlorine desorption. The loss energy refers to the energy away from the primary beam setting of 5 keV. In other data sets, the trend at higher loss energies is reversed (i.e. Cl present curve is greater than Cl removed curve.)

The low energy region of the spectrum was investigated using the CHA. A typical example of the low energy spectrum before and after chlorine desorption can be seen in Figure 5.11.

Although the Auger features change, their peak height is small, compared with the peak background, and are therefore unlikely to be the contrast mechanism. The remaining spectrum appears to change little during chlorine desorption, down to ~20 eV. It has been previously reported that the intensity of the secondary electron signal changes with adsorbate coverage.[63] In the very low energy region, the CHA transfer function is not well characterised and probably contributes to the shape of the secondary electron curves seen. However, the signal is consistently larger when chlorine is not present on the surface, indicating that this region may be responsible
for the contrast seen. If this is the case, similar contrast to that in the SAC images should be seen in the secondary electron images. Detector geometry may be responsible for a reduced signal at the low energy end of the spectrum, and is a suggested area for further study.

Figure 5.11 Auger spectra of InP acquired with the MULSAM CHA, showing the large change in intensity at very low energy. Spectra acquired with 50 ms per point acquisition time.

5.4.6 Comparison of GaAs(110) with InP(110)

The experiments conducted were repeated on a sample of GaAs, cleaved similarly, to yield the (110) surface. This was mounted alongside the InP in the copper block ensuring it was always treated in the same manner. The results from the experiments show broadly similar results. Results indicate that the chlorine is located preferentially on the As surface atoms and is present in a greater quantity than on InP.
Figure 5.12 The sample absorption current profile, representing the concentration of adsorbate across the surface of the sample. The red line represents the case where no diffusion occurs and the green line the case with diffusion.

It was again not possible to determine the correct model for the decay from a graph of the decay of the chlorine Auger peak alone. Sample absorption current images were again needed to verify surface diffusion. However, when the model was best fit to the data, the actual diffusion profile was less than predicted, seen in Figure 5.12. Therefore, it can be concluded that for GaAs, the desorption parameter is greater than for InP, with the effects of surface diffusion less pronounced.

5.4.7 Carbon contamination effects

Under normal circumstances, investigations were conducted on a freshly cleaved section of wafer, to ensure a clean surface. An experiment was conducted on a surface that had been exposed to the vacuum for several days preceding measurement. The results obtained differed from those previously observed.

With fresh samples, the absorption current was observed to fall with the removal of the adsorbate leading to a darker area in the region subject to electron bombardment. However, the image obtained in this case showed decreased levels
of adsorbate at the edges of the desorption region, with increased levels towards the centre. During acquisition, it was noticed that the sample adsorption current initially decreased, before beginning to increase. To monitor this effect, a series of images were obtained at increasing electron exposure times (a sample of which can be seen in Figure 5.13). Analysis of the Auger spectra obtained during electron exposure showed that the 176 eV LVV Cl peak decreased with time (i.e. chlorine was subject to electron stimulated desorption) but that the 263 eV KLL carbon peak increased with time (Figure 5.14).

Figure 5.13 A series of sample adsorption images showing that, after an initial decrease, the signal increases in the area under electron beam bombardment over time. The diagonal lines are predominantly interference from the scan-unit.

This increase in the carbon signal has been noted in other works,[64] being responsible for the appearance of patches in secondary electron images. This is often ascribed to the electron stimulated adsorption of residual gases to the surface. To test whether this effect was happening in this system, the diffusion/desorption simulation was adapted to take into account an additional adsorption. This generated a profile with a similar shape to the observed profile, assuming the adsorption of the carbon has a similar (but inverse) effect on the secondary electron signal to that of a desorption.

It is possible that surface diffusion causes the increase in the carbon signal,[65] though surface diffusion would require a higher concentration of carbon outside the
irradiated region and would lead to the lowest concentration of adsorbate being in
the centre of the irradiated region, but this is not observed. The carbon source is
most likely to be as modelled, being due to residual hydrocarbons present in the
vacuum system being cracked in the electron beam, then adsorbing to the surface.

Figure 5.14 The apparent build up of carbon within the electron bombarded area. A shows
the relative intensity change for the 263eV carbon peak, and B shows the relative change for
the 176eV chlorine peak. C shows example spectra obtained from the irradiated region (red)
and non-irradiated regions (blue).
5.5 Conclusion

Residual gas analysis of chlorinated adsorbate, present on the surface of InP, but liberated by electron stimulated desorption, determined it to be in the form of HCl. Using the rapid acquisition time of the HFA, a study of the rate of desorption was possible by extracting information from entire Auger spectra acquired, about the rate of decay of the 176 eV LVV chlorine Auger peak.

Since a large energy spectrum could be measured in such a short time, the emergence of the bulk components could be measured at the same time as the decay of the chlorine peak. From this, information about the location of the adsorbate was calculated. The adsorbate interaction with the surface seems to be via two sites of differing binding strength, of which the stronger are Cl–As and Cl–P.

Models were proposed to account for the shape of the Cl decay curve, one that assumed desorption occurred from two independent adsorption sites, and another that assumed the effects of surface diffusion moderated the effect of single site desorption. Both models showed good agreement with the Auger data, and hence the correct system could not be determined from these results alone.

SAC imaging enabled the boundary region between the irradiated and non-irradiated regions to be investigated. This method was remarkably sensitive to adsorbate concentration, considering it was at all times sub-monolayer. From adsorbate concentration profiles, it could be seen that surface diffusion was occurring. However, the actual data lay between the curves predicted by the two models, indicating that neither seems satisfactory in its own right and that it is likely that a combination of the effects of surface diffusion and desorption from two non-equivalent sites. The dominant desorption constant is $k = (3.75 \pm 0.3) \times 10^{-4} \text{A}^{-1}\text{m}^2\text{s}^{-1}$ and the diffusion coefficient gives an upper bound of $D = 7.0 \times 10^{-14} \text{m}^2\text{s}^{-1}$.

An investigation into the origin of the contrast showed there was little change in the high-energy end of the electron energy spectrum, before or after electron stimulated
desorption. Although affected by the transfer function of the CHA, a large change in signal intensity is consistently seen at low energy, possibly being the cause of the SAC contrast. The present detector geometry may be responsible for the reduced contrast seen in the secondary electron images.
Chapter 6

The CASE Partnership

6.1 Introduction

The work presented in this thesis was funded by the EPSRC CASE for New Academics programme, in conjunction with Shimadzu Research Laboratories (Europe) Ltd.\[66\] The provision of this award gave the opportunity for research to be conducted in partnership with the industrial sponsor at their facility.

Shimadzu Research Laboratories (Europe) Ltd, SRL, is a Manchester based, scientific instrument development company and is a research and design subsidiary of the Shimadzu Corporation. The main aim of the company is to develop ideas into working prototypes, which are then licensed to manufacturing companies. The design of the HFA developed at York was patented and this was sub-licensed to SRL who have been since developing a version of a HFA, for commercial exploitation. The SRL prototype is larger than the original York design, with various new features (such as individually adjustable field trimmers) to aid in the optimisation of the various analyser components. Construction materials differ, as is the design of the purpose built test chamber.

The author gave assistance with the final assembly of the SRL test system, modifications to the detector arrangement, characterisation experiments with the analyser and development of acquisition software for the device.
6.2 The SRL test system

The HFA test system consists of a vibration damping table, on which is mounted the vacuum system (Figure 6.1). This chamber, when running, is pumped solely by a large ion pump, a Varian VacIon Plus 300 Noble Diode pump, with an integrated titanium sublimation pump mounted below the chamber. Provision for changing the sample is provided by an airlock chamber, mounted on the side of the main chamber and isolated by a large gate valve. The airlock chamber is pumped by a turbo pump, which also provides the initial pumping for the whole system. To clean samples, an argon ion gun is fitted (Kratos Analytical, Mini Beam I).

The SRL HFA was mounted on a substantial support frame from a 12” flange, and projected into the centre of the main chamber. Electrical connections for the field were provided by a custom made 19-pin feed-through, located on a 4½” flange. The electrical connections to the detector were also mounted from the 12” flange with a liquid feed-through to supply the water for cooling.

Figure 6.1 The test system used at SRL. Photograph used by courtesy of SRL.
The electron gun was supplied by York Electron Optics, and has a differentially pumped two-lens field emission column. Beam scanning provision is provided by a scan box (of a similar design to that in use at York) or by an older image manipulation unit (a ‘Crystal’ unit from Quantel Ltd.), which is used for the acquisition of SEM images. The financial investment in the SRL system was considerably greater than that available at York.

### 6.3 The SRL HFA

The SRL HFA works on the same principle as the original analyser developed at York, with some slight differences in design. The SRL device is larger than the original York device, being 150 mm long, 50 mm wide and 50 mm high (Figure 6.2). The increased length ensures the main hyperbolic electrode is further from the entrance aperture reducing the chance of impact from high-energy electrons entering the analyser and thereby reducing the internal scattering effects.

![Figure 6.2 The SRL HFA. The screening case and water-cooling block can be seen. The inset shows a photograph of the SRL device, mounted to the support frame and main flange. Photograph and image used by courtesy of SRL.](image-url)
In the SRL device, the 16 electrodes used to approximate the field within the analyser are held at the appropriate potential by individual power supplies. This removes the requirement for an in-vacuum resistor chain (as used in the York device). This was done to enable empirical alterations to the focussing field, to improve focussing conditions. A specially constructed 19-pin high-voltage ceramic feed-through was used to connect the supplies to the analyser. Unfortunately, the perceived benefit of the added flexibility of this system was far outweighed by the engineering difficulties it presented.

The electrodes in the SRL device are attached to an insulating machinable ceramic. This is then fastened to a screened case. This has the advantage that the electrostatic field caused by the electrodes will not penetrate the vacuum system, especially around the entrance to the HFA.

The initial detector arrangement (MCP, phosphor screen and photodiode array) used in the SRL device was similar to that at York. To permit the testing of other detector arrangements, this was designed to be a modular component allowing the removal of the detector assembly as a single unit, which can be seen in Figure 6.3.

![Figure 6.3 The modular detector assembly used in the SRL HFA, showing how the assembly can be removed as a single unit. Image used by courtesy of SRL.](image-url)
The SRL device also included provision for active cooling of the photodiode array. A copper cooling-block, with circulating water, was attached to the rear of the HFA mounting frame. A thermocouple attached close to the PDA prevented the temperature reaching the maximum specified storage temperature of 85°C.

6.4 Comparative investigation of samples from ICT

During the course of HFA development at SRL, a company expressed an interest in the device – ICT (Integrated Circuit Testing GmbH), a subsidiary of Applied Materials. They were interested in the comparative performance of the SRL device, the York device and a more conventional analyser such as the CHA present in the MULSAM system. For this purpose, some samples were supplied; a small circuit made on BPSG (BoroPhosphoSilicate Glass), Si$_3$N$_4$, Ti and TiN. These were investigated using each analyser.

A difficulty that quickly became apparent was due to the insulating properties of BPSG, which, during investigation, showed evidence of charging, deflecting the main electron beam and affecting the spectrum obtained. This meant a reliable electron energy spectrum could not be obtained from this sample and this sample was not included with the comparison. Had longer time been available, various methods could have been applied to maintain the secondary electron yield at unity and reduce the effects of charging on samples. These include reducing the thickness of samples, tailoring the energy of the incident probe beam or charge compensation, using a low energy ion beam or second electron beam.

The ICT samples were first investigated using the MULSAM apparatus. The Ti, TiN, and Si$_3$N$_4$ samples were mounted on a standard tantalum sample plate and ion beam cleaning carried out using 4 keV Xe ions for 3 hours. Spectra were collected using a primary beam with energy 5 keV, the same energy being used in the other systems. The probe current was 4 nA and the total dwell time per channel was 500 ms, giving a total acquisition time of 885 s per spectrum. The analyser operated
in constant analysis energy mode, with a pass energy of 126 eV giving a resolution of 1 eV. Examples of the three spectra can be seen in Figure 6.4.

![Figure 6.4](image)

Figure 6.4 Electron energy spectra of Ti, TiN, and Si₃N₄ acquired with MULSAM. Total acquisition time 885 s, with a 4 nA probe current, giving a dose of 3500 nAs. The spectra are featureless above 800 eV. The spectra are offset in the y-axis for display.

Following analysis, the samples were transferred to the York HFA test system, using the transfer trolley. Once in position, the samples were then cleaned using 4 keV Ar ions for 30 minutes. The electron gun provided a beam current of 4 nA the total acquisition time was 100 s. The total acquisition range was 74 to 2600 eV. The spectra can be seen in Figure 6.5.

The York HFA spectra were subject to a correction factor, to reduce the effects of the transfer function, obtained using Be spectra acquired both by MULSAM and the York HFA (as described in Chapter 4).

The samples were then transported to SRL, where they were remounted and placed into the SRL test system. They were then subject to 4.5 keV Ar ion cleaning for 2 hours. Spectra were then recorded with a 10 nA electron probe, with a total
acquisition time of 50 s. The total acquisition range was 48 to 1245 eV. An example spectrum can be seen in Figure 6.6.

![Figure 6.5 Electron energy spectra of Ti, TiN, and Si3N4 acquired with the York HFA. Total acquisition time 100 s, with a 3 nA probe current, giving a dose of 300 nAs. The spectra are offset in the y-axis for display.](image)

Figure 6.5 Electron energy spectra of Ti, TiN, and Si3N4 acquired with the York HFA. Total acquisition time 100 s, with a 3 nA probe current, giving a dose of 300 nAs. The spectra are offset in the y-axis for display.

![Figure 6.6 Electron energy spectra of Ti, TiN, and Si3N4 acquired with the SRL HFA. Total acquisition time 50 s (TiN 100 s), with a 10 nA probe current, giving a dose of 500 nAs (TiN 1000 nA s). The spectra are offset in the y-axis for display.](image)

Figure 6.6 Electron energy spectra of Ti, TiN, and Si3N4 acquired with the SRL HFA. Total acquisition time 50 s (TiN 100 s), with a 10 nA probe current, giving a dose of 500 nAs (TiN 1000 nA s). The spectra are offset in the y-axis for display.
From the spectra above, all analysers show the presence of the main transitions in the Ti and TiN spectra, along with varying degrees of carbon contamination. In addition, the Si₃N₄ spectra acquired by the CHA and SRL HFA reveal the presence of the low energy 89 eV Si LVV Auger peak. The increased dispersion in the SRL HFA, due to the reduced field strength, enables spectra to be recorded over a smaller energy range (relative to the York HFA). This decreases the minimum recordable energy and increases the energy spread, therefore enhancing the lower energy part of the spectrum. Reducing the field strength in the York HFA becomes problematic due to the increased level of interference in the recorded spectra from internal scattering.

The Si peak is absent in the York HFA spectrum, due probably to the application of the comparative correction function. Be is used to generate this spectrum, as it has a generally featureless spectrum with the Auger transition peak occurring at 98 eV. In this case however, the effect of the Be peak is such that the applied correction spectrum becomes sufficient to mask the low energy Si peak. This is therefore an error in the calibration function. Problems with the calibration are also evident at higher energies as the 1614 eV transition is also absent. In this range, the errors are likely to be introduced by the interpolation of the MULSAM Be correction spectrum onto the York HFA channel scale. If acquisition time were not an issue, it would appear that the MULSAM CHA is the superior analyser.

In the world where ‘time is money’, the important criterion for comparing analysers is the ability to resolve spectral features in a limited time. For analysers with comparable energy resolution, the useful parameter is the signal to noise ratio (SNR). For the three devices, the signal to noise ratio was calculated as \((\text{Auger peak height} - \text{E}^m\text{ background})/\text{average channel to channel variation}\). This latter term was estimated from the standard deviation of intensity values over a 200 eV energy window in a featureless region of the spectrum. The relative SNRs for each of the three devices are shown in Table 6.1. Each value has been normalised to account for differences in the beam current and acquisition time. Note that a factor
of $x$ improvement in signal to noise ratio is equivalent to a reduction in the acquisition time of $x^2$.

<table>
<thead>
<tr>
<th>Sample and Auger Peak</th>
<th>MULSAM</th>
<th>York HFA</th>
<th>SRL HFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$ (N KLL 375 eV)</td>
<td>1.0</td>
<td>3.2</td>
<td>3.1</td>
</tr>
<tr>
<td>Ti (Ti LMM 381 eV)</td>
<td>1.0</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>TiN (Ti LMM / N KLL ~380 eV)</td>
<td>1.0</td>
<td>2.0</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 6.1 Relative SNR for each analyser, normalised to the value obtained by MULSAM.

It can be seen that the SNR for both HFA devices is greater than that of the CHA present in MULSAM. Both HFA devices have a smaller angular acceptance of electrons emitted from the sample, however this is more than made up for by the parallel acquisition.

The spectra obtained from the York HFA have had applied a calibration factor to reduce the transfer effects of the analyser. At SRL it was not possible in the time to obtain such a correction and as such the results shown represent the raw spectra. The indicated values for the SRL analyser therefore seem to represent a lower limit for the SNR, as the calculated noise factor does not take into account the inter-channel gain variations.

Further discrepancies in the values obtained for the SNR could be caused by the carbon contamination of the surface. Although ion beam cleaning was conducted, contaminants are still present to varying degrees in each vacuum system and will affect the magnitude of the recorded Auger features, and therefore the SNR.

One last effect is the background removal used to estimate the height of the Auger features. The method used was to fit a curve of the form $E^m$ (a Sickafus background as mentioned in Chapter 1). This curve was used as an approximation to the background trend as it provided a better approximation than that of the simple linear extrapolation. However, it should be noted that the Sickafus background
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can only be properly applied to the true $n(E)$ and that usually a high energy beam is used to ensure separation of the secondary electron and back-scattered components of the electron energy curve.

Taking the above factors into account, the SRL HFA is the best analyser of the three for this test. It can resolve features as well as the CHA, but in a reduced acquisition time.

6.5 Titanium and titanium nitride comparison

The electron-energy spectra of titanium and titanium nitride are very similar, as the principle transitions overlap in energy. Work with the ICT samples prompted an investigation into whether the HFAs could resolve these features.

The ability of an Auger spectrometer to resolve these features becomes important when considering an application in the semiconductor industry. Here, titanium and titanium nitride are used, often together as a bi-layer film, when working with aluminium. They improve the adhesion of materials (such as dielectrics, etc.) and act as a diffusion barrier, preventing migration between Al and Si in a multi-layer structure.\[69\] If Auger depth profiling is to be used as an analysis technique, the position of the different materials must be measurable.

Titanium is a very reactive material, rapidly combining with hydrocarbons and other residual gases in the vacuum system and for this reason, is often used as a ‘getter’ pump. Its reactive nature makes the Auger investigation of a clean titanium surface difficult, as carbon and oxygen contamination is usually present.

The spectra of Ti and TiN acquired by the analysers can be seen in Figure 6.4, 6.5, and 6.6. High-resolution spectra (0.3 eV for Ti and 0.5 eV for TiN) obtained by Pellerin et al.,\[70\] show a larger peak around 380 eV (Ti LMM + N KLL) in TiN compared to the LMM peak in pure Ti. To identify an unknown material as either
Ti or TiN, it would be more useful to be able to compare features within a single spectrum.

The spectra obtained from MULSAM and the SRL HFA both show an increased peak height in the overlap region corresponding to the presence of both Ti and N. This is not seen in the spectrum obtained from the York HFA, but this might be due to different levels of carbon contamination. If the spectra are viewed in differential form (as $dN(E)/dE$ spectra), other effects become apparent, as shown in Figure 6.7, 6.8, and 6.9. In particular, there is a consistent difference in the ratio of the 380 eV to the 416 eV minima. This is summarised in Table 6.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio of Ti/N peak to Ti peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MULSAM</td>
</tr>
<tr>
<td>TiN</td>
<td>2.57</td>
</tr>
<tr>
<td>Ti</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Table 6.2 Ratio of peak heights in differentiated Ti and TiN spectra.

The ratio of these peak heights varies with the addition of the nitrogen, such that the ratio is less in the absence of nitrogen. This change is apparent in the data from all analysers, even though it is not immediately apparent in the $N(E)$ spectra.

It should be noted that differential spectra are strongly influenced by the resolution of the analyser, resulting in changes to the amplitudes of the differentiated peaks. The energy resolution of the MULSAM spectra acquired was 1 eV, however that of the HFA varies as a function of energy. At these energies the York HFA resolution becomes comparable, with the SRL resolution being higher. This will affect the comparison of values between different analysers, though the values between peaks measured on the same analyser will be self-consistent making it a suitable method for industrial applications.
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Figure 6.7 Differentiated spectra of Ti and TiN from Figure 6.4 (MULSAM).

Figure 6.8 Differentiated spectra of Ti and TiN from Figure 6.5 (York HFA).

Figure 6.9 Differentiated spectra of Ti and TiN from Figure 6.6 (SRL HFA).
6.6 The effect of a second MCP

The detector in use in the York HFA, and the initial detector in the SRL device both used a single MCP to provide electron amplification. A dual MCP arrangement was tested in the SRL device, as specifications from an interested party required the analyser to work with low (100 pA) probe currents. Although the addition of a second MCP would not increase the number of events recorded, it was felt that the modest increase in gain and improvement in counting statistics would be of benefit.

An MCP detector\cite{71} is a glass plate containing an array of micro-pores. These pores are \(~10\ \mu m\) in diameter with a length to diameter ratio (L/D) of 60, in the case of the MCPs used in the HFAs. The glass is treated in such a way to increase the secondary electron emission of individual channels and cause the channel walls to be semiconducting, allowing electron replenishment. An electron incident on the top of a channel initiates a cascade that propagates down the channel, towards the output face held at high positive potential (Figure 6.10). This can yield up to \(10^4\) electrons at the output.

The output from a single MCP has a distribution of output pulse amplitudes (the pulse height distribution, PHD) that is a negative exponential\cite{72} (Figure 6.10a). However, if a pair of MCPs are used, stacked such that the output of the first supplies the input to the second, the PHD becomes quasi-Gaussian (Figure 6.10b), due to the large electron cascade becoming limited by space charge saturation near the output, yielding output pulses with very nearly the same amplitude. In this case, there would be an expected improvement in SNR over the negative exponential distribution. The reason for this is that the individual events are not being counted (unlike most single channel devices), rather the sum of the amplitudes of the events is being considered.
The signal to noise ratio was investigated using TiN spectra acquired with both 1 nA and 100 pA beam current at 5 kV. The potential applied to the MCP and phosphor were (respectively) the usual values of 900 V and 3 kV for the 1 MCP system and ~1700 V and ~3.7 kV for the two MCP system. The improvement in SNR for the two MCP system was found to be a factor of 3 when using a 100 pA primary beam current but only a factor of 1.5 when using a 1 nA probe.

6.7 Improvements to detector operating time

If the photodiode was run continuously for a prolonged period, of the order of a few hours, the high-energy channels began failing. The maximum working channel number would decrease in arbitrary, quantised steps until eventually the entire detector ceased recording, shown in Figure 6.11. Only after several hours of inactivity, during which all applied potentials were removed, would the PDA recover. This effect was noticed on both the York device and the SRL device.
Figure 6.11 A time series image (with colour representing intensity) showing the gradual failing of the PDA channels.

It was considered that the high potential applied to the phosphor could be creating a strong electric field, affecting the internal circuitry of the PDA. To test this theory, SRL supplied a non-functioning Hamamatsu PDA, from which the fibre-optic plate (FOP) was separated by immersion in strong solvent (dichloromethane). This was then coated with a transparent gold conductive layer, on which was deposited a phosphor coating. The plate was then incorporated into the SRL detector. The original conductive layer on the FOP nearest the PDA could then be grounded to reduce the field affecting the PDA. The assembly can be seen in Figure 6.12.

Figure 6.12 The SRL detector arrangement with 2 MCPs. The conductive layer on the lower FOP was grounded.
The detector was then run continuously for 36 hours and showed no sign of PDA breakdown (the effect noticed previously after approximately 4 hours). This increase in operation time enabled higher resolution spectrum-images to be acquired and greatly improved the operation of the HFA. Following this trial, a 1 mm thickness phosphor coated FOP (with ITO as the phosphor contact) was purchased from Hamamatsu.

### 6.8 Modifications to HFA acquisition software

Under the development arrangement with the University, SRL were able to use a copy of the same test software as used at York. This was used during the initial stages of construction and testing to ensure the correct functioning of the PDA. It was felt however, that it would be beneficial for SRL to adopt a version of the Semaphore program (Chapter 3) to give increased flexibility to the HFA device. The program was therefore modified to function using the SRL equipment. Since most of the hardware acquisition electronics were the same only minor changes to the program were required to take into account the slight differences (Figure 6.13).

![Figure 6.13 Schematic of the acquisition path used at SRL.](image)

A simple spectrum-image viewing program was also written for use at SRL, as their multi-dimensional visualisation software was, at the time, still under construction. Using the stored ASCII spectrum-image data file, the program displayed a two
dimensional map of the sample surface at a given energy, with the spectrum at a
given point displayed beneath, shown in Figure 6.14. The energy map and
spectrum were interactive such that selecting a point on the image caused the
spectrum at that point to be displayed, and selecting an energy on the spectrum
caused that energy map to be displayed. The energy spectrum can be displayed in
the differential format if desired.

Figure 6.14 A screenshot of the simple spectrum-image viewing program used at SRL.

6.9 Spectrum-imaging

The Semaphore program enabled the acquisition of spectrum-images using the SRL
device. The act of acquiring full-range spectrum-images using conventional
analysers is usually a lengthy process, often over a period of days. During this time
special precautions must be taken to reduce the effects of thermal drift, etc. These
become less important however, with the reduced acquisition time of the HFA.
The test of the SRL HFA spectrum-imaging capabilities was conducted on a region of the TiN sample, obtained from ICT. This had become contaminated with a small quantity of silver paint used to secure the samples. One of the first spectrum-images acquired was a $20 \times 20$ point square array, covering an area approximately $1.2 \text{ mm}^2$. At each point, an energy spectrum was recorded over 48 to 1221 eV, with an acquisition time of 15 seconds, giving rise to a total acquisition time of 100 minutes for all points. A 5 keV electron beam was used, with a probe current of 2 nA. SEM and SAC images of the region inspected can be seen in Figure 6.15 (a) and (b).

The surface under inspection is not ideal, as the painted region has strong topography. This causes a great deal of variation in the intensity of the electrons emitted from the surface, due to microscopic edge enhancement and shadowing. Methods exist to compensate, to varying degrees, for this effect, especially if extra information such as the back scattered electron signal is measured simultaneously. In this case however, the ratio $(N_1 - N_2)/(N_1 + N_2)$ is used to reduce topographic effects and changes caused by a slowly varying probe current. Here $N_1$ represents the intensity at the maximum of an $N(E)$ peak, and $N_2$, a point on the background above the peak.

Taking images at a constant energy shows the composition of the surface for a particular element. Since the entire spectrum is acquired, this can be done post acquisition. Figure 6.15 shows the relative distribution of carbon (c), titanium nitride (e) and oxygen (g). Note that the mapping of palette value to index value is different for each image.

Figure 6.15 (c) shows the relative distribution of carbon over the surface, with the threshold map shown in (d) shown to highlight the distribution and represents the intensity at a point, relative to the mean value. The image shows that the carbon is concentrated mainly over the rougher painted regions near the edge of the sample. In liquid form, the paint consists of colloidal silver suspended in the solvent isobutyl methyl ketone. Since the paint has an appreciable volume, it is likely that
complete evaporation of the solvent does not occur, with traces remaining. The large hydrocarbon presence in this remaining solvent is likely to be responsible for the increased carbon signal.

Figure 6.15 (e) and (f) show the distribution of TiN, or rather the overlap of the 375 eV KLL N peak and the 381 eV LMM Ti peak. This is present on the sample region alone, indicating that the sample is TiN, and the rough region visible on the SEM and SAC images is due to an overlayer of contaminant rather than damage to the TiN sample itself.

The oxygen distribution, (g) and (h), shows the lowest amplitude signal is from the region of the paint. The stronger signals come from the sample and the stainless steel sample plate holder (lower right hand corner). This is most likely caused by residual contaminants adsorbed on the stainless steel surface. Also, the sample plate was in atmosphere for an extended period prior to sample mounting and is therefore likely to have an oxide surface. Although the spectrum-image took 100 minutes to acquire, it could be done faster, simply with a reduced signal-to-noise ratio. This was the first test of the spectrum-imaging capability of the SRL HFA.
Figure 6.15 Constant energy images, extracted from a SRL spectrum-image, showing the distribution of carbon, titanium/nitrogen and oxygen.
6.10 Further work at SRL

Further development work has continued on the HFA, with a different type of detector, a delay-line detector, being designed and tested at SRL (Figure 6.16). The data collected in this section was acquired by D. Cubric.

Figure 6.16 The delay-line detector fitted to the SRL HFA. Photograph used by courtesy of SRL.

The delay-line detector is designed to be a replacement for the PDA based detector used in both the York and SRL devices. As covered in Chapter 2, this consists of an MCP to amplify an incident electrons that are then accelerated towards the high positive potential on a phosphor screen where they are converted to light pulses and integrated by the PDA. The one-dimensional delay-line detector (DLD) replaces the PDA and phosphor screen, with the signal generated by the electrons impinging on the detector. The position of the event can be determined by the difference in the time taken for the signal to reach the ends of the wire, which typically has a resistance between 5 Ω and 100 Ω end to end. The DLD performs
well with a low count rate as the signal received is not subject to a local gain variation (i.e. it is a single detector) and the dark current is greatly reduced.

The increased size of this detector required a modified analyser base plate. The delay-line detector was supplied by RoentDek and consisted of a pair of wires, helically wound in parallel around a support. These wires were held at a positive potential (~+500 V relative to the MCP exit side), with the signal wire being held at a slightly more positive potential. These wires are then connected to the input of a RoentDek DLATR6 unit. This unit combines the decoupling of the signal and DC offset, differential amplification of the wire pair signal, and a constant fraction stage to process the signals. The timing signals are then fed into a time to digital converter (TDC), from which position information can be determined and a spectrum generated (Figure 6.17).

A sample spectra obtained with this detector can be seen in Figure 6.18. The acquisition time for this spectrum was 300 sec. The distance from the sample to the entrance aperture of the HFA was 50 mm, rather than the 25 mm used with the phosphor/PDA detector.

Initial tests of the delay-line detector suggest the energy resolution of the phosphor/PDA detector arrangement give a superior resolution. The current
resolution limit is not the pitch of the wires, but the timing resolution of the TDC hardware.\textsuperscript{[77]} This implies that with improved external electronics, the energy resolution using this arrangement can be improved.

At higher beam currents, problems can occur with a delay-line detector due to nearly coincident electrons striking different positions along the length of the line. If an electron induces a signal in the transmission line near one end, then the longer signal path must remain event free until the signal is recorded. If another electron event occurs in the wire during this time, ahead of the pulse, then there will be an error in the position information obtained and hence a random contribution to the signal level.

The time separation of pulses arriving at a channel of the TDC must be separated by 15 ns. Further dead time is introduced by the processing electronics, limits the maximum count rate of the detector to \(~1\text{ MHz}\). In the case of the SRL analyser, this corresponds to a maximum probe current of \(<\sim0.5\text{ nA}\), if the analyser retains it 1 mm entrance aperture and is a distance of 50 mm from the sample.
Chapter 7
Design and construction of a new HFA

7.1 Motivation

In the previous chapter, it was shown that the SRL HFA is better than the York analyser, having a greater signal to noise ratio. It can also be used with a weaker dispersion field to expand the low energy range of the spectrum. The original York device is also relatively wide, which makes its incorporation into MULSAM difficult with current detector geometry. With the aim of fitting a HFA into the MULSAM system, a new analyser was designed, based on experiences gained from the previous two versions.

The main reason for the improved performance of the SRL analyser was due to the reduced internal scattering of high-energy electrons. This is a common problem with electron spectrometers and is the subject of some study.\cite{46,49,78,79} The original version of the HFA was a very compact device measuring only 100 mm in length, making it susceptible to collisions from high-energy electrons on the hyperbolic electrode (Figure 7.1). The secondary electrons emitted then impinged on the detector generating a broad feature in the background. In order to reduce this, a rectangular hole was cut from the electrode. This effect is greater at higher beam energies or equivalently weaker dispersing fields. The problem is solved in the SRL analyser by moving the main electrode further from the entrance. This results in a longer device, requiring a higher voltage power supply.
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Figure 7.1 High-energy primaries can strike the rear electrode, causing the emission of secondary electrons.

The original HFA was mounted on an 8” flange. This reduced the potential mounting configurations for the detector due to the large size. With the aim of fitting an HFA into the MULSAM system, it was decided that any future mounting be done from a 4.5” (2½” internal diameter) port.

A new analyser was constructed that addressed the following points

- The analyser must be able to fit through a 2½” tube.
- The design should be longer to reduce internal scattering from the prime electrode.
- The analyser must be capable of being used with up to a 10 keV electron beam without significant internal scattering.
- The design should incorporate water cooling, enabling in-situ baking of the photodiode array.
- The detector should accommodate a second FOP to prevent breakdown of the PDA.

7.2 Electron-optics modelling

The design of the new HFA was developed using the analytic methods described in Chapter 2 and SIMION 3D (version 7.0).[80] SIMION is an ion-optics simulation program, for ray tracing the trajectories of charged particles through electrostatic and magnetic fields. In this particular case, the program was used to determine the
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trajectories of electrons affected by a hyperbolic electrostatic field. The value of SIMION is in the modelling of the third dimension (i.e. the sides of the analyser) which is not included in the analytic models. The effect of approximating the field with a small number of electrodes could also be seen (Figure 7.2).

Figure 7.2 (A) A 3D rendition of the HFA as modelled using SIMION. (B) A cross section of the simulation through the XY plane. $E_1$ to $E_9$ represent the potentials (negative) applied to the electrodes, with the landing positions of energies given beneath.

SIMION approximates the Laplace equation to calculate the electric field strength, by averaging the value of the six nearest neighbours of a given point. The process is repeated until the field variation reaches convergence. The total potential distribution is calculated in parts, taking advantage of the additive solution of the Laplace equation. The electrostatic potential distribution for a given electrode is calculated, whilst keeping the potential of all other electrodes constant. When this
has been done for all electrodes present, the solutions are combined giving the total distribution. The individual electrode potentials can then be changed and the field is scaled accordingly.

In the new analyser, \( V_1 \) is -5 kV and \( b \) is set to 50 (equation 2.1). The field was approximated using a flat plate as the main electrode, with the field trimmed along the top edge of the analyser by 8 strips held at appropriate potentials.

To ensure the best approximation (and smallest perturbation caused by the grounded casing) to the hyperbolic field in the central region of the analyser, electrodes were placed on the sides of the analyser. These electrodes were extensions of the 8 electrodes running along the top of the device, with each following the contours of the appropriate field line. This is more complicated than the side electrodes in the original HFA, but allow it to be narrower.

The sample position is located at \( x_s = -13.9 \text{ mm and } y_s = 8.2 \text{ mm and } \alpha = 25.5^\circ \), giving good parallel acquisition in the energy range \( E_{\text{max}}/E_{\text{min}} \sim 30 \). The entrance to the analyser is defined by an aperture of width 1 mm, which restricts the angular spread to \( \sim 3.3^\circ \). The position for second order focussing is predicted at \( x_f = 14.9 \text{ mm, in agreement with SIMION modelling. If the energy range is from 70 eV to 2100 eV, second order focussing occurs at } E = 100 \text{ eV. The optimum energy resolution occurs at the position of second order focussing. Analytically it can be expressed as}^{[81]} \)

\[
\frac{\Delta E_b}{E} = \frac{\Delta S}{D} + C_a (\Delta \alpha)^n + C_b \Delta \beta^2, \tag{7.1}
\]

with the dispersion \( D = E \left( \frac{\partial x_f}{\partial E} \right) \), \( \Delta S \) is the spatial resolution of the detector, \( n = 3 \) for a second order focussing device, \( \Delta \alpha \) is the opening semiangle angle and \( \Delta \beta \) is the out of plane semiangle. The coefficient \( C_a \) is given by
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\[ C_\alpha = \frac{2\Delta x_f}{(\Delta \alpha)^3 D} \]  

(7.2)

This has been solved using MathCAD and is \( C_\alpha = 150 \) and \( D = 7.1 \) mm for the new design.\(^{[14]}\) Note that these values refer to the second order focussing position, as the dispersion in the HFA is energy dependent.

Figure 7.3 Landing positions at various energies for the latest HFA. The first and second order focussing position (stationary inflexion) can be seen at \( E/V = 1.19 \). If \( V \) is scaled so that the detector range is from 70 to 2100 eV, \( E \approx 100 \) eV.
7.3 The HFA construction

The new HFA is constructed from non-magnetic stainless steel throughout. The walls and base plate of the analyser were grounded to reduce field penetration into the vacuum system. A photograph of the device can be seen in Figure 7.4, along with a semitransparent illustration to enable a view into the analyser. An exploded view and diagrams of all the parts are given in the appendix.

Figure 7.4 (A) Photograph of the new HFA mounted onto the mini extension chamber. This chamber has the flanges containing electrical feedthroughs and those for water-cooling. A semitransparent view of the analyser (B) shows how the electrodes are mounted from the upper Kapton (DuPont tradename for polyimide) panel, to generate the focussing field. The PEEK (poly-ether-ether-keytone) bars visible in front of the hyperbolic electrodes prevent them touching the grounded case.
The analyser base plate provides the main attachment point for the sides and connects the HFA to the mounting frame. It was machined from a single block of stainless steel, and, to reduce the width of the analyser, all electrical connections required to run the PDA are contained within channels machined into the sides. Separate channels carry the high voltages required for the MCP and phosphor potentials. Considerable care must be taken to ensure the adequate shielding of the video data line from the lines carrying clock pulses. (The more common configuration is for the photodiode array to be mounted directly on the amplifier board, but this is not possible for vacuum applications).

The internal surface of the base plate contains grooves at the front to locate the parts required to secure the detector. Beyond the detector region there is a rectangular depression machined into the base plate to serve as an electron dump, reducing the probability of secondary electron emission from incident electrons. An acetylene flame (carbonising) was used to deposit a layer of carbon onto the recessed region, reducing the secondary electron yield.

To ensure the recess does not distort the field within the analyser, it is covered by high transparency mesh. This was etched from a thin (150 µm) stainless steel sheet covering the base plate, using a photochemical etching process known as chemical milling. Drawings were sent to Photofabrication Ltd., where the design was plotted onto film. A metal sheet was then laminated on both sides with a UV-sensitive polymer resist. The film was then used as a mask (on both sides) during UV exposure, after which the non-exposed regions of the resist were developed away. The sheet was then acid etched to the desired shapes before finally removing the remainder of the resist. This method has the advantage that the machining does not deform thin sheets of material.

The electrodes used to approximate the field within the HFA were also chemically milled, their design derived from the SIMION model. Partial etching, whereby a sheet is only etched to half its thickness, was used to create guide lines to produce a perfect fold, as shown in Figure 7.5. To ensure alignment of the electrodes, partially
etched spacer bars connected each element. Once all electrode fixings were in place, these were removed.

Figure 7.5 The field creating electrodes were manufactured as a planar sheet, with half etched fold lines. When bent, a cage, capable of reproducing the simulated field is created.

The electrodes are mounted, with appropriate spacer washers, to the underside of a Kapton sheet. Each electrode is connected to the next by a resistor located on the top of the Kapton sheet. The resistor chain (which is located in vacuum) enables a single -5 kV power supply to be distributed appropriately between the electrodes (values as seen in Figure 7.6), producing the desired field. The field can also be scaled by adjusting the potential on the primary electrode. Although painted resistors are not commonly thought of as UHV compatible, their use in the previous analyser design proved their use to be acceptable. After baking the system, the pressure increase during operation is only a few parts in $10^{-10}$ mbar.

To reduce the effect of field leakage (caused by the exposed resistors) in the region around the entrance aperture, a thin, grounded sheet of stainless steel was placed over the first few resistors with a thin backing of Kapton to prevent the guard from causing a short circuit. Without this guard, the field generated in the entrance
region is sufficient to disturb the trajectories of low energy electrons and prevent focussing on the detector plane.

For initial testing, a phosphor coated glass block was substituted for the PDA. A potential of +1 kV was applied across the MCP, with the phosphor held at a potential of +3 kV. The light intensity distribution corresponding to the energy spectrum could be recorded with CCD camera mounted outside the vacuum system. This meant the system could be baked without an active cooling mechanism and enabled any misalignment in the analyser to be quickly noticed.

The final detector arrangement is shown in Figure 7.7. A gap of 0.5 mm separates the MCP from the first of two fibre-optic plates. For the first FOP, a section of 3 mm thick, 1:1 fibre-optic plate was cut to size (15 × 65 mm) and both faces coated with a transparent layer of aluminium. A thicker layer was deposited at the ends provided an electrical contact. A layer of P22 phosphor was deposited on the upper face using a spraying method to provide a scintillator. The lower FOP face is kept grounded to prevent field penetration caused by the phosphor potential into the PDA. The second fibre-optic plate, which is bonded to the PDA, was not subject to any coating process. In this arrangement, the intensity distribution visible on the
phosphor screen is translated by the FOP arrangement to a linear photodiode array where it is detected. The PDA was the same model as in previous versions.

![Diagram of detector components](image)

**Figure 7.7** The in-situ detector used in the new HFA.

The PDA can be stored at temperatures up to 85°C. The usual temperature at which the MULSAM system is baked is 150°C, therefore active cooling is required to prevent damage occurring to the PDA during this time. This is provided by a cooling-block mounted to the rear of the analyser, with a copper base where it contacts the HFA. Water to the cooling block is supplied through liquid feedthroughs embedded in the mounting flange.

The HFA assembly is mounted from a 4.5” flange mounted to a small, multi-port extension chamber, to which all electrical feedthroughs were attached. The mounting flange also contains a thermocouple feedthrough enabling monitoring of the HFA detector temperature during baking. This arrangement enables the HFA and all connections to be removed as a complete unit.

### 7.4 Preliminary testing of the new HFA

The first modification required to the design was the adjustment of the analyser mount as it was discovered that the analysis position for the MULSAM system is offset from the chamber centre by 20 mm. The mount was modified by the
inclusion of a PEEK spacer block to provide the displacement, and also aid thermal isolation of the HFA.

Initial trials of the water-cooling arrangement gave temperature difference of about 10°C, meaning the maximum system bake temperature was only about 90°C. This resulted in extended bake out periods and a lower ultimate pressure. This poor performance was caused by the large distance between the heat sink and the PDA (which was necessary due to the geometry considerations with the MULSAM system). Since the primary mechanism of heating was through radiative transfer, a thin copper sheet was used to totally shield the PDA from line-of-sight heating effects. This shield was clamped between the cooling block and the HFA base plate, as it was felt that this sheet, with its improved thermal conductivity would keep the analyser cooler. With this in place, the water-cooling was able to generate a 34°C temperature difference. Though still not ideal, the water-cooling does provide a mechanism whereby both the chamber and PDA can baked in a single session. The bake-out control interlocks were wired so that the thermocouple mounted on the HFA would control the heaters, with the main chamber thermocouple set to prevent the system exceeding 150°C. However, it was quickly discovered that the thermal isolation of the HFA was sufficient to cause a large hysteresis chamber temperature, leading to a very inefficient bake. This was changed so that the HFA thermocouple became an indicator with the main chamber temperature being controlled.

With the phosphor screen detector and CCD camera arrangement, a simple test was conducted into the effects of internal scattering within the analyser. Reducing the potential applied to the field electrodes enables scaling of the analysing field to lower energies. The effect of this can be seen in Figure 7.8.
Figure 7.8 The effect on the energy spectrum of reducing the field strength, before any calibration has been applied. The dashed lines represent approximate constant energies.
In this example, the sample (copper) was not cleaned, resulting in a spectrum containing large carbon and oxygen features. Each spectrum was acquired with a 5 keV electron beam, probe current ~4 nA. The new analyser shows no signs of internal scattering until the field is considerably reduced to about 1000 V. At this energy, the range should be approximately 20 – 500 eV. Detector effects can be noticed also, as features that do not change with a change in field strength, as highlighted by vertical lines in the figure. These spectra show that the new analyser can operate with a variable field strength and will enable low energy features to be examined in greater detail.
Conclusions

After careful calibration and further development, the HFA can now be used to provide quantitative surface information. From the comparison of identical spectra taken with the HFA and MULSAM CHA, the HFA transfer function can be calculated. This can then be applied when inspecting other materials to remove the influence of the analyser on the energy spectrum. Software for analyser control has been developed, enabling the simultaneous acquisition of information from a range of detectors, including the HFA, to provide more information about the sample under inspection. Control of the beam scanning permits sample imaging which, when used with the HFA, enables rapid spectrum-imaging.

The usefulness of rapid acquisition is demonstrated by a study into the effects of electron stimulated desorption of HCl from the surface of InP (110). Auger spectra monitored the time evolving features during irradiation. The use of a fine focussed electron beam during this work permitted the effects of surface diffusion to be measured, using the novel approach of intensity profiles generated by sample absorption current imaging. From this work, the value of the main desorption constant was calculated to be \( k = (3.75 \pm 0.3) \times 10^{-4} \text{ A}^{-1} \text{m}^{2} \text{s}^{-1} \), with the diffusion coefficient being less than \( D = 7.0 \times 10^{-14} \text{ m}^{2} \text{s}^{-1} \). This technique shows high sensitivity to adsorbate coverage. It has been proposed that the contrast mechanism is due to a change in the low energy secondary electron yield. A more thorough investigation into the exact cause could perhaps yield a yet more sensitive surface inspection technique. It would be interesting to apply this method to other adsorbate systems and compare the performance against other methods of adsorbate analysis, such as infra-red spectroscopy.
Conclusions

Work has been conducted with the industrial sponsor, SRL, developing and testing the commercial prototype of the HFA. During testing, a means to prolong the detector operation time was implemented which, combined with modified York acquisition software, permitted the first collection of spectrum-images with the SRL device. Also, an investigation into the differences in the Auger signal from Ti and TiN showed both the SRL and York HFAs could resolve the two samples, even though the difference was not immediately apparent in the \( N(E) \) spectrum. This was achieved by measuring the height ratios of the \( \sim 380 \) eV Ti/TiN and \( 416 \) eV Ti peaks in the differential spectrum, which showed the ratio to be greater for TiN due to the overlap of the main Auger transitions of Ti and N. The next challenge would be to apply this technique to actual device samples (e.g., depth profiled Ti/TiN structures). Using line-scans or spectrum-imaging would enable the elemental distribution to be accurately determined over the whole sample.

A new HFA has been developed for inclusion into the MULSAM system. This is longer and narrower than the original design to reduce the effects of internal scattering and to fit with the other instruments. The analyser energy range can be as low as \( \sim 20-500 \) eV before internal scattering effects degrade the performance. It has been shown that at low energies, second order focussing occurs. The analyser has been fitted to the MULSAM system, but is not yet fully integrated. Once done this should provide a good compliment to the current MULSAM detectors. The calibration methods, which have been developed in this work, will be more accurate also, due to the standard samples being inspected under identical conditions. The control software for the HFA requires embedding into that of MULSAM.

The development of the HFA device has been possible due to advances in other technologies, such as photodiode arrays. It is therefore important to be aware of emerging future technologies, as these may enable the realisation of improved devices, as well as further applications.
Appendix 1

The following appendix contains technical drawings of the new HFA. Unless indicated otherwise, the material used is stainless steel.
An exploded view of the HFA, showing the relationship of the main parts.
Appendix 1

Front and rear plates (holes 2mm unless marked)

Front aperture

PDA securing plate

Primary electrode

Hole diam. = 2
Thickness = 0.5
Electrode attachment sheet (top of field box) - rear section

Trailing edge uppermost

All holes = 2
Material = Kapton
Thickness = 1

Electrode attachment sheet (top of field box) - mid section

Electrode attachment sheet (top of field box) - front section

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Appendix 1

MCP support and PDA assembly legs (2x each)

Sup. 1

Sup. 2 (mirror of sup. 1)

Material = PEEK

Electrode Rest (x2 front, x2 rear)

Shaped to increase path length

Material = PEEK

MCP/Phosphor electrode spacers

Holes = 2.1

Material = Kapton
Thickness = 0.25

Front Electrode Rest (x20)

Thickness = 3
Material = PEEK
Hyperbolic Electrodes

Material = Stainless Steel  
Thickness = 150um

The part was created by photochemical milling.
Base plate cover

Mesh region:
bars = 0.15
holes = 1

Thickness = 0.15
MCP/Phosphor contacts

Thickness = 0.05
References


36. MathCAD, Mathsoft Inc. USA.


66. Shimadzu Research Laboratory (Europe) Ltd., Wharfside, Trafford Wharf Road, Manchester, M17 1GP, UK.


