Application Note: 31055

Theta Probe: Small Spot XPS Spectrometer with Parallel ARXPS Capability

Key Words

- Parallel ARXPS
- Surface Analysis
- Ultra-thin Films

Description

The Thermo Scientific Theta Probe, Figure 1, is a high-performance XPS instrument. Our patented Theta technology provides the unique ability to collect angle-resolved XPS spectra over a 60° angular range, in parallel, without tilting the sample. This ability allows the instrument to characterize ultra-thin films non-destructively.

Key features of Theta Probe include:

- X-ray monochromator with user-selectable spot size in the range 15 µm to 400 µm
- Parallel angle-resolved XPS (PARXPS) analysis without sample tilting
- Ability to handle large samples
- Controlled by *Avantage*, a Windows®-based data system
- CCD sample alignment microscope perpendicular to the sample surface (when the sample is horizontal)

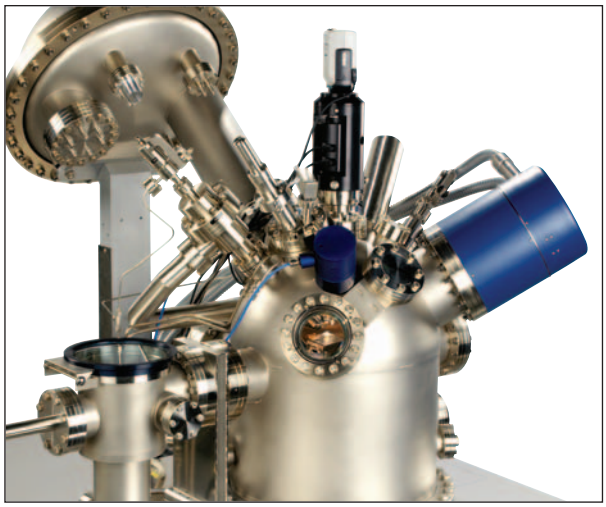

Figure 1: Theta Probe

Lens, Analyzer, and Detector

The arrangement of the components in Theta Probe is shown in Figure 2. In Theta Probe, the photoelectrons are collected by an electrostatic lens having a large angular acceptance (60°), the Radian lens. Such a large acceptance angle maximizes sensitivity and allows a large angular range to be collected in PARXPS measurements.

The axis of the lens is 50° from the sample normal and so electrons are collected over the range 20° to 80°. Note that all angles are expressed relative to the sample normal when the sample is in the usual, horizontal, analysis position.

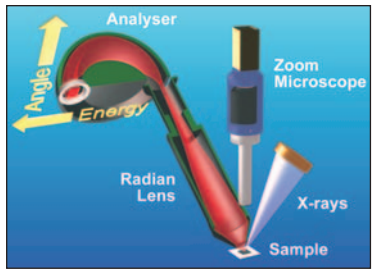

Figure 2: The arrangement of the analytical components on Theta Probe. The 2-D detector collects spectroscopic and angular information simultaneously.

The 180° spherical sector analyzer is fitted with a two-dimensional detector in the output plane.

The lens in Theta Probe is unique because it can be operated in either of two modes:

- Conventional mode, for spectroscopy when there is no requirement for angle-resolved information.
- Angle-resolving mode.

The two-dimensional detector provides a means of multi-channel detection, having up to 112 energy channels arranged in the radial direction at the output plane. This means that good quality snapshot spectra can be acquired without the need to scan the analyzer. This represents a significant time saving, particularly for experiments that require a large number of spectra to be acquired, such as depth profiling or XPS mapping. The reason why this method of acquisition is faster is explained in the application note AN31014. For survey spectra, the required energy range is too great for the snapshot mode to be used and the analyzer is scanned in the conventional manner.

In the angle-resolving mode, electrons are dispersed on the detector in two directions. They are dispersed, according to their energy, along the energy dispersive direction of the analyzer, as is conventional for a hemispherical analyzer. The electrons are also dispersed in the perpendicular direction according to the angle at which they were emitted from the sample.

This means that angle-resolved XPS spectra can be acquired in parallel and without tilting the sample. The instrument collects photoelectrons over a range of 60° and this can be dispersed into a maximum of 96 angular channels. As a compromise between angular resolution and sensitivity, the data are usually summed into 16 channels covering the whole 60° range.

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X-ray Source

All Theta Probe instruments are fitted with a microfocusing monochromator, this is often their only radiation source. The principles of the operation of an X-ray monochromator are described in application note AN31038. Two features of Theta Probe's monochromator must be mentioned:

- The Movable Anode. With use, the aluminum coating on any X-ray anode will wear, affecting the intensity of the X-rays and therefore the sensitivity of the instrument. When this happens on instruments from other manufacturers, the anode has to be replaced. On Theta Probe, the anode can be moved to expose a fresh area to the electron beam. This can be done without breaking the vacuum. This feature increases the lifetime of the anode significantly.
- The Probe Light. This is a light source, situated outside the vacuum system, which is focused onto the anode and reflected onto the crystal. The crystal focuses the light onto the sample at the analysis position. This provides a means of defining the analysis position with great confidence. Its operation is illustrated in Figure 3.

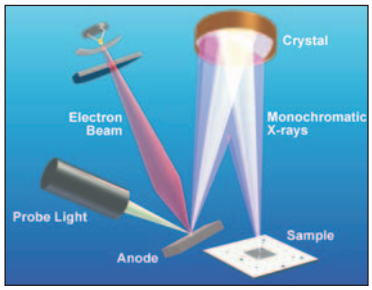

Figure 3: The microfocus monochromator on Theta Probe has a Probe Light to assist in sample alignment.

Small Area XPS (SAXPS)

In Theta Probe, the area for analysis is defined by the size of the X-ray spot (i.e. it is source-defined SAXPS). The relative merits of this approach have been described in application note AN31033. The lateral resolution available from the instrument is 15 µm to 400 µm.

Mapping

Mapping with Theta Probe is accomplished by moving the sample stage under the X-ray spot. The size of the X-ray spot therefore determines the resolution of the image.

Figure 4 shows an example of an XPS map acquired from a copper grid using the smallest X-ray spot size. A line scan constructed from the image showed that the average spatial resolution was 8 µm, Figure 5.

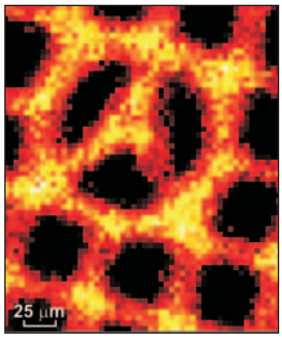

Figure 4: XPS map of copper grid acquired using Theta Probe

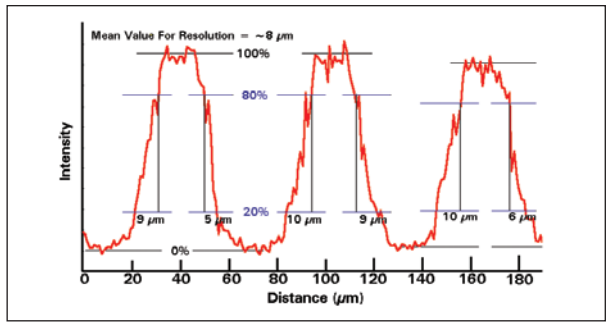

Figure 5: A line scan through the map in Figure 4 showing an average spatial resolution of 8 µm

Producing maps by scanning the sample stage is less rapid than other methods but has a number of important advantages:

- The spatial resolution is constant over the whole of the imaged area. This is not the case if the image is produced by scanning the X-ray spot.
- The detection efficiency is optimized. The image is produced with the lens operating at its maximum transmission. This is not the case if the map is produced by scanning the lens-defined analysis area.
- The instrument transmission function is independent of position. The transmission function can potentially be affected if the map is produced by scanning the lens-defined analysis area.
- The X-ray energy and intensity are independent of position. Neither of these remains constant if the X-ray spot is scanned over the sample to produce the image.
- A very large field of view is possible. The maximum field of view is determined by the range of movement of the sample stage, in the case of Theta Probe, this is 70 mm x 70 mm. Other methods of imaging or mapping are much more restricted than this.
- It is possible to produce a spectrum at each pixel in the image. The spectra can be processed in the normal way for maximum quantitative and chemical state information.
- With Theta Probe, PARXPS measurements are possible at every pixel enabling overlayer thickness maps to be obtained. No other XPS instrument can do this.

Ion Gun

Theta Probe is fitted with the EX05 ion gun. This has been in described in application note AN31017.

Sample Size and Sample Alignment

All Theta Probe instruments have a fully motorized stage capable of five axes of movement. The stage on Theta Probe can accommodate large samples. Its movement range in X and Y is 70 mm and 25 mm in Z (height). Figure 6 shows, schematically, the range of samples that can be analyzed in the system and Figure 7 shows a sample holder loaded with samples for analysis.

Figure 6: The range of sample sizes that can be accommodated in Theta Probe

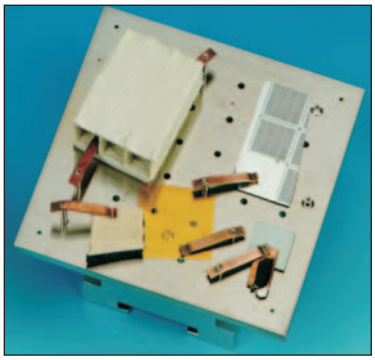

Figure 7: The standard sample carrier used in Theta Probe with a number of samples loaded ready for analysis

If sample tilt or rotation is required, samples must be loaded on the appropriate sample holder, Figure 8. Using this sample holder, the rotation is continuous and the tilt range is ± 45°.

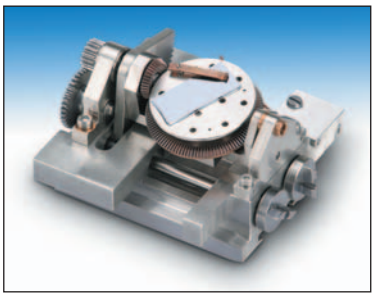

Figure 8: The sample holder used when sample tilt or rotation is required

All axes of movement on the sample stage are motorized and the controller is linked to the *Avantage* data system so that the data system can control the sample position.

Analysts who routinely perform rotation depth profiles should select the optional 8-sample multi-rotation holder. A different sample can be accommodated on each of the 8 sample positions and a rotation depth profile can be measured on each without any user intervention between profiles. This minimizes the time that Theta Probe remains idle.

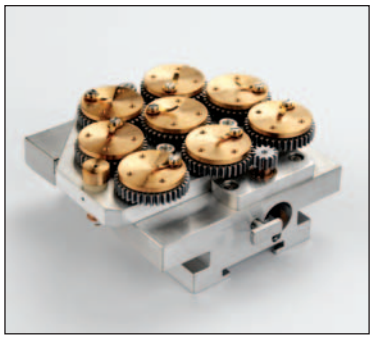

Figure 9: 8-sample multi-rotation holder

As can be seen in Figure 10, there is a zoom microscope positioned immediately above the sample, its axis is parallel with the sample normal when the sample is in its analysis position.

The field of view from this optical system is in the range of 400 µm to 4 mm. The analysis position is accurately aligned with the center of the graticule when the image is in focus. To align a feature for analysis it must be visible and in focus at the center of the graticule. This can be done by moving the sample using the tracker ball or pointing to a position on the optical image using the mouse pointer.

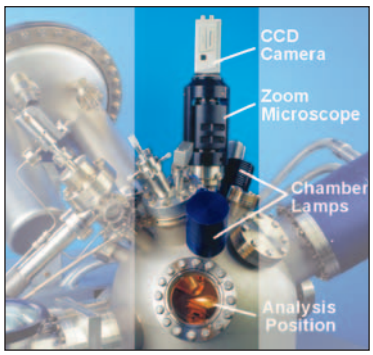

Figure 10: The alignment of the zoom microscope, sample and illumination on Theta Probe

Sample positions can be stored and recalled for unattended operation of the instrument. For accurate sample alignment, it is important that the sample height is set accurately. One of the features of Theta Probe is its ability to set the sample height automatically, using an XPS signal.

Vacuum System

The analysis chamber is constructed from 5 mm thick mu-metal to maximize the efficiency of the magnetic shielding. The analysis chamber on all Thermo Scientific XPS instruments are constructed this way. The use of internal or external shields, the shielding method used by other manufacturers, is not so effective.

The chamber is pumped using both a turbomolecular pump and a titanium sublimation pump. This arrangement allows the analysis chamber to achieve a vacuum better than 5 x 10^{-10} mbar.

The entry lock is pumped using a turbomolecular pump backed by a rotary pump. Differential pumping for the ion gun is provided by another turbomolecular pump and rotary pump.

The whole vacuum system can be baked in order to achieve the ultimate base pressure.

Sample Preparation

A sample preparation chamber can be added to Theta Probe, see Figure 11, to enable a variety of sample preparation techniques to be added. These facilities include, ion etching, heating, cooling, fracturing, parking etc.

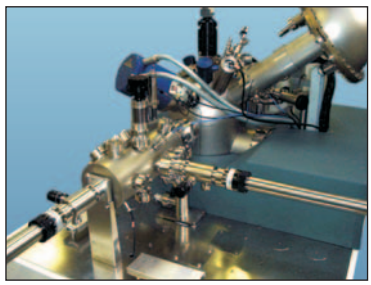

Figure 11: An example of a preparation chamber fitted to Theta Probe

Performance

Specifications

The Theta Probe specifications are defined under typical operating conditions. The microfocus monochromator is operated at the maximum power appropriate for each spot size. Count rate scaling is therefore not necessary.

The sample is placed on the normal sample holder with its surface horizontal. The sample remains in the same position for both spot size and count rate measurements.

When comparing specifications from different instruments, it is important to ensure that the conditions under which the data are collected are the same.

Small Area XPS

Figure 12 shows an area of a failed galvanized steel joint at each of two magnifications, as seen through the optical microscope on Theta Probe.

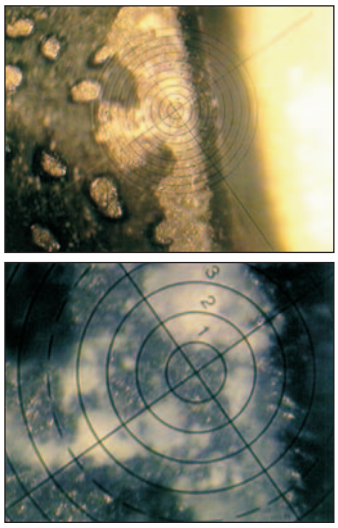

Figure 12: The failure area of a galvanized steel joint, as viewed through the microscope at two different zoom settings. The microscope graticule can also be seen.

Figure 13 shows a comparison of the XPS spectra obtained from the dark and bright areas visible in the optical image. In each case, the monochromator spot size was set to 20 µm.

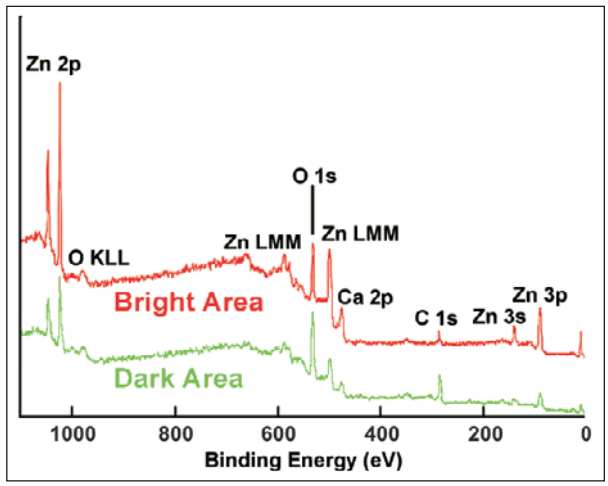

Figure 13: Survey spectra from light and dark areas of the sample shown in Figure 12

The SAXPS analysis revealed less Zn in the dark areas than the light areas. The presence of zinc in the spectrum is an indication that the phosphate layer, applied before the galvanizing process, has been depleted by corrosion and dissolution. This causes a weakening of the adhesion of zinc to steel in the galvanized material.

Multi-point, small-area analysis is available using Theta Probe. Figure 14 shows the optical view of a 100 µm bond pad in the analysis position. Seventy of these pads were analyzed in a single, unattended operation. The results are shown in Figure 15.

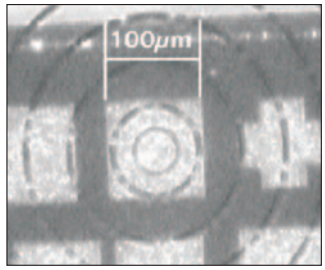

Figure 14: Optical view of a sample having a large number of Al bond pads

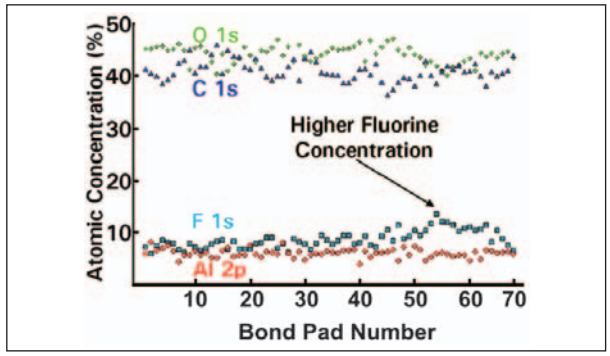

Figure 15: The composition of 70 of the bond pads similar to those shown in Figure 14. These data were acquired during an automated, unattended acquisition.

Parallel Angle Resolved XPS (PARXPS)

ARXPS is being used increasingly to determine the composition and thickness of ultra-thin surface layers. At grazing emission-angle, XPS data are only collected from the near surface. At nearer normal emission, the information depth is larger.

The radian lens spectrometer on Theta Probe provides both energy dispersion and angular dispersion on the 2-D detector. Both are collected simultaneously. Angle resolved XPS is now possible without tilting the sample.

Figure 16 shows an image of the channel plate output when the analyzer is tuned to the Si 2p region of the spectrum. In this example, the sample is 4 nm of silicon dioxide on silicon. The elemental and oxide peaks are clearly visible but the intensity of the signal from elemental silicon decreases more rapidly with increasing angle than the oxide peak.

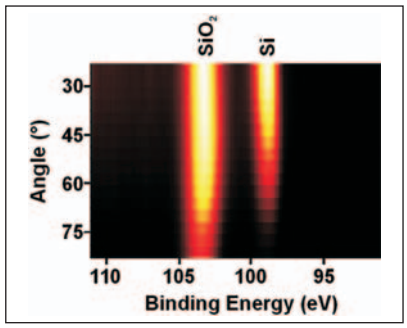

Figure 16: An image of the 2-D detector output when the analyzer is tuned to the Si 2p region of the XPS spectrum during the analysis of a 4 nm layer of SiO_2 on Si.

Figure 17 shows the same data as Figure 16 but displayed as a montage of spectra.

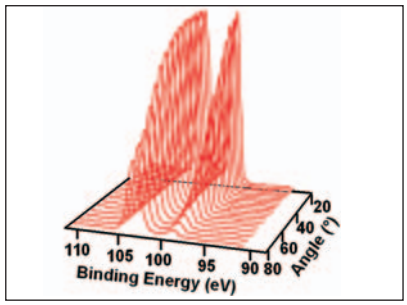

Figure 17: The same information as that shown in Figure 16, shown graphically as a montage of spectra

Layer Sequencing

The simplest use of angle-resolved XPS data is to produce a relative depth plot, see Figure 18. This shows the sequence of layers in a sample but does not provide thickness or depth information. The way in which this plot is constructed is described in application note AN31014. Figure 18 is from a layered structure consisting of Al_2O_3 on HfO_2 on SiO_2 on Si. The sequence of these layers and the carbon contamination layer is clearly visible in Figure 18.

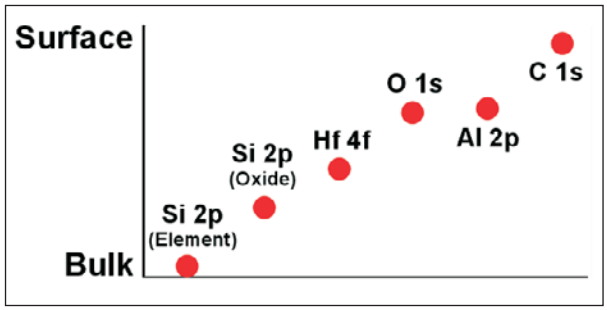

Figure 18: A relative depth plot, derived from PARXPS data, showing the sequence of the layers in a multi-layer material

Thickness Measurement

Data such as Figure 17 can be used to measure the thickness of the oxide layer. For this, the overlayer thickness calculator software, integrated into the *Avantage* data system, is used. The principles on which this is based are described in detail in the application note AN31005.

Thickness measurements from a number of oxide on silicon samples were compared with ellipsometry measurements and the results are shown in Figure 19.

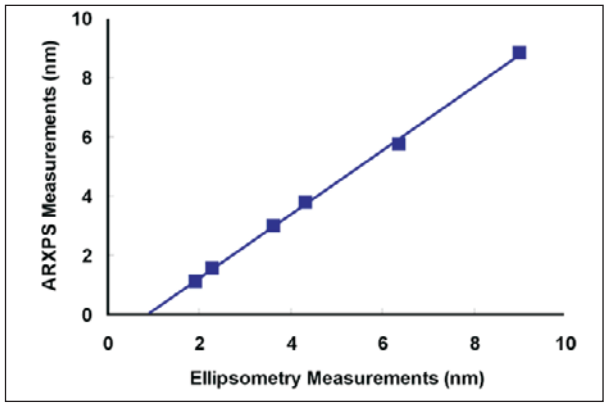

Figure 19: Comparison of ARXPS and ellipsometry for the measurement of the thickness of SiO_2 layers on Si

In this Figure, the linearity is excellent and the gradient is very close to unity, but there is a 0.8 nm intercept on the ellipsometry axis. This is commonly observed in such comparisons and occurs because ellipsometry measures both the oxide layer and the contamination layer present at the surface. PARXPS, however, measures only the oxide. The contamination layer was formed at the surface during exposure of the material to air. The thickness of the contamination layer can also be measured by PARXPS, if required.

The thickness of multiple layers can be measured using PARXPS, see, for example, Figure 20. This is data from a series of Al_2O_3 layers grown by atomic layer deposition (ALD) on 0.9 nm SiO_2 on Si. For each sample, the three thickness measurements were made simultaneously.

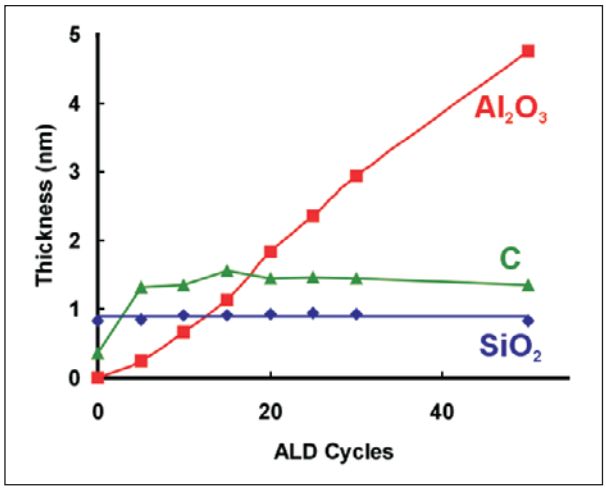

Figure 20: The thickness of C, Al_2O_3, SiO_2 and Si as a function of the number of cycles of ALD growth of the Al_2O_3

Depth Profiles

Using a method involving maximum entropy, described in application note AN31014, it is possible to extract depth profiles from PARXPS data. Figure 21 shows an example of such a profile from one of the samples whose thickness is shown in Figure 20.

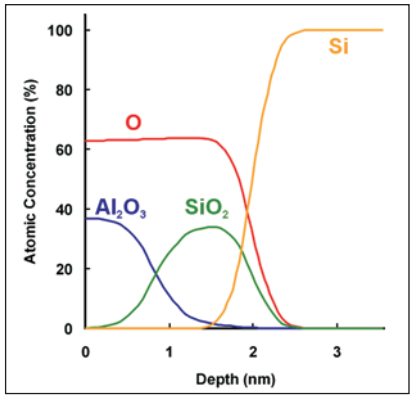

Figure 21: A depth profile of one of the samples plotted in Figure 20. The profile was constructed from the PARXPS data.

PARXPS is a powerful technique for examining surface modification of insulators.

Using Theta Probe, the sample does not have to be tilted so the charge compensation conditions remain constant. The analyst can be certain that changes in peak shape with angle are due to the chemistry of the surface.

Sputter Profiles

For layers whose thickness is greater than a few nanometers, concentration depth profiles can be generated by sputtering using noble gas ions.

Theta Probe provides depth profiles from a small area with high sensitivity. Small sputtered areas ensure high etch rates and short acquisition times.

Many features of Theta Probe have been developed for optimum sputter profiling performance:

- The EX05 ion gun may be operated at high current for maximum profiling speed and at low energy (down to 100 eV) for optimum depth resolution. The low energy performance is enhanced by use of a 'floating drift tube' in the ion gun (see the application note AN31017 for details).
- Multi-sample sputter profile acquisition allows unattended operation for maximum sample throughput
- The data system includes Target Factor Analysis (TFA), Linear and Non-Linear Least Squares Fitting (LLSF and NLLSF). These functions are fully integrated and ensure that the maximum possible chemical information is extracted from every profile.
- Azimuthal rotation of the sample during sputtering minimizes the development of sputter induced topography.

As an illustration of the ability of Theta Probe to produce high quality profiles, Figure 22, shows the profile through the layered structure of a hard disc.

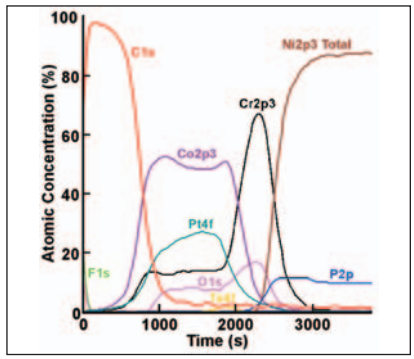

Figure 22: Sputter depth profile of a hard disc

Mapping

Theta Probe provides:

- Quantitative elemental and chemical state maps
- A spectrum at every point
- A set of angle resolved spectra at every point, if required.
- Thickness maps

The multi-channel detector on Theta Probe allows the collection of up to 112 energy and 96 angle channels simultaneously at each point on a line or map.

Spectra or PARXPS data can be derived retrospectively from any area in the map or even from a single pixel.

Maps can be constructed following the application of advanced data processing techniques such as NLLSF. This enables accurate mapping of chemical states.

Collection of angle-resolved data simultaneously with the spectral data allows thickness maps or sub-surface images to be constructed.

Theta Probe uniquely combines mapping with PARXPS. This capability adds a new dimension to XPS mapping.

In this example, a masked sample of oxidized tin was prepared by sputtering with argon ions using a grid as a mask, as illustrated in Figure 23.

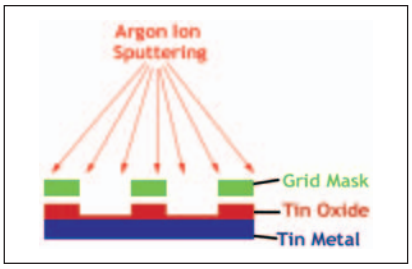

Figure 23: Method of sample preparation for the mapping experiment.

A chemical state map of the sample was generated from PARXPS data. Reconstructed PARXPS spectra were then generated from masked and unmasked areas of the sample, Figure 24. The spectra from the unmasked area showed an increased in the amount of tin present in relative to oxidized tin.

By applying peak fitting and LLSF to the data set, the metal and oxide peaks can be mapped. Figure 25 shows the map of oxidized tin.

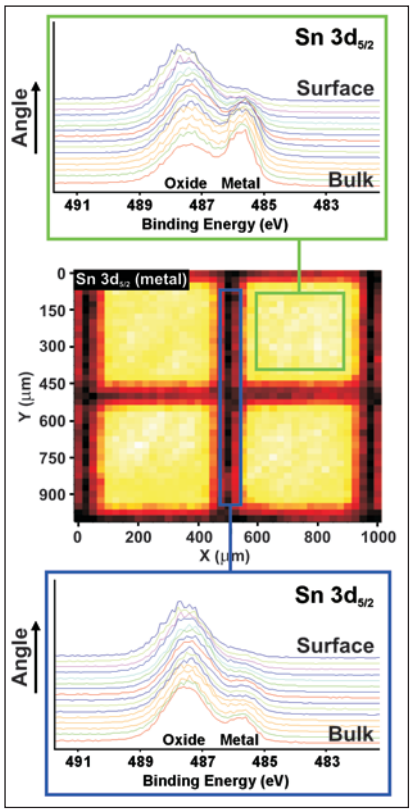

Figure 24: Reconstruction of PARXPS data from two areas of the elemental tin map

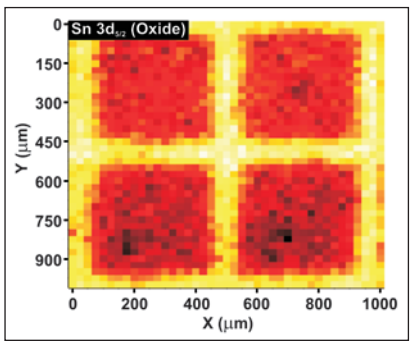

Figure 25: XPS map of oxidized tin

PARXPS data is collected at every pixel, which means that a thickness map can be constructed using the overlayer thickness calculator in the *Avantage* data system. Such a thickness map is shown in Figure 26.

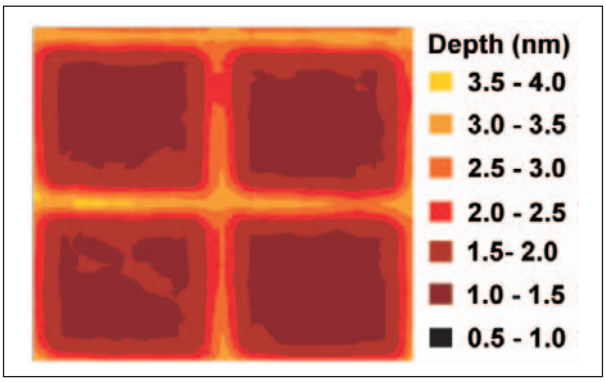

Figure 26: Oxide thickness map constructed from the PARXPS data

Configuration

Theta Probe comprises a UHV mu-metal chamber fitted with:

Electron Analyzer

- Double-focusing full 180° spherical sector analyzer
- Multi-element electrostatic Radian input lens for spectroscopy
- Two-dimensional, multi-channel spectroscopic detector for spectroscopy and mapping

Microfocused Monochromated X-ray Source

- 250 mm Rowland circle monochromator
- Microfocused electron gun and multi-position aluminum anode X-ray source
- Thermostatically controlled quartz crystal and crystal manipulator

Combined Low-energy Electron/Ion Flood Gun

- Charge Neutralization
- Flood gun assembly incorporating electrostatic deflection for precise alignment.
- Low energy-spread, high brightness electron source (fitted into the above).
- Leak valve and manifold for inert gas admission.
- Differential pumping

Ion Gun

- Sample cleaning
- Depth profiling
- Digital power supply
- Beam scanning
- Differential pumping
- Faraday plate SEM detector

Sample Viewing

- X-ray shielded viewport
- Zoom microscope sample alignment facility with CCD camera
- Multiple light sources

Fast Entry Chamber

- UHV compatible sample transfer mechanism
- Fully safety interlocked pneumatic 98 mm gate valve to analysis chamber
- Turbomolecular pump and rotary backing pump

5-axis Sample Stage

- High precision, automated sample stage with internal stepper motors
- Stage controller with trackball and joystick, interfaced to the *Avantage* datasystem

Avantage Data System

- Instrument control
- Multi-sample analysis
- Linescan
- Depth profiling
- Mapping
- Advanced software for processing PARXPS data including multi-overlayer thickness calculation and non-destructive depth profile construction

Options

Sample Holders

- Multi-sample holder
- Tilt and rotate sample holder
- Heated sample holder (1000 K) with thermostatic temperature control
- Sample cooling
- Three axis rotating sample holder

Closed Circuit Water Chiller

- Water chiller unit with 1000 W at 20 °C cooling capacity
- Water temperature regulator and flow control

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