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Applications of high lateral and energy resolution imaging XPS with a double hemispherical analyser based spectromicroscope

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ABSTRACT

The design and applications of an instrument for imaging X-ray photoelectron spectroscopy (XPS) are reviewed. The instrument is based on a photoelectron microscope and a double hemispherical analyser whose symmetric configuration avoids the spherical aberration (α^2-term) inherent for standard analysers. The analyser allows high transmission imaging without sacrificing the lateral and energy resolution of the instrument. The importance of high transmission, especially for highest resolution imaging XPS with monochromated laboratory X-ray sources, is outlined and the close interrelation of energy resolution, lateral resolution and analyser transmission is illustrated. Chemical imaging applications using a monochromatic laboratory Al Kα-source are shown, with a lateral resolution of 610 nm. Examples of measurements made using synchrotron and laboratory ultra-violet light show the broad field of applications from imaging of core level electrons with chemical shift identification, high resolution threshold photoelectron emission microscopy (PEEM), work function imaging and band structure imaging.

1. Introduction

Since the beginning of X-ray photoelectron spectroscopy (XPS) with Siegbahn's Nobel Prize winning work [1] in the 60 s and 70 s of the last century, XPS has evolved into a standard technique for acquiring chemical and elemental information of surfaces [2,3]. Although first attempts in acquiring lateral information with XPS started more than 20 years ago, these techniques have not, as yet, achieved widespread use. Until recently, acquisition times in imaging XPS have been comparatively slow and for most applications local spectra from a small area $\geq$10 μm (small spot spectroscopy) will provide sufficient information within reasonable time.

A different situation is found for highest resolution imaging XPS with a lateral resolution in the range of several hundred nm where local XPS maps can provide rich information from the analysed sample area, such as the chemistry of interfaces. Other element sensitive imaging methods with high spatial resolution such as Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) or imaging Auger Electron Spectroscopy (Scanning-Auger) will not provide enough sensitivity to extract the full chemical information, especially the elemental bonding states. Compared with the above-mentioned methods, XPS has the advantage of being a quantitative and non-destructive method.

In contrast to Scanning-Auger, a technique directly derived from scanning electron microscopy, the methodology of imaging XPS is not so straightforward. In the past, several different types of instruments have been proposed and build as single instrument prototypes and today a variety of imaging XPS instruments are commercially available. Reviews of laboratory [4] and synchrotron based work [5,6] can be found in literature.

There are basically two approaches to design a XPS instrument allowing laterally resolved chemical imaging. The most common technique is to utilize an electron energy analyser with the capacity to simultaneously image and energy-filter the photoelectrons [7–11]. The other approach is to focus the X-ray beam into a micro-spot and scan the beam or the sample while acquiring the photoelectron signal with a standard analyser. This has been implemented by several projects at synchrotron beamlines, where zoneplate- or mirror-optics are used to focus spot sizes down to some 100 nm [5].

While the majority of commercially available imaging XPS systems follow the concept of an imaging analyser with a fixed X-ray beam position, one instrument [12] makes use of a scanned Al Kα laboratory X-ray source, but the spot size of the scanned X-ray source limits the instruments lateral resolution to about 10 μm.

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Among the imaging energy analyser based instruments, two types can be distinguished, not primarily by the working principle, but by the emphasis of the instruments' use.

Instruments using a fixed X-ray source with an imaging energy analyser set-up are derived from photoelectron spectrometers dedicated for laboratory applications. The imaging properties of a hemispherical analyser are used to generate energy filtered maps. The entrance lenses typically accepting large field of view of some 100 μm have only limited lateral resolution of some micrometers, but are capable to transmit a sufficiently large phase space to enable elemental mapping in reasonable time.

A second class of instruments is derived from photoemission microscopes or low energy electron microscopes [10,11] and typically aim for the highest lateral resolution within a small field of view. A direct consequence of the high lateral resolution is a considerably reduced overall transmission of the analyser. Although the use of these instruments for laboratory experiments may be limited to low energy applications in the Ultra-violet photoelectron spectroscopy (UPS) range, this disadvantage can be overcome when using today's high brilliance undulator beamlines at the synchrotron for imaging XPS experiments.

The instrument whose results are presented here is called the NanoESCA [13] which combines advantages of both approaches. It overcomes the strict limitation of energy filtered PEEM based instruments to synchrotron radiation and UV laboratory sources on the one hand and on the other hand it pushes back the longstanding lateral resolution barrier for imaging XPS in the laboratory of several micrometers by an order of magnitude to the 500 nm range. The entrance lens, being derived from a photoelectron emission microscope, provides also an ultimate lateral resolution better than 40 nm for secondary electron imaging, while a double hemispherical analyser or Imaging Double Energy Analyser (IDEA) [14] with a suitable retardation system allows for transmission of a large phase space.

A short description of the instrument is given in Section 2. In Section 3 the close connection of the instrument's transmission to its lateral and energy resolution will be addressed. Some of the recent laboratory and synchrotron radiation applications are reviewed in Section 4.

These have been chosen from a wide selection of case studies related to various fields of material science: (i) nanostructures (single silicon nanowires [15] and semiconductor heterostructures [16,17]); (ii) patterned surfaces (selective electrografting on silicon substrates [18,19], p and n doped silicon patterns [20] and layered hydrogels [21]); (iii) polycrystalline materials (grain boundaries of intermetallic alloy surfaces [13,22,23], orientation dependent surface chemistry in oxide ceramics [24], work-function and d-band states imaging of single copper grains [25,26] or magnetic domain imaging on the Fe $2p_{3/2}$ core level [27]); and (iv) granular materials (trace elements in pre-solar meteorites [25,28]). Finally the most recent instrumental achievements from k-space imaging are highlighted with results on a copper single crystal [29].

We conclude with some indications on promising instrumental developments for future work.

2. Description of the instrument

The NanoESCA is an imaging analyser derived from an electrostatic photoemission electron microscope (PEEM) column, combined with the aberration compensated double hemispherical analyser. A schematic of the optical layout and a photograph of the instrument indicating the operation modes are shown in Fig. 1, further details of the instrument can be found in [13].

Photons are incident on the sample surface at an angle of 65° with respect to the sample normal resulting in photoelectron emission which is imaged by the microscope. The instrument can work with various excitation sources to obtain comprehensive spectromicroscopic information from all spectral feature of the photoemission spectrum (UV and VUV photons, laboratory and synchrotron X-rays). Three operating modes are available: direct non-energy-filtered PEEM; small spot, area selected spectroscopy; and energy filtered imaging. The fully electrostatic PEEM column is either used for direct (secondary electron) PEEM-imaging or as the entrance lens for the analyser.

The good lateral resolution of the microscope is accomplished by the immersion objective lens with an extraction voltage of up to 16 kV. In contrast to other cathode lenses described in literature [30,31] the objective lens works with asymmetrical voltages where the electrons are decelerated in the focussing field of the lens towards the low voltage column typically at 1000 eV drift energy. The objective lens is equipped with exchangeable and adjustable contrast apertures of different sizes and an octopole stigmator to compensate for axial astigmatism. A continuously adjustable iris acts as a field aperture for small spot spectroscopy or angular imaging. The low column energy allows the retardation of the electrons toward the low pass energies which are needed for high transmission operation.

The projection lenses project and retard the electrons into the analyser entrance or, in PEEM-mode with the energy analyser deactivated, magnify it onto the image intensifier for non-energy filtered operation. A channeltron detector located behind the first hemisphere can be used to acquire fast small-spot overview spectra. Using an additional transfer lens after the contrast aperture the angular distribution of the photoelectrons can also be imaged. This version of the NanoESCA instrument is also called momentum microscope [29]. A set of projection lenses after the second analyser is used to obtain the final magnification in energy filtered operation. The magnification can be adjusted over a large range between <5 μm up to >650 μm field of view.

In energy filtered operation, image stacks are recorded by scanning the sample voltage with fixed analyser pass energy and automatic refocussing of the objective lens. The three-dimensional data stack, $I(x,y,E)$, therefore contains at each image pixel microscopic and spectroscopic information, and can be analysed off-line by standard data reduction techniques, e.g. removal of photoemission background or principal component analysis to reduce the noise in core level images [32].

3. Options and limits of imaging XPS

The analyser and the entrance lens used for imaging of the photoelectrons set the limits to the performance of the instrument, as the energy resolving power and lateral resolution are closely linked to the achievable transmission. A higher resolution is generally only feasible if the transmission of the instrument is reduced by inserting apertures, either angular apertures to enhance the lateral resolution or apertures in a dispersive plane to achieve a higher energy resolution.

Here the interrelationships for a single hemispherical analyser (HSA) will be discussed and compared to the properties of the double hemispherical analyser IDEA. The HSA is the most popular type of analyser used for imaging [7,8,11] and therefore can be used as a benchmark for the new IDEA analyser.

3.1. Energy resolution and transmission of the analyser

Most of the properties of an ideal HSA can be easily deduced from its approximate (second order) imaging properties in the dispersive plane. Neglecting the fringe field effects at the entrance and exit slits, electrons entering the hemispherical field at the entrance slit with an excess energy of ΔE_{kin} over the pass energy E_{pass} of the