

K-Alpha: Chemical State Mapping of Polymers



Key Words

Surface analysis, chemical state mapping, polymer analysis, quantitative maps

Abstract

Thermo Scientific™ X-ray Photoelectron Spectrometers are equipped with a microfocusing monochromator and a multi-channel detector. This combination makes the instrument ideal for chemical state mapping. The spatial resolution of the maps is determined by the user-selected, X-ray spot size. The multi-channel detector allows snapshot spectra to be collected at each pixel of the map; this is much faster than scanned acquisition. The charge compensation system on these spectrometers allow chemical state maps to be produced very easily from insulating materials.

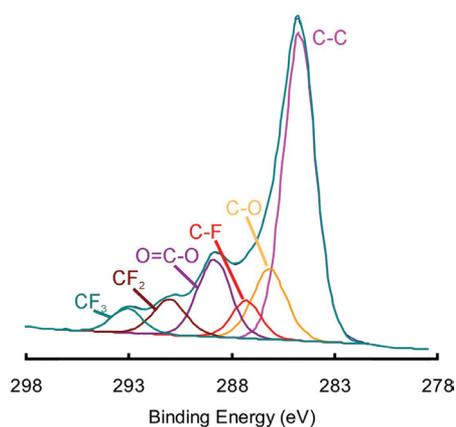


Figure 2: Peak fitting of the C 1s spectrum obtained by summing the spectra in each of the pixels of the map.

Sample preparation

A copper grid was attached to a substrate consisting of silicon coated with an acrylic acid plasma polymer. The substrate was then placed in a plasma containing a fluorocarbon monomer. This caused the fluorocarbon to polymerize on the areas of the substrate exposed to the plasma. After exposure to the plasma, the grid was removed from the substrate leaving a patterned, polymeric fluorocarbon. Figure 1 illustrates the method of preparation and the area of the sample that was analyzed in the Thermo Scientific™ K-Alpha™ XPS system..

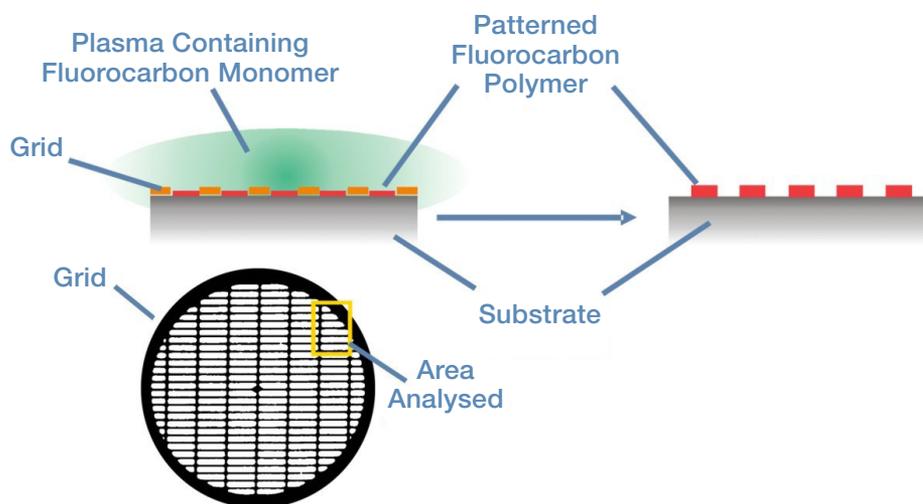


Figure 1: An illustration of the sample preparation, the grid used in the preparation and the area of the sample analyzed in K-Alpha.

Analysis conditions

The monochromated X-ray spot size was set to 30 μm . Snapshot XPS spectra of C 1s and F 1s were collected into 64 channels for each element. These spectra were acquired at each pixel in an array of 67 x 94 pixels with a 10 μm step size by scanning the sample stage.

Peak fitting spectrum

Figure 2 shows the C 1s spectrum that was obtained by summing the C 1s signal from the whole of the image. This spectrum clearly shows the existence of both ester and fluorocarbon species.

Image construction

One method by which a map can be produced is simply to display the image produced at a selected binding energy. Figure 3, shows the images formed at 10 of the 64 binding energies collected for this measurement.

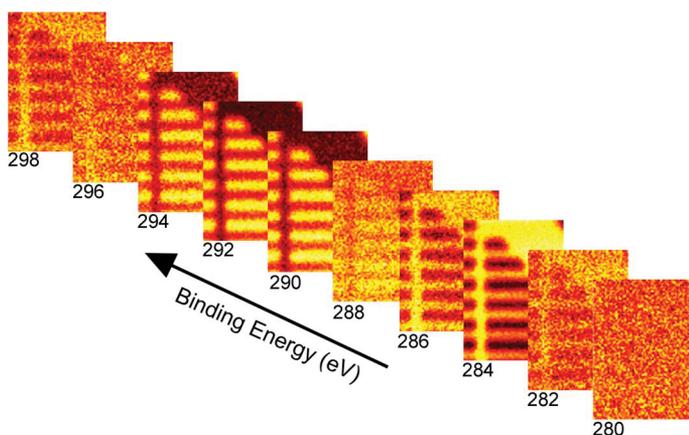


Figure 3: Maps constructed at 10 of the 64 binding energies collected.

Figure 4a shows an image constructed from a binding energy of 284.7 eV (hydrocarbon) Figure 4b shows an image of the peak at a binding energy of 291 eV (a fluorocarbon peak) and Figure 4c shows an overlay of these two images.

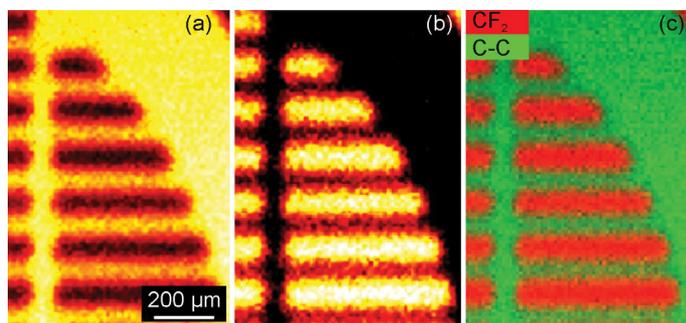


Figure 4: (a) Map obtained from the signal at a binding energy of 284.7 eV (the hydrocarbon peak) (b) Map obtained from the signal at a binding energy of 291 eV (a fluorocarbon peak) and (c) an overlay of the maps shown in (a) and (b).

Having performed the peak fit, as shown in Figure 2, all of the individual spectra that constitute the map can be fitted with the same set of peaks. This enables images to be produced from any of the fitted peaks showing fitted peak areas or atomic concentration. As an example, Figure 5 shows the atomic concentration images, in this case non-linear least squares fitting was applied to the data set to produce atomic concentration maps for the two components.

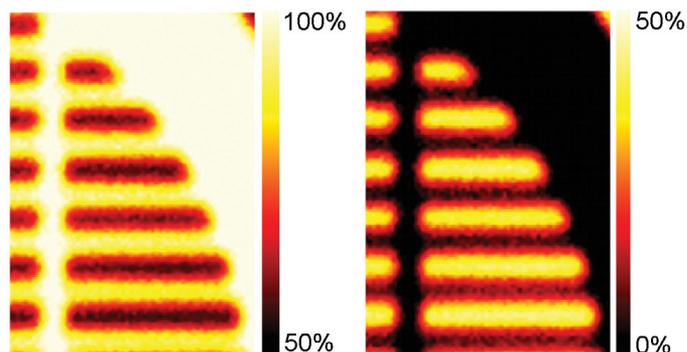


Figure 5: (a) Atomic concentration map from the hydrocarbon peak following peak fitting at every pixel. (b) Atomic concentration map from the fluorocarbon peak.

Reconstructed spectra

Each pixel of the image contains a spectrum and so it is possible to sum the spectra from defined areas on the image to produce a small area spectrum. Figure 6 shows two spectra constructed from the indicated parts of the image. From this it is clear that the substrate peaks can be seen in the fluorocarbon region but no fluorocarbon is visible in the substrate region.

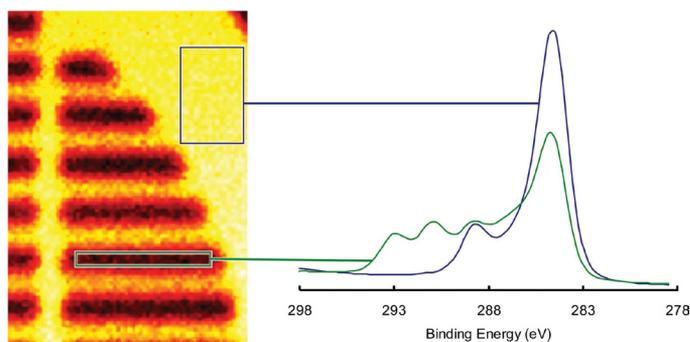


Figure 6: C 1s spectra reconstructed from the areas indicated on the map.

Thickness map

In the areas of the sample that are covered by the fluorocarbon material it is possible to detect the peaks from the substrate. This means that the fluorocarbon layer is only a few nanometers thick. It is therefore possible to construct a thickness map of the sample using the 'Overlayer Thickness Calculator' which is an integral part of the Advantage data system. The only assumption made in the calculation was that the density of each polymer is equal to its bulk density. Figure 7 shows the results of the measurement.

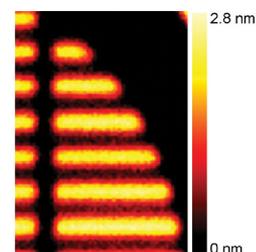


Figure 7: Thickness map of the fluorocarbon layer.

Advantages of stage scanning

To produce a map using the K-Alpha spectrometer, the sample stage is scanned. This method of map acquisition has a number of advantages over the other methods available:

- Spatial resolution is determined only by the X-ray spot size which is constant throughout the acquisition. There is no degradation of the image quality at the edges.
- Having a spectrum at every pixel means that quantitative maps of chemical states and thickness maps can be constructed easily.
- The spatial resolution is independent of the settings of the transfer lens and so the spectrometer is always operated at its maximum transmission.
- The point on the sample being mapped is always in the optimum analysis position and so there can be no changes in the sensitivity over the field of view.
- X-ray energy and intensity are independent of position on the sample.
- Very large field of view possible (up to 60 x 60 mm for K-Alpha).

Conclusions

The K-Alpha XPS system is capable of producing high-quality images. The parallel acquisition of spectral information (snapshot spectra) means that acquisition is rapid and the large number of channels collected in each spectrum means that quantitative, chemical state mapping can be performed reliably.

The advanced features present in the Avantage data system provide clear chemical state information and show how the chemical states are distributed in two dimensions. When there is a thin overlayer present, as in this case, it is possible to measure and map the thickness of that overlayer non-destructively.

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