Fundamental Aspects of XPS and the Development of XPS Imaging

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Introduction

Our common introduction to the laws of chemistry is rooted in the bulk, steady-state phenomena of solution and gas chemistries. This eases the introduction of the mathematical structure required to explain our macroscopic measurements. We come to understand that chemical change is driven by local gradients in the bulk and that gradients are steepest where properties change most rapidly. This is exactly what happens at material interfaces, where the mathematics get complicated, chasing infinities, and approximations often have to suffice. This confirms what we intuitively knew from everyday observation, that chemical dynamics take place at the interfaces between materials. The interfaces are where the action is.

Many important processes inherently depend on interface properties. From adhesion between materials to corrosion, lubrication, semiconductor and thin film growth, heterogeneous catalysis, and even many biological interactions, the chemistries at the very surface of a material determine the outcome for a wide range of industrial processes.

Discontinuity at a material interface breaks the equilibrium symmetry of the bulk interior, with the interface region at this boundary often having a markedly different chemical nature from the bulk, as unsatisfied bonds rearrange to minimize energy. We often refer to these as surface properties because we are usually investigating the material interface with the constancy of air or partial vacuum on the opposite side of the interface. The scale over which the interface chemistry differs from the bulk can vary, but many effects and reconstructions happen in just a single atomic layer.

Traditional analytical chemistry tools are insensitive to such surface differences. Even SEM-EDS, which traditionally is considered to have some surface sensitivity, usually gives information from about a micrometer into a material or about one thousand times deeper than the extent of the surface chemistry differences. Optical probes also penetrate on the order of the wavelength used, still much deeper than surface effects extend. What the researcher requires is information with great chemical and surface specificity.

X-ray Photoelectron Spectroscopy

In the 1950s Kai Seigbahn discovered that electrons, excited from a material using monochromatic X rays, carried elemental core binding information. When measuring the energies of electrons emitted from the surface, he found that sharp photoelectron emission lines exhibited shifts related to the local chemical environment [1]. He went on to win a Nobel Prize for this discovery, fundamentally based on the photoelectric effect, which was no mean feat, considering Albert Einstein had already been awarded a Nobel Prize for the photoelectric effect.

The technique that Kai Siegban developed is equivalently referred to as either X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA). When atoms are illuminated with X rays, electrons are excited from all populated orbitals where electrons are bound at energies lower than the photon energy. The electrons leave the surface with a kinetic energy (KE) equal to the X-ray photon energy ($h\nu$) less the energy that bound the electron (BE) and work function of the material (wf).

$$KE = h\nu - BE - wf$$

If a narrow-energy X-ray source, such as the characteristic X-ray emission from a metal (often Mg Kα or Al Kα in laboratory sources) is used to illuminate the sample, the emitted electrons can be dispersed by energy into a spectrum showing the number of electrons at each energy. While we measure the kinetic energy of the electrons, the energy distribution spectrum of the electrons is usually shown with binding energy BE as the abscissa. Only electrons that have not lost energy in exiting the specimen contribute to the discrete nature of the spectrum. Electrons that were scattered inelastically contribute to the background at lower kinetic energy (Figure 1) [2] .

When dense materials such as solids or liquids are illuminated in this way, the distance an electron travels in the material before it inelastically scatters and loses energy is quite short, falling off exponentially into the bulk. This exponential decay of the signal strength with depth gives XPS its surface sensitivity, the outer atomic layers contributing the most to the signal, with only a small contribution coming from deeper than 5–10 nm. The minimum detectable amount of an element is generally considered to be a 0.1 atomic %, depending on the element of interest. Quantitative analysis is straightforward because the method exhibits few matrix effects.

Chemical Shift Information

While XPS readily provides useful elemental information from the first several atomic layers of a surface, its true power lies in the chemical information it reveals about the constituent elements. Figure 2 shows the high-resolution carbon 1s and oxygen 1s photoelectron spectra from the polymer polyetheyene terepthalate (PET), along with the molecular structure showing how the chemical bonding of each element relates to the peaks in the spectra. The chemical shift observed in these deep core-level electrons is due to charge screening from the atom's local bonding environment, which modifies the potential well that the electron must overcome.

Angle-Resolved XPS

Figure 3 illustrates that the chemical information is surface-sensitive. The native, room-temperature oxide on a silicon wafer is only about 0.8-nm thick, but the signal from

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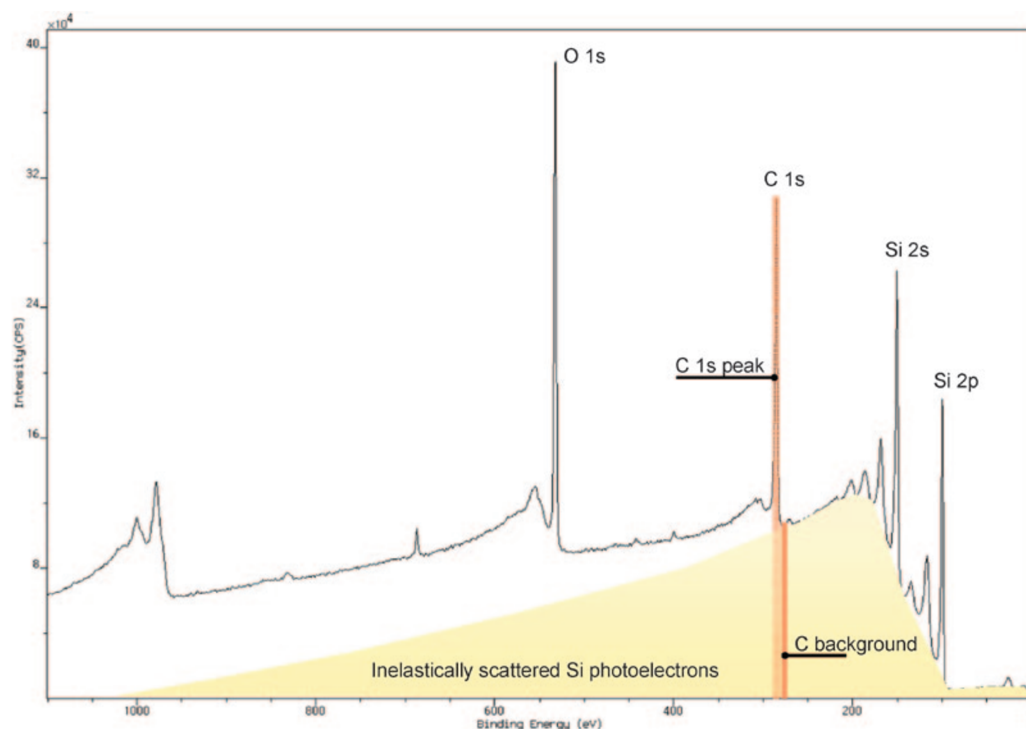

Figure 1: XPS survey spectrum of a self-assembled monolayer (SAM) on a Si substrate. Around 40% of the total intensity at the C 1s energy is due to inelastically scattered Si photoelectrons.

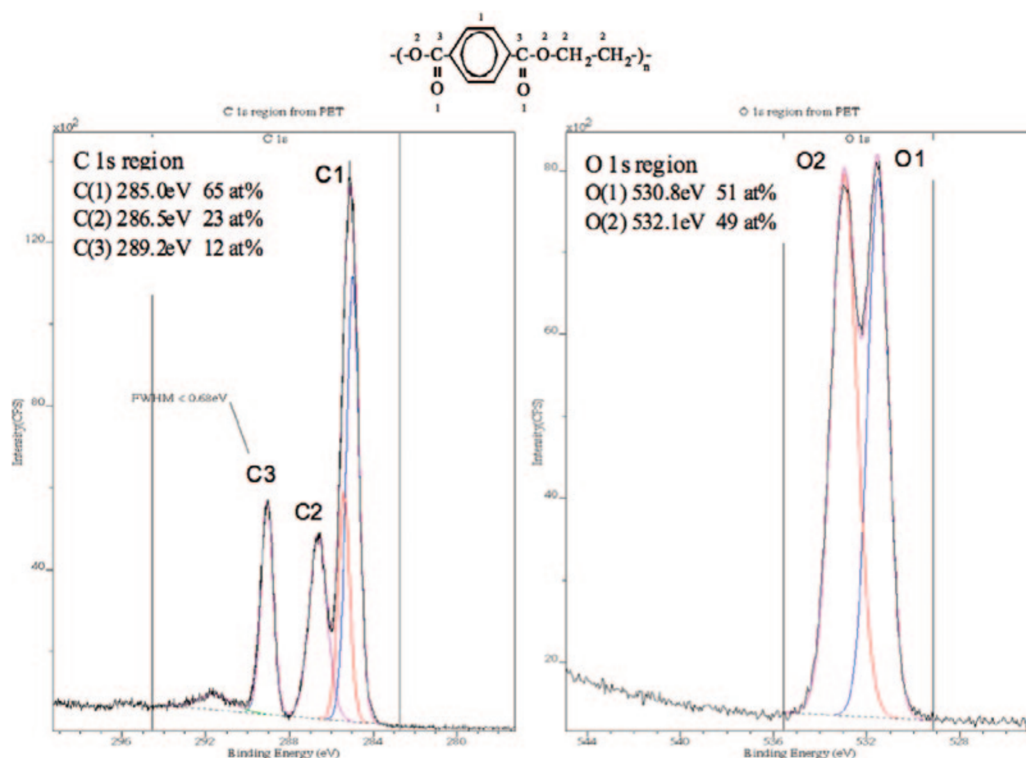

Figure 2: High-resolution C 1s and O 1s spectra from poly(ethylene terephthalate) (PET), along with the molecular structure of PET, identifying the relationships between the peaks and the atomic positions in the molecule.

this thin layer can be enhanced by collection of the spectrum at a glancing angle using angle resolved SPS (ARSPS) [3] protocol.

Careful refinement of ARXPS data can reveal detailed chemical information from near-surface layers and readily identify surface differences. Figure 4 shows the reconstructed depth profile resulting from maximum entropy method refinement [4] of ARXPS data. These data show which end of a molecule is attached to the substrate for a self-assembled monolayer system by reconstructing the depth of an attached fluorine atom [5].

Sample Charging

The complementary technique of Auger electron spectroscopy (AES) provides elemental, and some chemical, information on a similar depth scale, but with significantly higher spatial resolution than XPS. However, its use of an electron beam for excitation can cause difficulties in the analysis of insulating samples. For example, the sample charging can deflect the electron beam. Although sample charging will not deflect the excitation source in XPS, changes in the surface charge can compromise the high-resolution information in the spectrum. The FWHM resolution of metal peaks is commonly less than 0.5 eV in XPS with a monochromatic source, while just a few volts of differential charging across the analysis area destroys the energy resolution and the chemical state specificity.

To overcome these sample-charging issues, modern photoelectron spectrometers employ some form of charge neutralization scheme using electron bombardment of the sample surface during analysis, with occasional addition of low-energy argon ions in some approaches. Charge neutralization allows high-energy resolution analysis to be obtained with nearly all types of samples that can withstand the ultra-high vacuum (UHV) of the measurement chamber. Figure 5 shows a frizzy cotton-like sample and high-resolution spectra obtained from it when the surface was sufficiently neutralized. Even with the most advanced neutralization, AES

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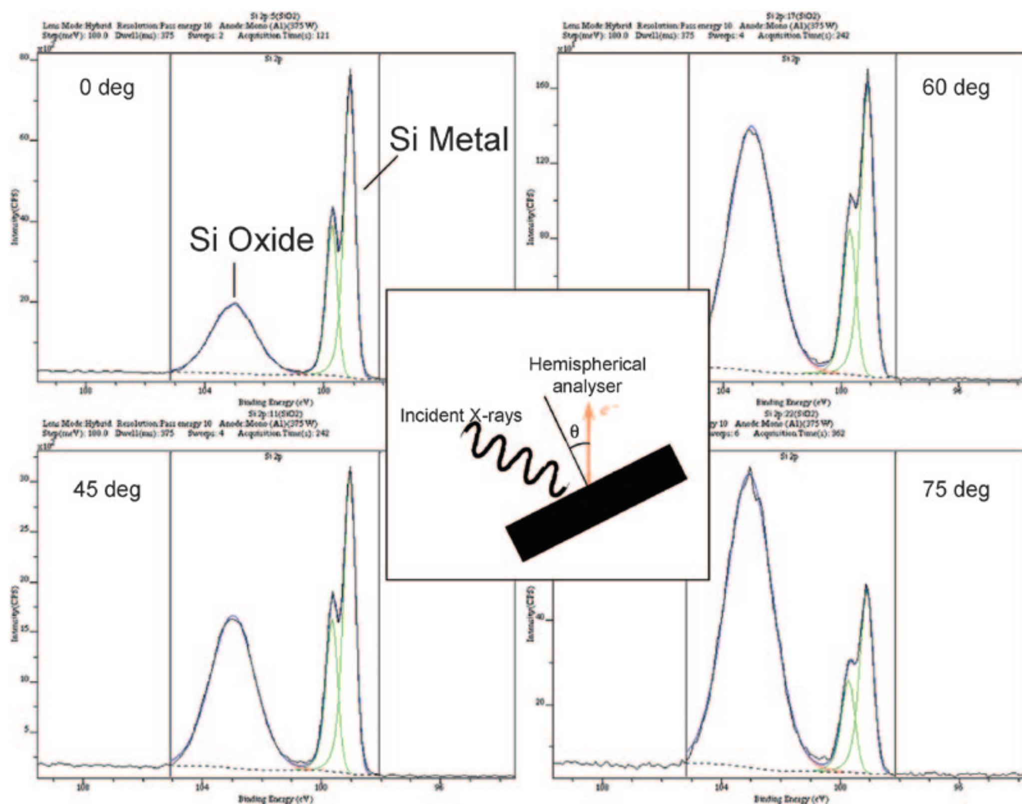

Figure 3: Angle-resolved photoelectron spectra from a room-temperature native oxide on a silicon wafer sample about 0.8-nm thick, demonstrating increased surface sensitivity at a more glancing angle with the sample surface (greatest at theta = 75°).

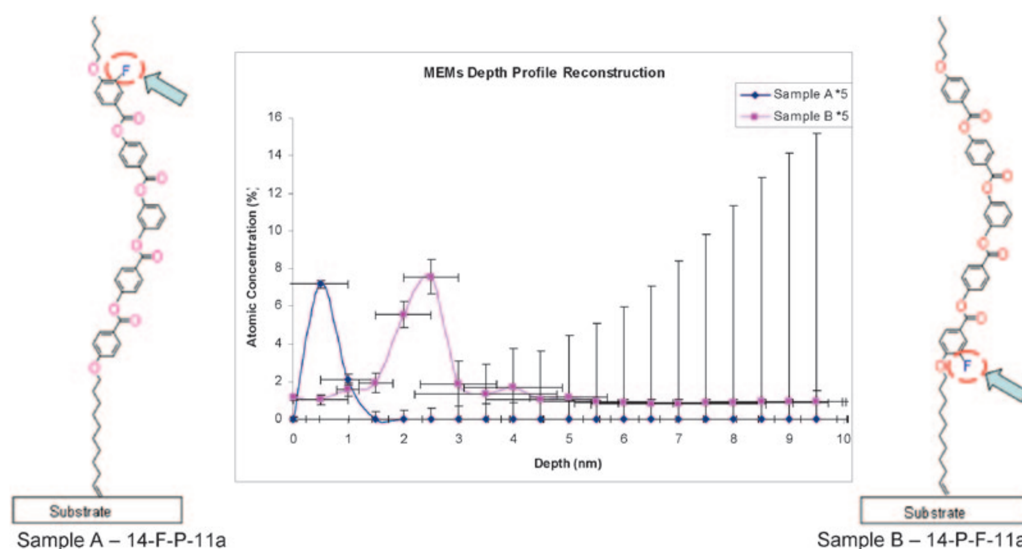

Figure 4: "Banana shaped" molecule self-assembled monolayer (SAM). A depth distribution of fluorine from a reconstruction of ARXPS data distinguishes between two locations of the fluorine. Detailed studies using AFM, water contact angle, and ATR-FTIR techniques have shown that the monolayer is densely packed and well ordered. (Sample provided by H. Zuilhof, Wageningen University, the Netherlands.)

from insulating samples such as this is not possible, cementing XPS as the more universally employed surface analysis technique, even with its more limited spatial resolution.

XPS Elemental Mapping

Spatially resolved XPS initially developed following two general approaches. One method is based on the use of highly focused X-ray beams to limit the sample exposure while collecting all possible electrons emitted from the illuminated region of the sample. To perform mapping analysis of samples, either the stage is moved serially, or in a more novel approach, the monochromatic X-ray beam is moved across the sample surface by scanning the electron beam generating the X rays on the anode.

The second approach uses apertures and electromagnetic lenses to limit the collection and analysis of electrons to those coming from a small region of the sample. In this approach, deflection plates in the lens stack can be used to deflect this virtual probe across the sample surface, serially collecting electrons from different points along a raster pattern—somewhat the inverse of a scanning electron microscope.

Both of these approaches continue to be employed in the generation of small spot spectra, with analysis spot sizes in the 10-µm range. The inefficiency of the photoelectron process itself ultimately limits the ability to collect statistically reasonable count rates without requiring X-ray fluxes that would damage either the source or the sample itself. The time then required for reasonable intensities and counting statistics in two-dimensional maps with scanned probes becomes quite long for higher spatial resolutions over reasonable fields of view. This is particularly true when considering the additional collection of background references, which is critical in XPS. The background increase at lower kinetic energy (higher binding energy in the spectrum display) from one material in a spatially distributed sample may be much higher in absolute intensity than from an adjoining region having a peak from a different element on

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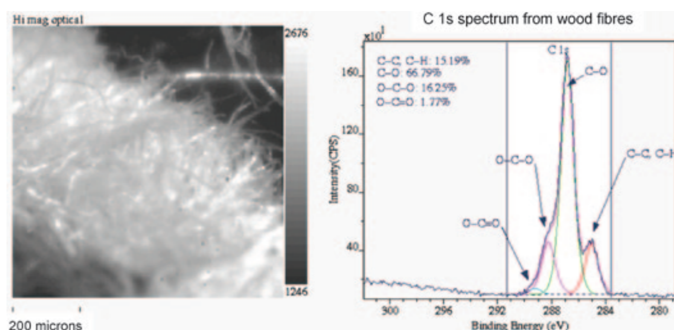

Figure 5: Neutralization of rough insulating samples. The sample of wood pulp fibres shown in the light optical image would traditionally be a difficult sample to charge neutralize. The charging on samples such as this can now be controlled to maintain peak resolution well below 1 eV.

top of its own locally low background. However, both will have the same intensity.

Figure 6 shows a contrived example of this effect, displaying the overlay of two large area survey spectra from different materials, Au and CdSe. One could imagine a region of gold deposited next to a region of CdSe and the analysis of oxygen across the interface between these two materials. If a single-peak intensity map were obtained at just the position of the O 1s peak, the image would show absolutely no contrast between the two regions. To get realistic elemental distribution information, careful attention must be paid to the use of background points in the XPS spectrum, because the background on one material may be of higher intensity than a peak in an adjoining region. Subtracting even a simple single-point background image from the peak intensity image in the above example would show the desired material contrast.

The push for higher spatial-resolution XPS imaging with reasonable acquisition times was met by the development of

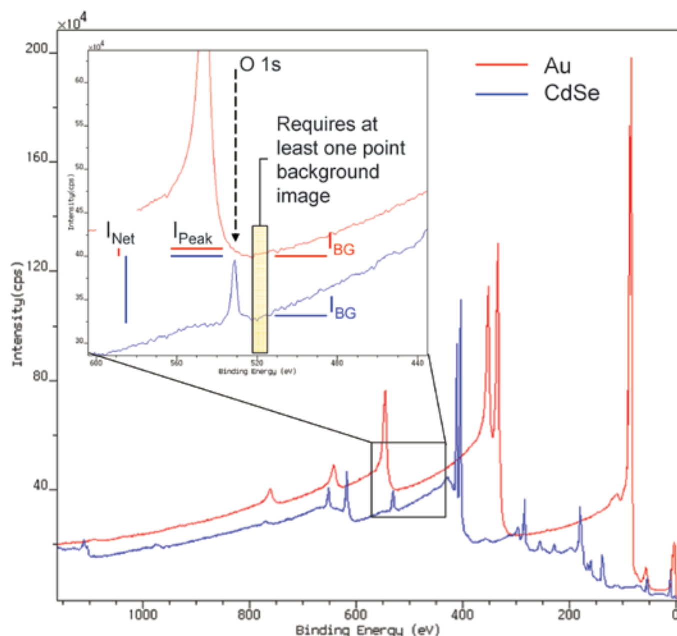

Figure 6: Example showing why the use of background reference images is critical in XPS mapping. The background intensity may be larger in one material than the peak of an adjoining material, masking or inverting the chemical contrast in a map of pure peak intensity.

parallel imaging analyzers, with the capability to magnify and detect the two-dimensional electron emission from a surface at selected energies [6, 7]. These parallel approaches currently yield maps with metal edge resolutions (20–80% drop-off) in the 2–3 micron range. The inefficiency of the photoelectron process and the nature of counting statistics still limit the spatial resolution.

These parallel imaging systems make XPS elemental mapping a practical tool with the ability to visually distinguish regions of different surface chemistry. Advances in detector technology, allowing position-sensitive pulse counting of two-dimensional electron distributions, have turned what were initially qualitative contrast images into quantitative data for stoichiometric comparison. This quantification can be localized within an image down to the pixel level. Individual pixel resolution in the 1-um range is now possible on commercial instruments.

Quantitative XPS images (maps), accessible over reasonable acquisition times, allow the reconstruction of spectra from small regions. XPS is after all a spectroscopy-based technique, and the spectroscopy carries the chemical state information. A reconstruction of spectra from images taken at multiple energies is shown in Figure 7. The energy-selective analyzer can be stepped through a series of energy steps, with an image taken at each step. Each pixel of the image contains one point on a spectrum, and running through a stack of these images produces a spectrum at that pixel. A set of energy-stepped images, with 256 × 256 pixels in each, represents more than 65,000 spectra. Stated another way, an energy spectrum can be generated at each pixel (a spectrum image). Summing spectra from a group of pixels aids in the retrieval of surface chemical information from restricted regions on the sample surface. Multivariate approaches to the processing of XPS images and surface chemical information [8], as well as multivariate coordination of spectroscopic XPS data [9], provide new ways to exploit the information accessible with the technique.

Additional Resources

ASTM has maintained a surface chemistry committee, E42, for over 35 years, and the ISO surface chemistry committee, TC-201, has be active for nearly 20 years. Both serve as valuable resources for the analyst working with XPS and other surface analysis techniques by providing standards, guides, and practices for things such as terminology, instrument calibration, charge neutralization practices, sample preparation, and data reporting. As part of its handbook series, ISO has just released a CD-ROM including the 34 standards and 6 technical reports maintained by TC201 on surface chemistry.

Conclusion

Recent trends have shown strong growth in the referencing of XPS in research articles [10]—much more so than other traditional surface analysis techniques. The need for the crucial information obtainable using this technique can only continue to grow as nanomaterials development expands. In many cases the entire volume of these nanostructures is within the surface region, and the surface effects can dominate the material properties.

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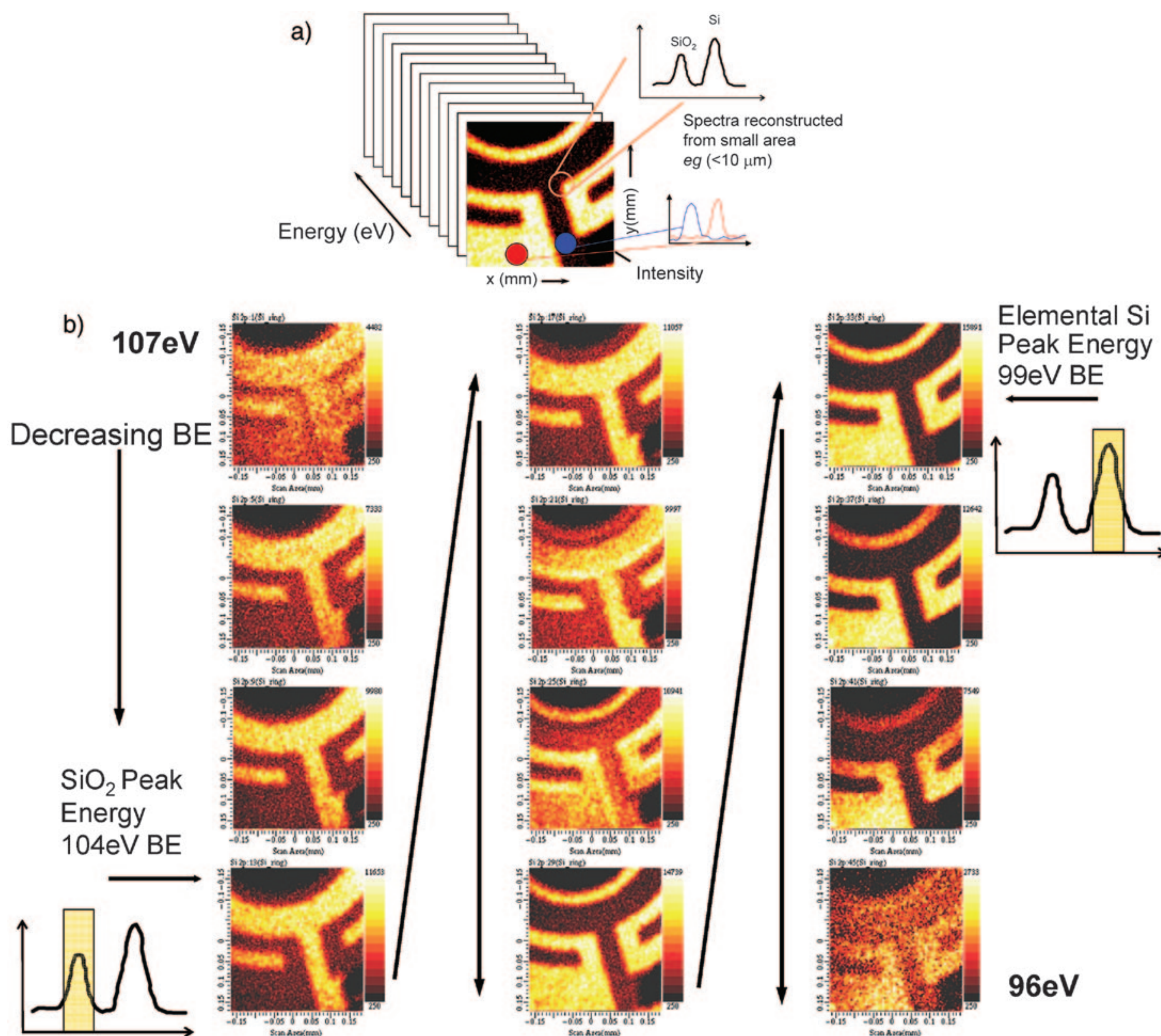

Figure 7: Chemical state images are accessible with the ability to collect multiple images in a reasonable time frame, each image often taking only 30–120 seconds. The sample is patterned SiO_2 on Si, and the semicircular dark region at the top is photoresist. (a) Stacking of parallel images allows the generation of a representative spectrum from a region of interest projected into the stack. (b) Each panel reveals the spatial distribution of the intensity for a given energy-integration window.

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