Experimental setups for XPS measurements beyond the instrumental lateral resolution limit

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The lateral resolution of an X-ray photoelectron spectroscopy instrument, which is equipped with a focused X-ray beam, is limited by the nominal X-ray beam diameter and the long tail intensity distribution of the X-ray beam. The long tail intensity distribution of the X-ray beam impedes to perform a measurement with good lateral resolution and low detection limits at the same time. Two experimental setups are described which allow examining sample structures that are smaller than the X-ray beam dimensions. The first method uses differential sample charging on partly nonconductive samples by low-energy electron flooding. The spectra of the nonconductive sample areas are shifted towards lower binding energy. That way, the surface composition of conductive and nonconductive sample areas are estimated independently. The second method utilizes the limited dimensions of the energy analyser acceptance volume. Here, only the sample is placed inside the energy analyser acceptance volume. That way, signals from the illuminated sample contribute exclusively to the measured photoelectrons intensity, independent from the sample size.

KEYWORDS
energy analyser acceptance volume, ESCA, focused X-ray beam, lateral resolution enhancement, quantitative lateral resolution, sample charging, XPS

1 | INTRODUCTION

The resolvable sample structures of X-ray photoelectron spectroscopy (XPS) microprobes, which are equipped with a focused X-ray beam, are defined by the minimal X-ray beam diameter of this focused X-ray beam. This minimal X-ray beam diameter is given by the beam width at the half maximum intensity level or a similar vendor’s definition. Such a definition of the beam diameter ignores the long tail intensity distribution of the X-ray beam. In case of trace element detection on small sample features, it is impossible to decide whether this signal refers to a contamination of the small sample feature or if it comes from the surrounding of the small sample feature due to the long tail intensity. Therefore, an XPS measurement with higher lateral resolution using an instrument with a focused X-ray beam is limited by the nominal X-ray beam diameter and the long tail intensity distribution of the X-ray beam.

In this article, two approaches are presented, which overcome this limitation by dedicated experimental setups. The approaches allow examining sample structures, which are smaller than the X-ray beam dimensions. The first method utilizes differential sample charging on partly nonconductive samples to discriminate conductive and nonconductive sample regions. The second method utilizes the limited dimensions of the energy analyser acceptance volume. If exclusively the sample is placed inside this volume, this way, only the illuminated sample contributes to the measured photoelectron intensity, independent from the X-ray beam diameter and the sample size.

2 | INSTRUMENTATION

Two XPS microprobes were used for the XPS measurements presented here: A Surface Science Laboratories X-probe instrument and a
Physical Electronics XPS Quantum 2000, respectively. Both XPS instruments achieve the spatial resolution by the combination of a fine-focused electron beam generating the X-rays on a water-cooled Al anode and a mirror quartz monochromator, which monochromatizes the AlKα radiation and refocuses the X-rays to the sample surface. This way, the beam diameter of the electron beam, which generates the X-rays on the Al anode, defines the X-ray beam diameter on the samples surface. Both instruments have a low-voltage electron gun for charge compensation and a differentially pumped Ar⁺ ion gun for sample cleaning and sputter depth profiling.

The Surface Science Laboratories instrument is equipped with an 6'' wafer sample handling system. Sample features are selected and adjusted at the instrument’s measurement position utilizing an optical microscope. The instrument has nominal X-ray spot sizes of 150, 300, 600 and 1,000 μm. The X-ray beam, the mean take-off angle of the energy analyser and the Ar⁺ ion gun have an angle of 55° relative to the surface normal of a flat-mounted sample. The hemispherical energy analyser has a collection lens with 30° acceptance angle and multichannel detection via a microchannel plate electron multiplier and a position-sensitive detector. A more detailed description of the instrument can be found in the literature.1,4

The Physical Electronics XPS microprobe Quantum 2000 represents the further development of the primary focused XPS microprobe concept. By controlling the electron beam diameter, nominal X-ray beam diameters between 10 and 200 μm are selectable with the instrument used here. The X-ray beam scans across the sample as the electron beam is scanned across the Al anode by applying electrostatic deflection voltages to the electron beam. On the sample surface at maximum, an area of approximately 1.4 mm² can be scanned. With a fine-focused rastered X-ray beam, a sample can be depicted by an X-ray beam-induced secondary electron image. This way, sample features are localized. An optical microscope utilized for sample inspection at the measurement position becomes unnecessary thanks to this imaging capability. Therefore, in a Quantum 2000, the space directly above the sample is used for the X-ray source mounting. For a flat-mounted sample as used here in a Quantum 2000, the incoming X-rays are parallel to the surface normal. In this geometrical situation, the mean energy analyser take-off axis and the Ar⁺ ion gun are oriented approximately 45° relative to the sample surface normal. The hemispherical energy analyser has a collection lens with an acceptance angle of 30° and a 16-channel detector. A more detailed description of the instrument and its performance is found in the literature.1,4–10

3 | QUANTITATIVE LATERAL RESOLUTION OF AN X-RAY MICROPROBE

The X-ray beam diameters of XPS microprobes with a focused X-ray beam are measured using a vendor-specified measurement procedure. For the Quantum 2000, the manufacturer defines this beam size as the distance between the points at which the signal amplitude is 20% and 80% of the maximum value when the beam is scanned over a material edge.6 However, for a more precise determination of the intensity distribution within the X-ray beam, the long tail contributions of the X-ray beam have to be taken into account.1

The long tail intensity was measured using Pt apertures of different diameters, which were mounted over drilled holes. If the X-ray beam is centred in the aperture, only long tail X-ray beam intensities from outside the aperture diameter produce a Pt signal. This measured Pt intensity is normalized by a second measurement on massive Pt. Per definition, the quantitative lateral resolution of an X-ray microprobe is the diameter of an aperture, which produces a normalized intensity of 1%. It is approximately 450 μm for the Quantum 2000 used here.1

4 | EXPERIMENTAL APPROACHES

Due to the instrumental design, the smallest area, which can be analysed by an XPS microprobe with a focused X-ray beam, is defined by the beam’s lateral dimensions. On one hand, it is the nominal diameter of the X-ray beam. On the other hand, there exists a trade-off between a good lateral resolution and the detection of low elemental concentrations, due to the tailing of the X-ray beam intensity. As discussed above, the quantitative lateral resolution of an XPS microprobe can describe this property.

Two experimental approaches are applied to examine sample structures independently, which are smaller than the X-ray beam’s dimensions. First, differential sample charging on partly nonconductive samples is utilized to discriminate conductive and non-conductive sample regions.2 Second, by using the energy analyser acceptance volume method, only the sample is placed inside the energy analyser acceptance volume. This way, exclusively the sample contributes to the signal independent from the sample size if it is illuminated by X-rays.

5 | DIFFERENTIAL SAMPLE CHARGING

The sample used to demonstrate the differential sample charging method is a microelectronic silicon device with Al bond pads of a size of approximately 120 × 120 μm². The silicon device was covered with a 30-μm thick polyimide (PI) protective layer. The bond pads were opened by plasma etching of the PI. The quality of this etch process was controlled by XPS measurements using the Surface Science Laboratories X-probe (SSI) instrument. The nominal X-ray beam diameter is 300 μm, which is quite larger than the bond pad.

Figure 1 shows the high-resolution N1s and O1s spectra with the flood gun switched off or switched on using electron energies of 5, 10 and 15 eV, respectively. Both graphs show an overlay of spectra measured in different experiments. O is present in the PI and in the Al oxide at the bond pad surface. On the conductive bond pad surface, the position of the O signal remains nearly constant independent from the flood gun energy. Without energy flooding, the PI becomes positively charged by photoelectron emission. The O1s signal of the PI is
detected at a binding energy, which is approximately 7.4 eV higher than the value measured on the Al bond pad. The nonconductive PI surface becomes negatively charged by the low-energy electron flooding. The photoelectrons from PI are accelerated, and therefore, they are measured at lower binding energy. For a flood gun energy of 5 eV, the O1 signals of the oxide and the PI superimpose. The N is only a component of the nonconductive PI because the peak position changes in all spectra. In the spectra, some smaller peaks are visible indicating some limitations of the differential sample charging method. These additional peaks are attributed to particular surface areas. For example, the transition area between the conductive Al and the nonconductive PI at the edge of the bond pad may be a candidate.

Figure 2 depicts a survey scan of the bond pad and the PI recorded with 15 V flood gun energy. If a binding energy shift of approximately 15 eV is observed, the measured intensities are assigned to the PI surface. The peak intensities attributed to the conductive Al bond pad appear at the expected binding energies. From the measured peak intensities, the apparent atomic concentrations of the detected element for the PI and the Al bond pad were estimated separately. The calculation uses the instrumental sensitivity factors and assumes that the detected elements are distributed homogeneously within the information volume, which is mainly defined by the information depth of the measurement. The table, which is inserted in Figure 2, summarizes the results. The Si on the PI is a hint to a residue of the mask, which is necessary for the bond pad opening etching. As expected, the Al bond pad surface is oxidized. On the bond pad surface, we detect F, which is due to an etch residue of the bond pad opening etching. Additionally, we have some ambiguous C contamination on the bond pad surface. But there is no N on the bond pad detectable. This indicates that there are no PI residues at the bond pad surface and that the bond pad opening was perfect.

### 6 | ENERGY ANALYSER ACCEPTANCE VOLUME METHOD

The second experimental approach uses the limited spatial extension of the energy analyser acceptance volume. Figure 3 shows a plot of...
the analyser acceptance dependency of a Quantum 2000 as function of the z position of an Au foil. The z position gives the distance of the sample from the X-ray source because the incoming X-rays are parallel to the surface normal. The intensity of a normalized Au 4f signal is plotted against the samples z position. Starting from the optimum sample position, the intensity decreases drastically for a misalignment of less than 1 mm. Due to the rotationally symmetry of the analyser input lens, the acceptance in x and y direction is expected to be comparable with this result. Therefore the analyser acceptance volume of the Quantum 2000 has an extent of a few cubic millimetres only. In praxis, the analyser acceptance in the x-y plane cannot be determined by a measurement. This is unfeasible because electrostatic deflection plates at the energy analyser entrance synchronize the analyser acceptance with the position of the rastered X-ray beam on the sample surface by dynamic emittance matching.

The energy analyser acceptance volume method involves placing only the sample inside this volume. This way, only the illuminated sample contributes to the measured photoelectrons intensity, independent of the sample size.

The analysis of Cu bond wire surfaces is discussed as an example of such a measurement approach. The bond wires have a diameter of approximately 80 μm. Figure 4 shows the mounting of the bond wires. The bond wires are mounted completely free over a hole of the sample holder. The inset shows the experiment in detail. The measurements were done with a 100-μm spot size of the X-ray beam. From each wire, a survey spectrum of the surface ‘as received’ was recorded. From the detected peak intensities, the surface composition of seven wires were estimated by standard data evaluation using the vendor’s software package. Table 1 summarizes the results. On all bond wires, a higher amount of C was detected. Most likely, this C is due to the lubricant utilized during the wire drawing. Additionally, C contaminations are due to sample handling in ambient air. The detection of N at the surface of wire 3 is a strong hint to an antioxidant chemical on the surface of this wire. On some wires, corrosive S and Cl contaminations are present.

Please notice that the X-ray beam size is larger than the bond wire diameter. As demonstrated, it was possible to perform a reliable measurement of the bond wires surface contaminations down to the 1% level, if only the sample and nothing else is placed within the energy analyser acceptance volume.
This article presents two experimental approaches, which overcome the lateral resolution and low-elemental concentration limit defined by the X-ray beams lateral dimensions and tailing.

On partly nonconductive samples, differential sample charging is used to separate spectra of different sample areas with dimensions below the X-ray beam diameter. Using low-energy electrons with a kinetic energy in the range of a few electron volts nonconductive areas are charged negatively. The photoelectrons from this surface area are accelerated, and therefore, they are measured at lower binding energy.

The energy analyser acceptance volume method utilizes the rather limited dimensions of the energy analyser acceptance volume. Applying this approach, only the sample and nothing else is mounted inside this volume. Therefore, the sample has to have a suitable shape, which can be produced by a sample preparation if necessary. The use of an adapted sample mounting where only the sample is probed is important.

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REFERENCES
1. Scheithauer U. Quantitative lateral resolution of a Quantum 2000 X-ray microprobe. Surf Interface Anal. 2008;40(3-4):706-709.
2. Boland JJ. Voltage contrast XPS - a novel scheme for spatially resolved XPS studies. Surf Interface Anal. 1987;10(2-3):149-152.
3. Chaney RL. Recent developments in spatially resolved ESCA. Surf Interface Anal. 1987;10(1):36-47.
4. Scheithauer U. Long time stability of the energy scale calibration of a Quantum 2000. J Electron Spectrosc Relat Phenom. 2012;184(11-12):542-546.
5. Scheithauer U. Characterisation of the primary X-ray source of an XPS microprobe Quantum 2000. J Electron Spectrosc Relat Phenom. 2014;193:58-62.
6. Physical Electronics Inc. System specifications for the PHI Quantum 2000. Eden Prairie, MN 55344 USA. 1999
7. Iwai H, Oiwa R, Larson PE, Kudo M. Simulation of energy distribution for scanning X-ray probe. Surf Interface Anal. 1997;25(3):202-208.
8. Larson PE, Palmberg PW. Scanning and high resolution XPS and imaging. United States Patent, Patent-Number: 5315113. 1994
9. Physical Electronics Inc. The PHI Quantum 2000: a scanning ESCA microprobe. Eden Prairie, MN 55344 USA. 1997.
10. Scheithauer U, Kolb M, Kip GAM, Naburgh E, Snijders JHM. Round Robin: quantitative lateral resolution of PHI XPS microprobes Quantum 2000/Quantera SXM. J Electron Spectrosc Relat Phenom. 2016; 210:13-15.
11. Physical Electronics Inc. MultiPak Software Manual - Version 6. Eden Prairie, MN 55344 USA. 2000.
12. Sastri VS, Packwood RH. Surface analysis in corrosion inhibition mechanisms. Mater Corros. 1987;38(2):77-82.

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