Analysis of Image Data from the Thermo Scientific K-Alpha

XPS imaging is performed in a variety of ways, one on which involves directing a small spot x-ray source at the sample and measuring a spectrum from the irradiated area. The focused spot of x-rays permits spectra to be collected from a set of well defined positions on the sample surface and these analysis positions can be so defined to provide spectra at the set of pixels forming an image of the sample surface. The K-Alpha adopts the x-ray probe approach coupled with stage movements to change the x-ray probe position. The advantage of moving the stage rather than changing the x-ray spot position is that the acquisition conditions are maintained as a constant; an important consideration when quantification is performed. Spectra are acquired at each pixel using either a *snap shot* mode, where the detector measures in parallel a set of energy channels determined by the pass energy of the analyser or *scanned mode* typical of most XPS spectral measurements. The snap shot mode offers a reduction in acquisition time since the spectral data are acquired in parallel. The spectra in Figure 1 are acquired from a K-Alpha using snap shot mode all using pass energy 148, hence the common energy width of about 20 eV for each spectrum. The parallel acquisition of the spectra in snap shot mode at PE 148 utilises 128 energy channels with an energy step of about 0.156 eV, resulting in very respectable spectra for an investigation of a sample.
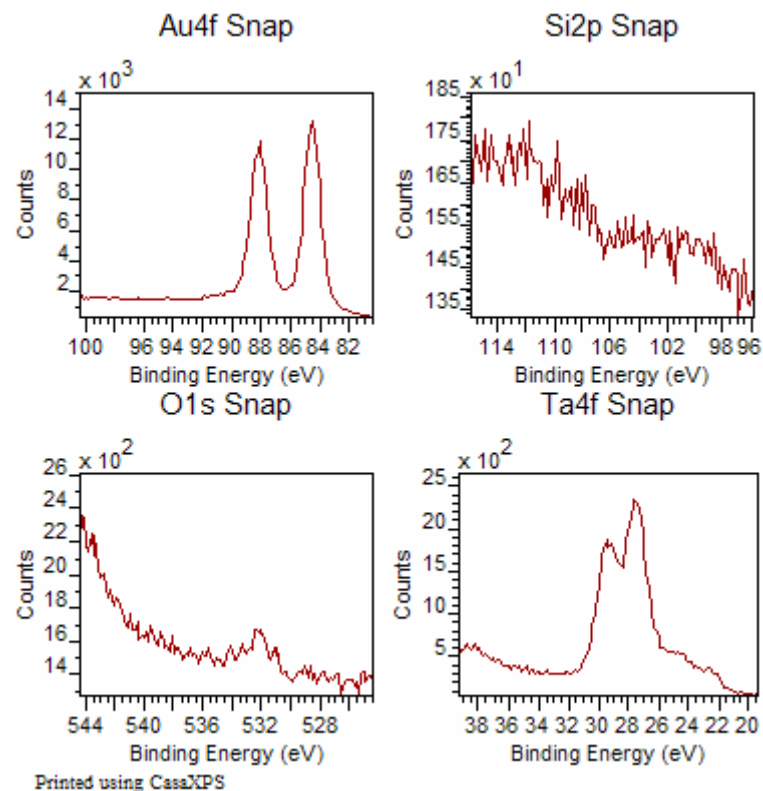
Converting the Image Data Set

Figure 1: Spectra acquired in parallel using Snap Shot Mode.

The image data set from which the spectra in Figure 1 were taken consists of a 21 x 21 array of spectra. These spectra are exported from Avantage in ASCII files where each element appears as a separate file with the extension .avg. To convert

these data into a suitable format for image processing in CasaXPS, the .avg files within a directory must be processed using a file extension of .ivg entered on the Convert to VAMAS File dialog window in CasaXPS. Figure 2 depicts a directory containing four .avg files. To create a VAMAS file formatted for image processing, the filename for the new VAMAS file must be entered as a base-name followed by the file extension .ivg. The name entered in Figure 2 is destination_filename.ivg, where the key string .ivg causes the conversion of the .avg files in the directory to the spectromicroscopy formatted VAMAS file shown in Figure 3.

The significant structure for image processing of the VAMAS file in Figure 3 is that each VAMAS block contains a row of spectra rather than the more usual one spectrum per VAMAS block. The set of spectra within each VAMAS block are stored as corresponding variables and enables the data to be presented in the browser using the compact format shown in Figure 3. If the same .avg ASCII files were converted using the file extension .avg for the destination file name rather than .ivg, the VAMAS file would be created where 1764 = 21x21x4 VAMAS blocks would be created each containing a single spectrum. This alternative representation of the data with one spectrum per VAMAS block would not be suitable for image processing in CasaXPS.
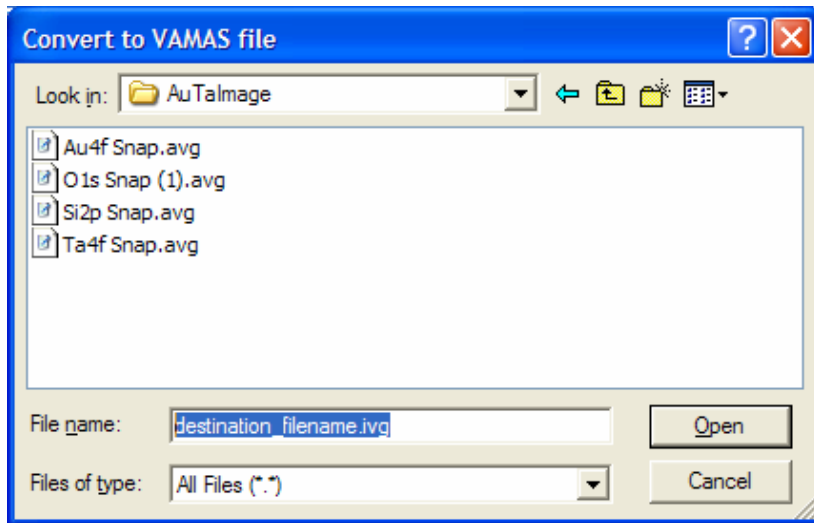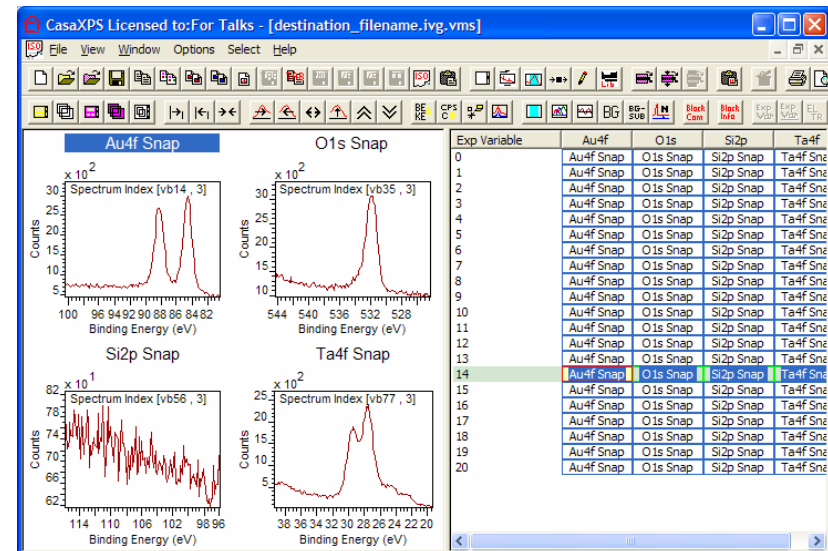

Figure 2: Convert to VAMAS File dialog window. Note that the data files are still assigned the .avg file extension and that it is only the name in the File name text-field that is given the new .ivg file extension.

Figure 3: Image Data Set from K-Alpha

The image data set shown in Figure 3 differs from the typical spectral data set created from the Avantage avg files in that the spectra are already transmission corrected. Treating the spectra in the avg files as spectra-at-pixels alters the way the transmission function is included in the data. For data treated as spectra, the second corresponding variable in each VAMAS block is the transmission function for the spectrum in the first corresponding variable. Since image data sets are typically large, the spectra are divided by the normalised transmission function, thus reducing the overhead of recording the transmission function separately. Spectra converted using the .ivg conversion filter will not cause the Automatic tick-box on the Regions property page to be ticked; this indicates the VAMAS block does not explicitly contain the transmission information.

Processing Images from the Image Data Set

The data shown in Figure 3 represent four images of size 21x21 where each pixel in each image contains a spectrum. To obtain images from these spectra requires the use of standard XPS quantification techniques for spectra. That is, for each VAMAS block, one or more quantification regions must be defined and, possibly, synthetic components used to identify chemical state information within these spectra. The simplest route to creating a meaningful XPS image is to define quantification regions and apply the **Convert Regions to Images** button on the Image Processing property page.

Images from Regions

The advantage of using spectra-at-pixels when generating images lies in the use of quantification regions to define a background and also the RSF for the integrated area between the peak and the background. It should be pointed out that these data are identical to spectra used in spectroscopic mode, therefore the same transmission and RSF apply to the image data as those used for spectroscopic data. Not all XPS imaging instruments can make these statements.
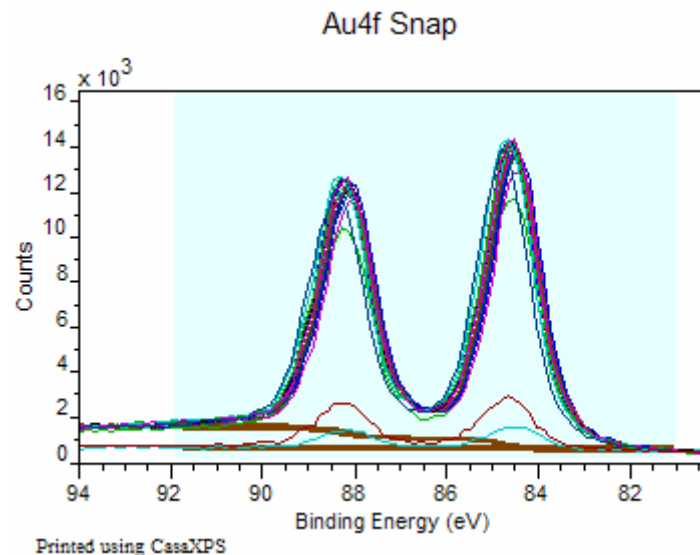

Figure 4: Quantification regions define on each Au 4f VAMAS block in Figure 3.

Figure 4 illustrates the required state of the Au 4f spectra in Figure 3 for creating an image based on quantification regions, namely:

1. A quantification region is defined on each VAMAS block in the column of Au 4f spectra shown in Figure 3.
2. The correct RSF is assigned to the quantification region for the Au 4f transition and the appropriate background specified.
3. The set of VAMAS blocks containing the Au 4f spectra are overlaid in the active tile. Only those VAMAS blocks in the active tile are used to create the image.
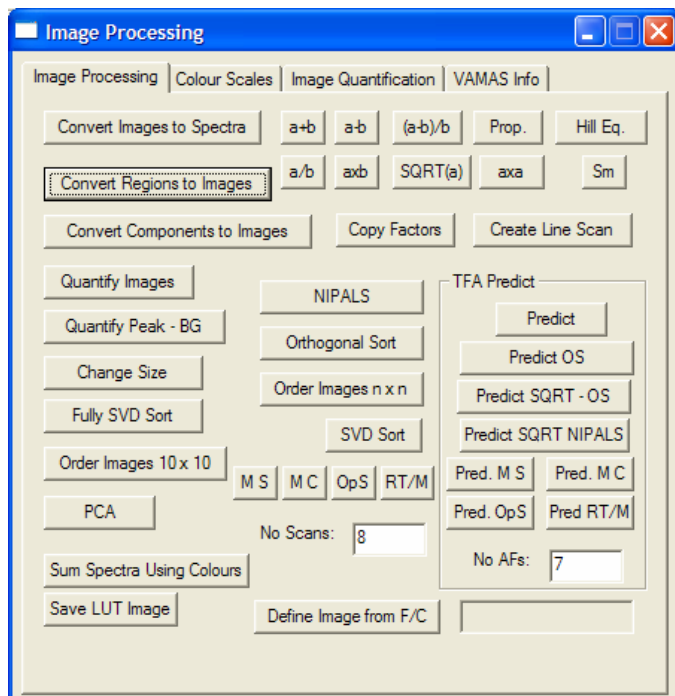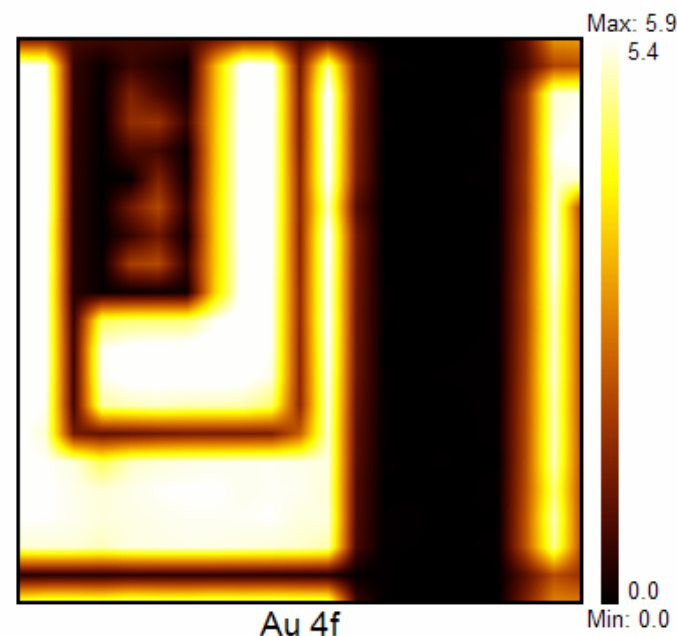
Once the VAMAS blocks are prepared as described above, pressing the **Convert Regions to Images** button on the Image Processing property page, shown in Figure 5, causes a new Experiment Frame to appear containing the Au 4f image of peak area adjusted by the RSF from the region.

Figure 5: Image Processing property page.

Figure 6: Au 4f image calculated from the data in Figure 4 scaled up using the Change Size button on the Image Processing property page in Figure 5.

The Au 4f image displayed in Figure 6 is scaled up from the original 21x21 pixel image created by pressing the **Convert Regions to Images** button.

The steps performed for the Au 4f set of spectra can be repeated for each of the O 1s, Si 2p and Ta 4f columns in turn; until four new Experiment Frames are generated each containing the RSF scaled element maps corresponding to the four columns in the data shown in Figure 3. The important step for understanding XPS images is the quantification step. To quantify these images, each of the individual element images must be copied (see below) into the same Experiment Frame. Once in the same Experiment Frame the images are overlaid in the active tile and the **Quantify Image** button pressed. Again, on pressing the **Quantify Images** button a new Experiment Frame is created containing atomic concentration images expressed as a percentage. The images in Figure 7 are atomic concentration images based on the raw spectra using regions to measure the intensities.

To copy the VAMAS block, select the VAMAS blocks for each of the images, holding down the Control Key to add to the selection, and press the ▣ toolbar button to transfer the selected blocks to the Experiment Frame with the current focus.

The raw images generated from the spectra are 21x21 pixels and too small to be viewed comfortably on the screen. The **Change Size** button on the image processing dialog window allows the creation of a new Experiment Frame from those

images overlaid in the active tile. The images in Figure 7 were created using the **Increase Image** radio button on the resulting dialog window invoked by pressing the **Change Size** button (Figure 5).
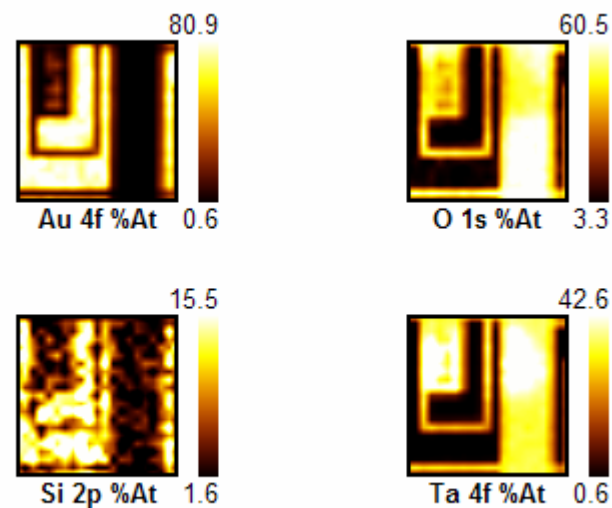
Figure 7: Atomic Concentration images created from regions.

The Ta 4f spectra and also the image in Figure 7 show structure which can be investigated by defining three regions on the Ta 4f spectra before conversion to image data. The three regions are defined such that one region spans the same energy interval used to create the Ta 4f image in Figure 7 specified with a

Shirley background. The two further regions use the background type *skip*, which simply defines region limits but leaves any previously calculated background unaltered. That is, the data are integrated using the Shirley background of the first region, while the end limits for the integration are defined by the regions labeled Ta 4f L and Ta 4f R in Figure 8. The image in Figure 8 shows how changes in the energy-position of the Ta 4f peak can be correlated with sample position.
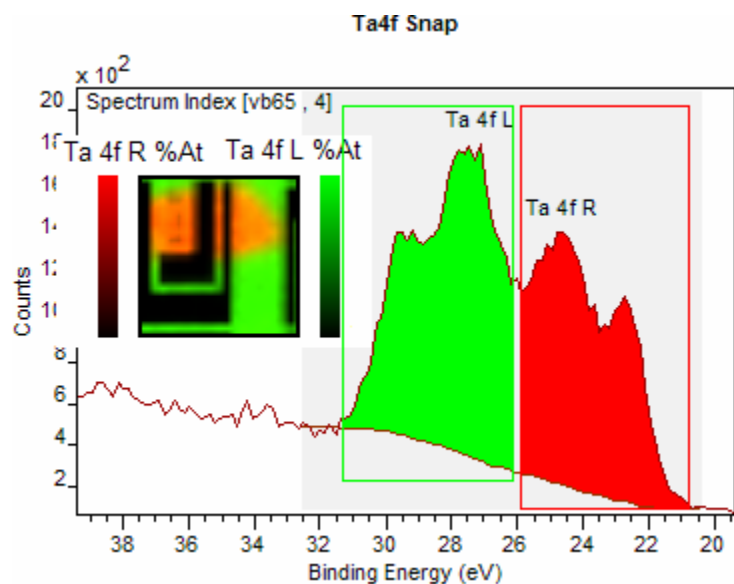

Figure 8: Ta 4f chemical state images based on regions.

The use of quantification regions is a quick means of extracting chemical state images from a spectromicroscopy data set, however not all data are open to such an analysis. For more correlated peak structures, peak models become more necessary when allocating intensities to images.

Images from Components

The spectrum in Figure 8 is only roughly partitioned using the quantification regions as described above. The two obvious peaks towards the middle of the data envelope are correlated and therefore a peak model should help to identify chemical state information in the data with respect to sample position.
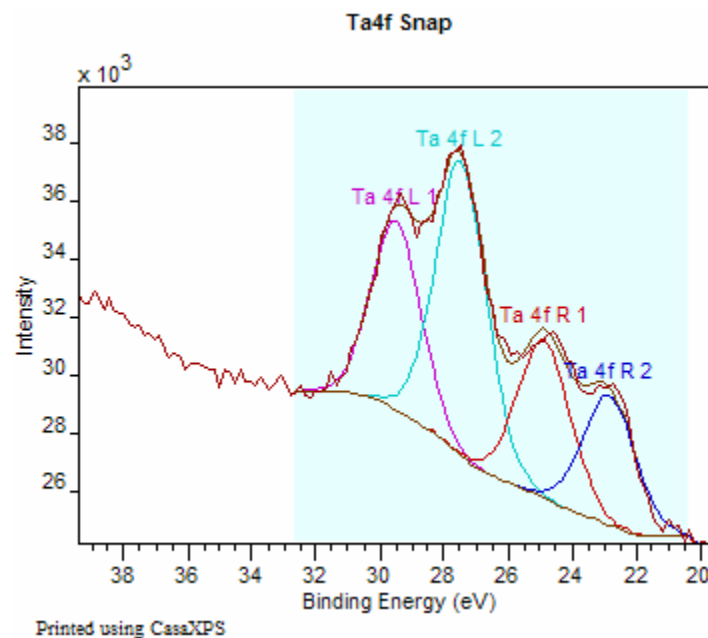
Figure 9: Simple peak model used to create images from the spectra-at-pixels.

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The spectrum in Figure 9 offers a simple peak model for the features apparent in the Ta 4f image data set. Each of the four synthetic peaks fitted to each of the spectra-at-pixels provides a means of generating four images from the Ta 4f spectra. Figure 10 displays a set of four 21x21 images corresponding to the peak model in Figure 9. Note how the contrast between the two least correlated peaks Ta 4f L 1 and Ta 4f R2 is the strongest, possibly suggesting the constraints were too loose for the more correlated central peaks Ta 4f L 2 and Ta 4f R1.
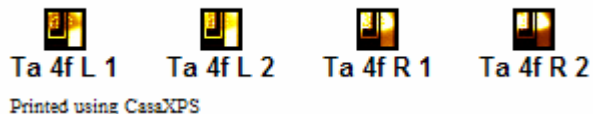

Figure 10: Ta 4f images generated using the peak model in Figure 9.

The analysis performed to produce the images in Figure 10 requires the column of Ta 4f spectra to be copied to a new Experiment Frame. However, apart from extracting the Ta 4f spectra, the procedure for analyzing the chemical state information from spectromicroscopy data sets using false colour images to guide the fitting of the peak models is identical to that described elsewhere in the CasaXPS manual.

Noise Reduction in the Images

The images in Figure 7 were computed using the raw spectra and quantification regions. The most note-worthy image out of these four images is the Si 2p image; principally because the Si

2p image in Figure 7 shows evidence of a poor signal to noise ratio. Data sets such as these are open to noise reduction based of Principal Component Analysis (PCA), where the raw spectra are replaced by a set of spectra constructed from a limited number of PCA abstract factors. For the case of the Si 2p spectra, applying PCA using Optimum Scaling shows that these Si 2p spectra can be adequately described using three abstract factors. After applying the **Pred. OptS** button shown in Figure 5 in the **TFA Predict** section of the Image Processing property page, the Si 2p spectra are significantly enhanced.

Figure 11: Si 2p image is enhanced using a PCA reconstruction technique based on Optimum Scaling.

The images in Figure 11 are calculated from the raw spectra for the Au 4f, O 1s and Ta 4f transitions; however the Si 2p image is computed using three abstract factors to reconstruct the spectra before determining the peak area for the Si 2p transition via quantification regions. Comparing the images in Figure 7 to those in Figure 11 reveals a much cleaner image for the Si 2p transition.

The key observation about performing noise reduction based on PCA is that the acquisition time for the entire data set could be reduced or alternatively, the number of pixels could have been increased by reducing the dwell-time per pixel to maintain the same overall acquisition time. PCA provides the means of recovering the quality in the final images. These PCA based techniques are discussed at length elsewhere in the CasaXPS manual.

A further observation from Figure 11 is that the Si 2p image appears to be very strongly correlated with the gold image; a result not expected for this particular sample. On further inspection of the processed data, it is clear the source of the error lies in the selection of the quantification region limits for the Si 2p transition. Figure 12 shows the region used to estimate the area of the Si 2p transition, where it is clear that the structure initially assigned to the Si 2p data is in fact a loss structure associated with the Au 4f peak. Both the raw spectrum and the same spectrum after processing using the Optimum Scaling technique are displayed in Figure 12. The shape of the loss structure is obvious in the processed spectrum, but not so clear in the raw data.
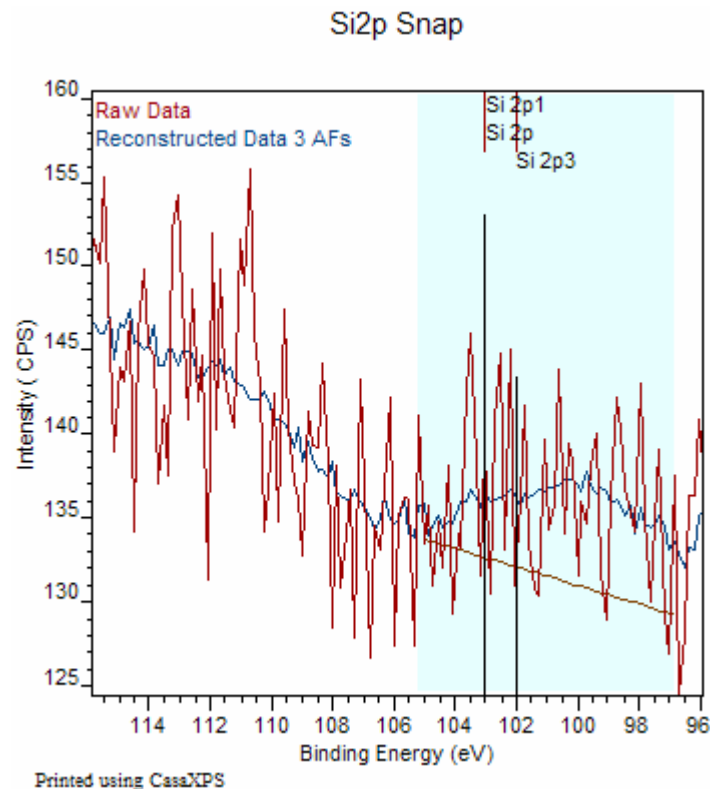

Figure 12: An example of a spectrum from the Si 2p region.

On closer analysis, the location of a possible Si 2p transition requires a refinement to the quantification limits. The same data in Figure 12 is shown in Figure 13, where a new quantification region attempts to isolate the Si 2p signal from the loss structure associated with the Au 4f peak.
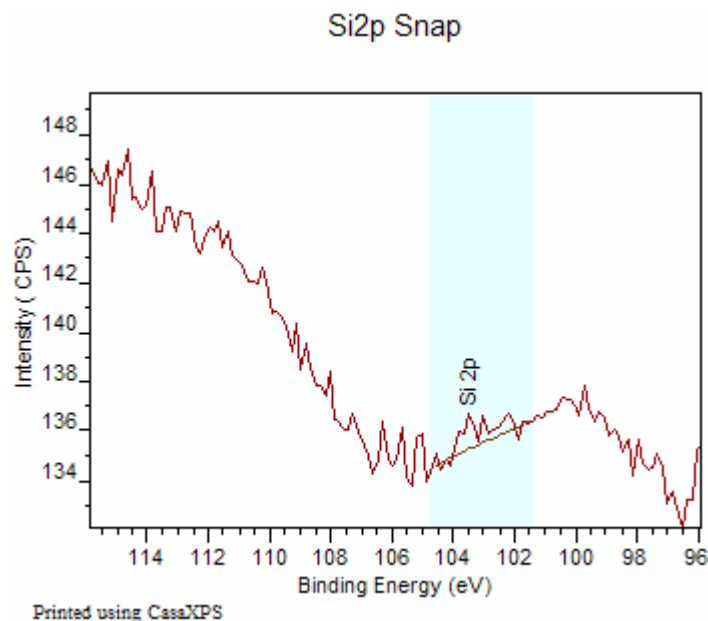
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Figure 13: A refinement of the Si 2p quantification region.

The images in Figure 14 are equivalent to those in Figure 11; the difference lies in the positioning of the quantification region in Figure 13 compared to the region shown in Figure 12. The upper portion of the imaged area was ion gun etched prior to the acquisition of the image data set. The atomic concentration of silicon is clearly small, but the image in Figure 14 for the Si 2p transition is more in line with the history of the sample.

This example highlights the power of cross referencing the spectroscopic data with image data. The flaw in the original analysis was picked up by noting the correlation between the Au and Si images in Figure 11. It would have been easy to miss this erroneous quantification if spectra alone were used to analyse the sample.
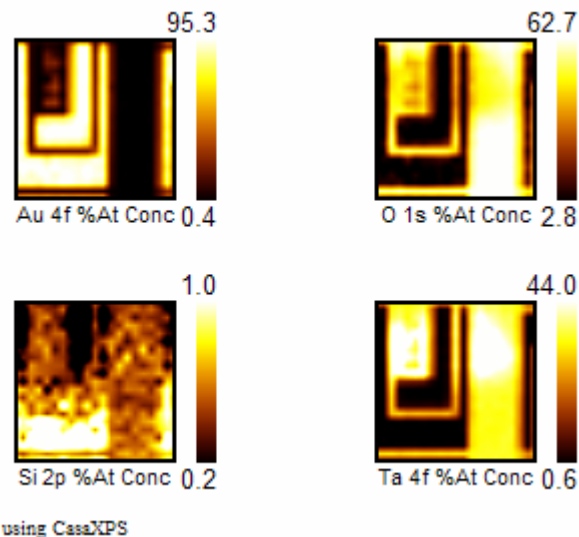

Figure 14: Atomic Concentration images after refining the Si 2p quantification region.