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Quantified imaging of silicon dioxide particles

Keywords
Imaging XPS, spectra from imaging (SFI), spectromicroscopy, silicon dioxide, parallel imaging, spherical mirror analyser (SMA), multivariate analysis

Application Note MO421(1)

Further application/technical notes are available online at:
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Overview

XPS imaging is an important tool for investigating the lateral distribution of surface chemistry on the micron scale. Photoelectrons emitted from core electronic levels of surface atoms may be focused to form a two dimensional image on a suitable detector to allow the lateral distribution of the photoelectrons to be determined. AXIS spectrometers have a pulse counting delay line detector (DLD) system which allows images to be quantified. Spectra may be generated from every pixel in an image hence the chemical state of a sample surface may be quantitatively determined at high lateral and high energy resolution. In this example silicon dioxide particles dispersed on the surface of a silicon wafer were analysed to demonstrate the flexibility of XPS imaging.

Introduction

Commercially available instruments with the ability to record XPS images have been available for more than 30 years. Early implementations were limited due to low sensitivity and the inability to accurately quantify the images produced. Current state of the art instruments such as the AXIS spectrometers have overcome these problems such that XPS imaging may be routinely used to measure quantitatively the lateral distribution of surface species.

The electron optics of the AXIS spectrometers is described in detail elsewhere. In brief the system comprises: a magnetic lens to focus a magnified photoelectron image of the sample surface into the electrostatic lens column;[1] a series of electrostatic lenses to form an energy retarded photoelectron image at the entrance to the energy analyser; a spherical mirror analyser (SMA) to transmit an energy filtered subset of the photoelectrons from the analyser entrance to reform an energy filtered photoelectron image on the detector;[2] a pulse counting delay line detector (DLD) to record the two dimensional photoelectron image projected onto the detector by the SMA.[3]

The SMA, Figure 1, first developed by Sar-El[4], transmits a narrow energy range of photoelectrons through the analyser and projects them onto a two dimensional detector.

Figure 2 shows electron trajectories through the SMA of a parallel beam of electrons with energy E_0 + 4%. The point at which the energy dispersion is at a maximum is coincident with a second minimum in the spatial distribution of the electrons. By inserting a baffle into the SMA at this position, electrons with energy equal to that of the pass energy are transmitted, whilst those with energies higher or lower than the pass energy are removed. Crucially this has no effect on the spatial resolution of the image formed at the exit plane of the analyser.[2]

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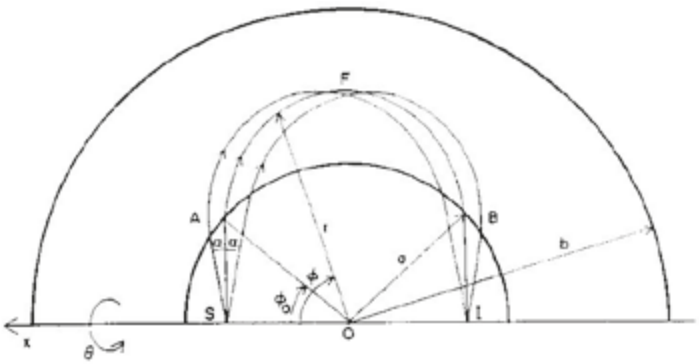

Figure 1: Spherical Mirror Analyser.

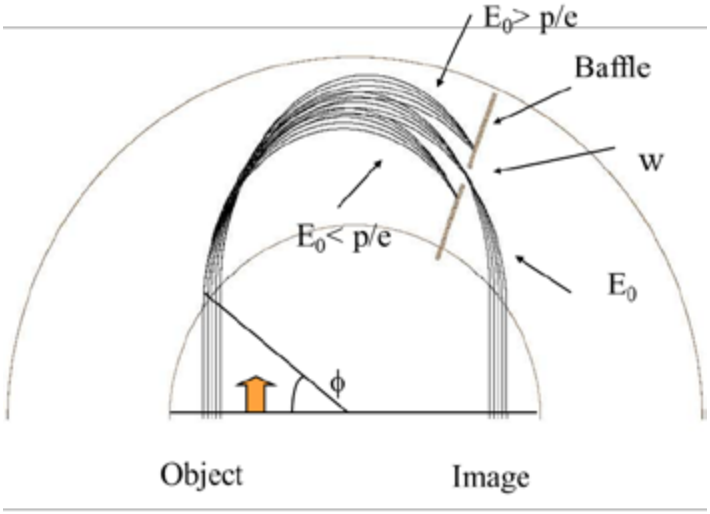

Figure 2: Electron trajectories through the SMA.

The Delay Line Detector (DLD) positioned at the image plane of the analyser detects energy and spatially resolved photoelectrons. The DLD is a genuine electron pulse counting detector which is used to acquire X-Y coordinates for each electron event. Integration of the signal over several seconds allows the generation of a truly quantitative elemental or chemical state image of the surface over a 256 x 256 pixel array. In the highest magnification mode the spatial resolution of the AXIS Supra at the surface is 1 micron.

In imaging mode the AXIS Supra has 3 predetermined fields of view (fov): fov1 800 x 800 µm; fov2 400 x 400 µm; and fov3 200 x 200 µm. The approximate lateral resolution in each fov is 15 µm, 7 µm and 1 µm. Images may also be recorded from areas larger than 800 x 800 µm by combining automated stage movements with image acquisition. This mode of operation is termed image stitching. Using this combined approach large areas of the sample surface (currently up to 8 x 8 mm) may be imaged. Alternatively, smaller areas of the sample surface may be imaged at high lateral resolution, for example, an 800 x 800 µm area can be investigated at a lateral resolution of up to 1 µm by the automatic stitching together of 16 fov3 images.

Experimental

To illustrate the performance of the XPS imaging system a Silicon Oxide (SiO_2) powder sample, supported on a Silicon substrate, was analysed. A large area (700 x 300 microns) survey spectrum was recorded from the sample surface to identify the surface elements present, Figure 3. This confirmed that one of the major surface constituents was indeed silicon. A high resolution spectrum of the Si 2p region, Figure 3, identified different silicon chemistries on the sample surface: SiO_2 at 103.8 eV; and elemental Si at 99.0 eV.

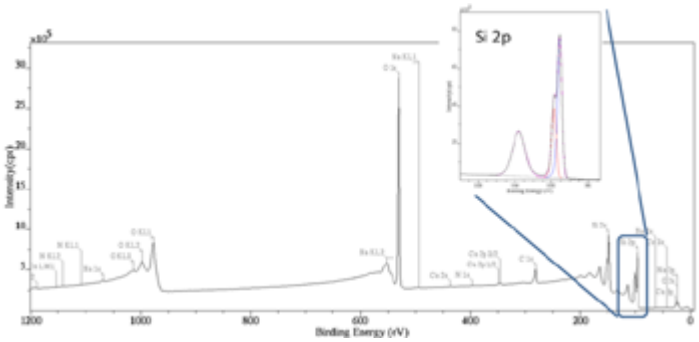

Figure 3: Survey and Si 2p narrow region spectrum of the sample surface.

Si 2p XPS images were recorded over a large area (2 x 2 mm) to investigate the lateral distribution of surface elemental Si, Figure 4. In parallel imaging mode individual parallel photoelectron images with a field of view of 400 x 400 µm were recorded at a binding energy of 99.0 eV. Photoelectrons at a predetermined binding energy are transmitted to the detector and all of the 256 x 256 pixels collect data in parallel. Stitched images are generated by automatically stitching together, via stage movements, the individual 400 x 400 µm images to produce images over a large area. A major advantage of image stitching is that although images from a large surface area are recorded, the lateral resolution is maintained independently of the eventual image size.

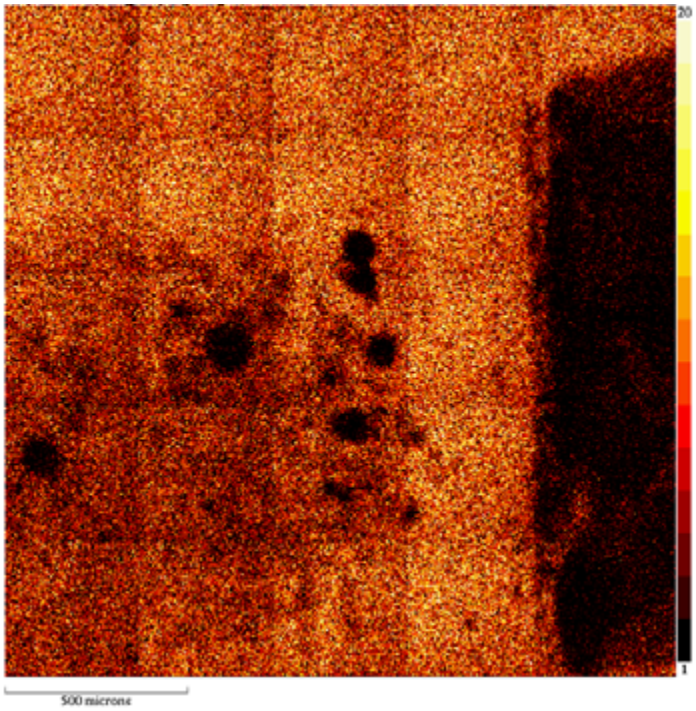

Figure 4: Large area, 5 x 5 (2 x 2 mm) field of view 2 automatically stitched parallel photoelectron image of the elemental Si peak at 99.0 eV.

A region was selected for further investigation from the large area stitched image, Figure 5. Here two smaller stitched images (1.2 x 1.2 mm) of elemental Si and Si oxide were recorded to highlight the different Si chemistries detected in the surface of the sample.

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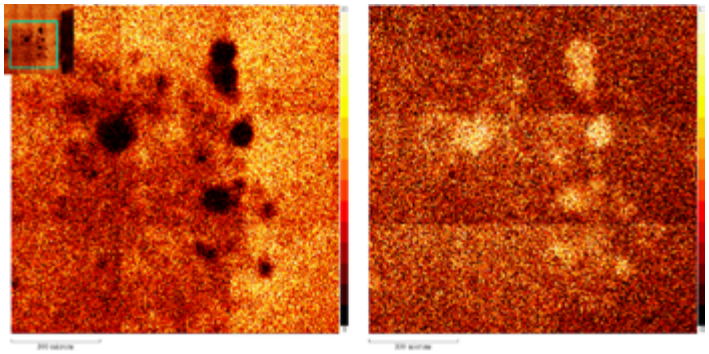

Figure 5: 3 x 3 (1.2 x 1.2 mm) field of view 2 stitched parallel photoelectron images of the Si elemental (99.0 eV, left) and Si oxide (103.5 eV, right) peaks.

Single fov2 images of the surface O, C, SiO_2 and elemental Si distributions were also recorded to reveal the surface chemistry from a selected area in greater detail, figure 6. The two Si images (oxide and elemental) are overlaid to demonstrate the chemical resolution achieved in the imaging mode, figure 7.

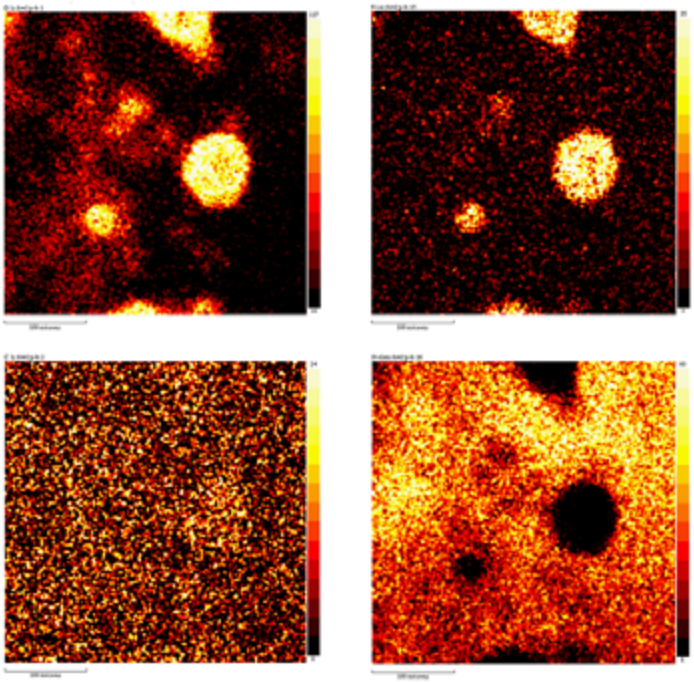

Figure 6: FOV2 parallel photoelectron images of the surface O (top left), C (bottom left), SiO_2 (top right) and elemental Si (bottom right) distribution.

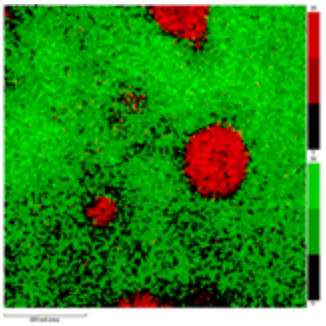

Figure 7: Overlay of elemental Si (green) and SiO_2 (red) fov2 images.

The parallel imaging system may be used to collect a series of images at small energy steps across a photoelectron peak. Using this data, spectra may be reconstructed from each pixel and the images quantified. This method is discussed in detail in applications note MO328. In the present example images were recorded in fov 2 from 110 eV to 85 eV binding energy in 0.5 eV steps. The pass energy used was 80 eV and each image was collected for 2 minutes resulting in a total acquisition time of 50 minutes, figure 8. The data produced was analysed using principle component analysis (PCA) and this allows the noise to be separated from real chemical information.[5]

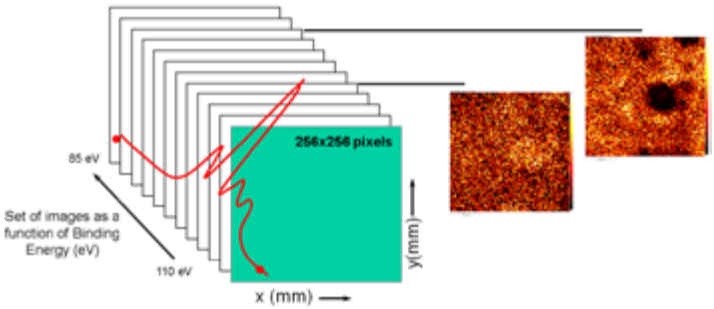

Figure 8: A series of fov2 images were recorded in pass energy 80 eV from 110 to 85 eV.

Results

The image data recorded across the Si 2p energy window were loaded into CASAXPS. The images are automatically combined and a spectrum generated at every one of the 65,536 pixels. An SVD sort was performed followed by PCA to remove the noise from the spectra at every pixel. peak and a Si elemental peak, Figure 9. This peak fit was then automatically propagated thought out the set of 65,536 spectra.

One of the 65,536 pixels was then curve fitted with a background and two chemical components, a Si Oxide peak and a Si elemental peak, Figure 9. This peak fit was then automatically propagated thought out the set of 65,536 spectra.

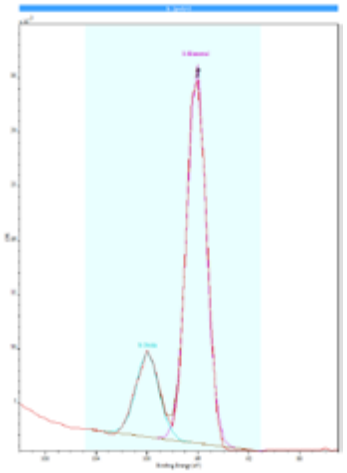

Figure 9: A spectrum from a single pixel after removal of noise by SVD sort / PCA. The spectrum is curve fitted with a Si Oxide and a Si Elemental curve.

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The peak fits generated at every pixel may then be quantified in the same way as standard spectra allowing an Si Oxide and Si Elemental images to be reconstructed from the measured peak areas, Figure 10. The images are now quantified, the scale on the right hand side of each image is measured in relative Si Oxide / Si Elemental percentage and every pixel has a percentage Si Oxide / Si Elemental composition, see overlay of the quantified Si Oxide and Si Elemental images, Figure 11.

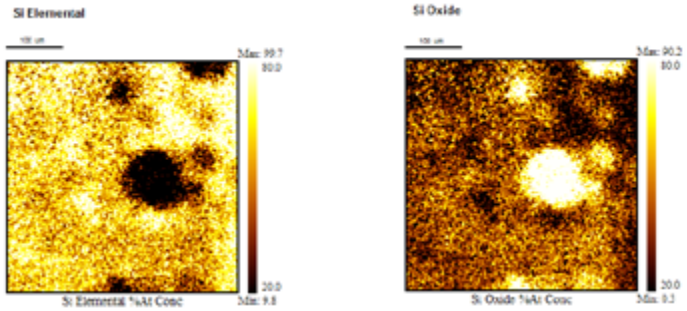

Figure 10: Si Elemental (left) and Si Oxide (right) reconstructed images.

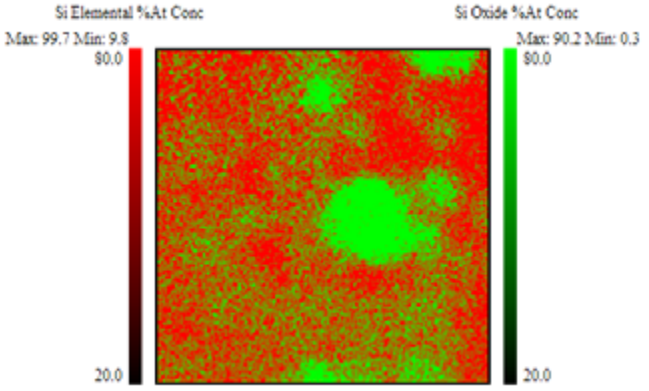

Figure 11: Overlay of Si elemental (red) and Si oxide (green) quantified images.

The data now contains the information necessary to calculate the Si Oxide / Si Elemental ratio at any pixel or area on the image. In this example 4 areas approximately 5 x 5 microns in size were selected from the sample surface and the relative composition at the selected points was automatically calculated, Figure 12 and Table 1. The number and size of the selected regions is unlimited. As all the data is stored quantification results may be acquired from different regions off line at any time in the future.

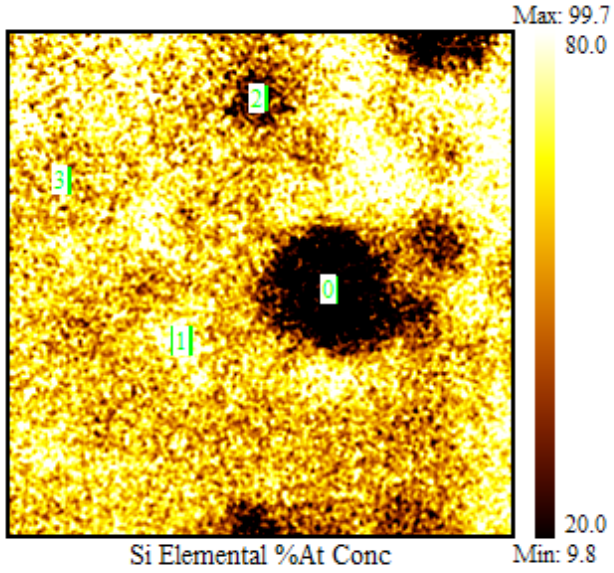

Figure 12: 5 x 5 micron regions for quantification selected from the image.

Element	% Si Elemental	% Si Oxide
0 (high SiO_2)	15.7	84.3
1 (high Si elemental)	79.6	20.4
2 (high SiO_2)	16.6	83.4
3 (mixed region)	54.5	45.5

Table 1: Relative Si / Si Oxide composition at the 5 micron square areas selected from the image displayed in Figure 12.

Conclusion

XPS imaging and in particular SVD/PCA image quantification has been shown to be a useful technique in determining the surface chemistry of a Si Oxide / Si Elemental sample. The spectra from images method followed by noise reduction via principle component analysis is a powerful analytical technique which can provide quantitative surface chemical characterisation at the micron scale.

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Acknowledgments

SVD sort and multivariate data analysis was performed using CasaXPS processing software.

Related documents available online:

Getting more from XPS imaging: multivariate analysis for spectromicroscopy

Applications note MO328

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