Nanoscale Imaging and Spectroscopy with XPEEM

Stefan HEUN
Laboratorio TASC-INFM, Area di Ricerca, I-34012 Basovizza (Trieste), Italy
(Received May 25, 2005)

The continuous miniaturization and increasing complexity of the materials used in modern technology requires to have access to chemical composition, electronic structure, magnetization, and fluctuations in these properties at sub-micron and nanometer scales. X-ray photoemission electron microscopy (XPEEM) can provide this information. The recent years have seen a strong increase in XPEEM activities worldwide. This paper reviews the present situation and future developments of XPEEM in combination with synchrotron radiation. In particular, the role of energy filtering, aberration correction, and temporal resolution is discussed.

1. Introduction
X-ray photoelectron spectroscopy (XPS) and the related technique, X-ray absorption spectroscopy (XAS), are powerful tools for the analysis of surfaces, as widely discussed in this issue. In a traditional experimental setup, the spectroscopic signal is obtained from a spot of some 100 μm to millimeters in diameter, and therefore averages over this area. On the other hand, the progress in modern nanotechnology has fueled an evergrowing demand to perform XPS and XAS from areas as small as the smallest building blocks of those nanostructures. This has triggered the development of special instruments which combine spectroscopy and microscopy and allow to perform XPS and XAS with the highest possible lateral resolution of less than 100 nm.1)

More than 10 years ago, two basic, complementary design principles have been identified to achieve this goal:2) the scanning and the direct imaging type instruments. In the scanning type instruments the photon beam is demagnified, i.e. the X-rays are focused by an optical system (like a Fresnel zone plate or a Schwarzschild objective) on a small spot on the sample. The photoelectrons excited from this area are then collected by a detector. The lateral resolution of the instrument is given by the size of the illuminated area. A surface map can be obtained by scanning the sample relative to the beam. More details of this kind of instruments can be found in the article of T. Munakata in this issue.

On the other hand, in the direct imaging type instruments, the sample is illuminated in a larger area and the photoelectron yield image is magnified by an electron optical system. The most popular instrument of this type is the photoemission electron microscope (PEEM) which will be discussed in the following in this article.

2. PEEM
A PEEM employs electrostatic or magnetic lenses to form a magnified image of the local photoelectron yield of the sample on a screen. Typical fields of view of the microscope range from 1 μm to 100 μm. To excite the photoelectrons, the sample is homogeneously illuminated by monochromatic X-rays in a spot the size of which matches ideally the field of view of the microscope. This spot size is small relative to what is typically used in integral photoelectron measurements, but it can still be achieved with conventional optical elements (mirrors). A PEEM allows continuous imaging with video rate. No sample scanning is necessary. A basic PEEM is shown in Fig. 1. The photoelectrons emitted from the sample are accelerated by a high electric field between the sample and the objective lens. The image produced by the objective lens is magnified by the projector lens onto a detector, where it can be observed with a CCD camera. High fields at the sample are generally needed for collection efficiency and lateral resolution. Therefore samples with sharp tips cannot be studied since field emission starts at fields well below those used for imaging.

The lateral resolution of a PEEM is determined by
three quantities: (a) spherical aberrations, (b) chromatic aberrations, and (c) diffraction. Spherical aberrations can be reduced by cutting the rays which pass the lenses far from the center, i.e., by reducing the angular acceptance of the microscope. For this purpose, a contrast aperture is usually placed in the back focal plane (or an equivalent plane) of the PEEM. Furthermore, due to the chromatic aberrations, a focal point of the microscope is smeared out along the optical axis. Only electrons with the proper energy are focused into the aperture, which reduces the width of the energy distribution of the electrons transmitted through the PEEM. Therefore the use of a contrast aperture reduces the aberrations of the lenses of the microscope, at the expense of transmission. Reducing the diameter of the contrast aperture, the lateral resolution of the microscope can be improved, until finally the diffraction at the aperture becomes the dominating effect, and further reduction of the aperture diameter reduces the transmission of the microscope without further improvement in lateral resolution. With X-ray illumination, a standard PEEM like the PEEM 2 at the ALS can reach a lateral resolution of 20 nm.

3. LEEM

A PEEM can be equipped with an electron gun and operated as a low energy electron microscope (LEEM). This combination allows to perform electron microscopy and X-ray microscopy on the same sample area. The separation between incoming and outgoing electron beams is achieved by a magnetic prism (sector field). A LEEM can be used to obtain real space images of the sample with a lateral resolution of 8 nm, or to measure the intensity distribution in reciprocal space (low energy electron diffraction (LEED)). The LEED can be obtained from a micrometer spot on the sample.

4. Contrast Mechanisms

A photoelectron spectrum obtained with X-rays consists of three parts: the secondaries peak at low kinetic energies (≈0–20 eV), the core level and Auger peaks at energies characteristic for the elements and their chemical state, and the valence band or Fermi edge at the high kinetic energy cutoff. The width of the spectrum (i.e., the difference between high and low energy cutoff) equals the photon energy minus the work function of the sample, and can therefore be several 10 to 100 eV large in synchrotron radiation experiments. However, lowering the photon energy to the UV, the valence band moves closer to the secondaries peak, and the photoelectrons' energy distribution curve gets narrower, thereby reducing the effect of chromatic aberrations. Under such conditions a lateral resolution of up to 7 nm has been achieved.

The early PEEM work has been performed with deuterium or mercury lamps. In these experiments, lateral variations of the work function of the sample were used as contrast mechanism. However, to do real elemental sensitive work, higher photon energies are necessary to excite atomic core levels. Therefore spectroscopic work with PEEM is usually done at a synchrotron. Most of this work has utilized soft X-rays and ultraviolet photons (10–2,000 eV) in order to achieve high surface sensitivity. However, there are first attempts to use PEEM also in combination with hard X-rays which allows to image buried interfaces. Alternatively, the use of PEEM in transmission mode makes PEEM a bulk sensitive probe.

Spectroscopy with a PEEM can be performed by scanning the photon energy and measurement of the optical absorption edge of elements of interest. This technique is called μ-XANES (X-ray absorption near edge spectroscopy). It allows to perform spectroscopy with the lateral resolution of the PEEM. A requirement for this kind of experiments is a tunable X-ray source, which is naturally given in a synchrotron. As an example, Fig. 2 shows the Co L₂₃ edge spectra from a GaAs sample which was partially covered with a Co film by selective metal electrodeposition (for details, see Ref. 10). The GaAs sample is a lay-
Fig. 2. (a) Optical microscopy image of a patterned Co/GaAs sample. (b) Co L23 edge spectra from the sample shown in (a). The integration areas from which the spectra in (b) were obtained are shown in (a).

Fig. 3. Ga 3d and In 4d core level photoelectron spectra taken from an InAs/GaAs sample. The spectra were obtained from the center of the island indicated by a circle in the inset and from the wetting layer (W.L.) close to the island. Inset: XPEEM image of the sample surface which was obtained with In 4d photoelectrons. The energy range used for imaging (76.9 eV ± 0.9 eV) is indicated by the horizontal bar above the In 4d core level spectrum. Photon energy 99.0 eV.

Processed structure with a n-doped layer grown on a p-type substrate. Figure 2 (a) shows an optical microscopy image of the sample. The horizontal and vertical lines visible in the image are grooves created by lithography and etching, in which the n-type GaAs layer was removed to expose the p-type GaAs substrate. In a subsequent electrodeposition step, Co was deposited only on the n-type areas, as demonstrated by the spectra shown in Fig. 2 (b): the spectrum from region A (n-type) clearly shows the presence of Co in this region, while the micron-sized region B (p-type) was not covered by Co, as shown by the corresponding spectrum.

Even with sufficiently high photon energies, a basic PEEM (as described above) cannot be used for µ-XPS because it is not equipped with a photoelectron energy analyzer. Therefore, in order to perform photoelectron spectroscopy with a PEEM, the system has to be equipped with an energy filter. As an example, Fig. 3 shows the Ga 3d and In 4d core level spectra taken from an InAs/GaAs sample. During the growth of InAs on GaAs, after the formation of a two-dimensional wetting layer, the growth of islands is observed which is driven by the strain in the growing film due to the lattice mismatch between InAs and GaAs. The inset of Fig. 3 shows an XPEEM image of these islands which was obtained with In 4d photoelectrons. The energy range used for imaging (76.9 eV ± 0.9 eV) is indicated by the horizontal bar above the In 4d core level spectrum. The two spectra shown in Fig. 3 were obtained from the center of the In(Ga)As island indicated by a circle in the inset and from the wetting layer close to the island. The energy resolution set for spectroscopy was approximately 1 eV. The integration area for both spectra was 25 nm × 25 nm. From each spectrum, the local Ga/In concentration ratio can be deduced.

Forming such an analysis pixel-by-pixel allows to obtain a map of the Ga/In concentration ratio of the sample surface with the lateral resolution of the microscope (~25 nm). However, the implementation of an energy filter in a PEEM is not only useful to obtain energy filtered images and to collect photoemission spectra. It also allows to reduce chromatic aberrations. Therefore, even for µ-XANES experiments the use of an energy analyzer is beneficial: it allows to select a narrow energy window around the maximum of the secondary electron energy distribution and to improve the lateral resolution without unacceptable loss of intensity.

In combination with circularly polarized light, the X-ray magnetic circular dichroism (XMCD) effect can be employed as a contrast mechanism for magnetic domain imaging. It arises from the dependence of the photoabsorption coefficient on the relative orientation of the sample magnetization direction with respect to the helicity of the incident X-rays: it is maximal for parallel alignment, minimum for antiparallel alignment, and zero for perpendicular alignment. Since electrons are excited from core level s to empty states, XMCD is element-specific. This is very useful especially for the study of magnetic multilayers and alloys. Furthermore, the XMCD measurements can be quantitatively evaluated via sum rules to obtain the spin and orbital magnetic moments and their anisotropies. Figure 4 shows images obtained from a Co film deposited on a patterned Si substrate.
Fig. 4. XMCD-PEEM images of a Co film deposited on a patterned Si substrate, measured at the Co L₃ edge. (a) and (b) show the images taken with negative and positive helicity, respectively; (c) is the difference image between the two images. (d) Co L₂₃ edge absorption spectra measured on the same sample with photons of positive helicity. The spectrum indicated by the dashed line was measured on an area where the magnetization was parallel to the helicity vector of the X-rays (equivalent to a bright area in Fig. 4 (b)), while the spectrum indicated by the full line was measured in a dark area. The intensity difference in the spectra at the Co L₃ edge explains the contrast observed in the image shown in Fig. 4 (b). At the Co L₂ edge, the spectral intensity is inverted, which reflects also in a contrast inversion in the XPEEM image (not shown here). Inverting the helicity of the X-rays, the two spectra show an inverted behaviour (not shown here), which reflects in the contrast inversion observed between the images in Fig. 4 (a) and (b). In a similar fashion as XMCD, also the X-ray magnetic linear dichroism can be employed for the study of antiferromagnetic thin films.¹⁴

5. Temporal Resolution

From video rate, the temporal resolution of PEEM can be dramatically enhanced by a pump and probe approach with two pulsed excitation sources which are synchronised for stroboscopic imaging. Using a laser for pumping (the width of the laser pulse can easily be less than 1 ps, down to some fs), the X-ray pulses from a synchrotron can be used for probing. In a third-generation synchrotron, the X-ray pulses have a typical width of 50–100 ps (At BESSY-II operated in low alpha mode, even sub-ps X-ray pulses are already available.¹⁵). In multi-bunch operation of the light source they are repeated every few ns, which is too short for most experiments, given the X-ray pulse width. However, when the synchrotron is operated in single bunch mode, the distance between X-ray pulses is around 1 µs, which is sufficiently long compared to the X-ray pulse width.

Recently the pump and probe technique has been used in combination with XMCD-PEEM to obtain the response of a magnetic pattern to a short (~ns) external magnetic field pulse, which has been synchronized to the X-ray pulses. The vortex dynamics of Landau patterns has been measured with sub-ns-resolution.¹⁶⁻¹⁸ Other groups have investigated the magnetic switching of spin-valve samples¹⁹ and the magnetization processes in a permalloy ring.²⁰

The principle of these experiments is sketched in Fig. 5: The pump pulse excites the sample, after a
constant delay $\Delta t$ the X-ray pulse from the synchrotron probes the sample, and then the sample returns to its initial state before it is pumped again. Averaging over many pulses allows to obtain images with a useful signal-to-noise ratio. This method can therefore be applied only to systems which return to their initial state between two probe pulses. By changing $\Delta t$, the temporal evolution of the sample can be obtained with a time-resolution given by the X-ray pulse width. Using the combination of a Ti:sapphire laser and a PEEM, the surface plasmon dynamics in nanoscale roughness on a silver grating has been investigated with sub-fs temporal resolution.\textsuperscript{21)} Pulse length of some ten fs are expected for X-ray free electron lasers (XFEL) which are now under construction in several places worldwide. Furthermore, XFEL sources will deliver such a high photon flux that single shot measurements will become feasible, which would allow to achieve fs-time resolution even with samples which show non-periodic behaviour.

6. Energy Filter

Two principal ways lead to an energy analysis of the photoelectrons with lateral resolution. One possibility is to perform area selective spectroscopy: an aperture is used to select an interesting region within the field of view of the microscope. Photoelectrons from other parts of the sample are blocked, and only the photoelectrons from the interesting region can reach the analyzer. Therefore, the PEEM acts as a high-performance transfer lens for the analyzer. The diameter of the analyzed region can be as small as 1 µm. A commercial energy analyzer (hemispherical or cylindrical) can be used for this purpose, which allows to rely on tested standard equipment. An energy resolution of 190 meV has been demonstrated with such setup.\textsuperscript{22)}

The second possibility is to filter the whole PEEM image energetically. Several methods have been proposed to achieve this goal. In a simple setup, a mesh is inserted in the PEEM. If the mesh is biased, only photoelectrons with a kinetic energy higher than the bias can pass the mesh which therefore acts as a high-pass filter. By taking two images at slightly different bias and calculating their difference, energy-filtered images can be reconstructed (spectromicroscopy). By increasing the bias of the mesh, more and more photoelectrons are cut out, and the energy spread in the image is reduced. By differentiation, the energy distribution curve of the photoelectrons from the sample can be obtained from an area as small as 1 µm (microspectroscopy). An energy resolution of about 1 eV is reported for this setup with synchrotron and laboratory X-ray sources.\textsuperscript{23)}

In a more sophisticated setup, the whole PEEM image is energy filtered by a band-pass filter, i.e. only electrons with a certain energy $E \pm \Delta E$ can contribute to the image. Different solutions have been proposed and realized.

In a time-of-flight (TOF) analyzer, photoelectrons excited by a pulsed light source are dispersed by the time $T$ they need to pass a drift tube of length $L$ with a velocity $v = L/T$. The dispersion is given by $dT/dE$ with $E = \frac{m}{2} v^2$ ($m$: electron mass). For $L = 30$ cm we obtain a variation of $dT/dE$ from 8 ns/eV at 10 eV to 0.25 ns/eV at 100 eV. Therefore, the single light pulses should be separated at least by some 10 ns in order to avoid an overlap of spectra from consecutive pulses, which means that measurements with TOF require a synchrotron operated in single- or few-bunch mode. Obviously, this kind of PEEM requires a detector with high temporal resolution, which is the main technical difficulty in this approach. With a delay line detector, a time resolution of 0.5 ns has been achieved,\textsuperscript{24)} which corresponds to a theoretical energy resolution of 60 meV at 10 eV and of 2 eV at 100 eV. In first test experiments, an energy resolution of 400 meV at 43 eV has been achieved, while a lateral resolution of less than 100 nm has been reported.\textsuperscript{24)} In the future, PEEM systems with TOF analyzer might become very useful in combination with XFEL sources.

A Wien filter uses electric and magnetic fields...
which are perpendicular to each other so that only electrons with a particular energy can pass the filter without deflection.\textsuperscript{25} Although an energy resolution of 0.1 eV has been calculated for this design, only 1 eV has been demonstrated so far, mainly because at higher resolution the intensity would be unacceptably low.

The analyzer type most commonly used in photoelectron spectroscopy is the electrostatic spherical energy analyzer. Such analyzers were also combined with PEEM. Systems with 90° analyzer\textsuperscript{26} and 180° analyzer\textsuperscript{6} have been built and successfully operated. A combination of two 90° analyzers has been proposed,\textsuperscript{27} as has a system of two opposite concentric spherical deflectors connected by a relay lens.\textsuperscript{28} Recently a double hemispherical 180° analyzer has been built and connected to a PEEM (NanoESCA).\textsuperscript{29} The NanoESCA provides a high transmission even at high photoelectron kinetic energies and is therefore particularly suited for use with laboratory X-ray sources (Mg K\textsubscript{α} and Al K\textsubscript{α}). Electrostatic spherical analyzers in connection with PEEM have demonstrated an energy resolution of better than 200 meV.\textsuperscript{29, 30}

An Omega filter consists of four sector magnets arranged in the form of the greek capital letter Omega. It is used in the SMART microscope at BESSY-II. A best energy resolution of 0.1 eV has been calculated, and 0.5 eV have been achieved so far with this analyzer.\textsuperscript{3}

7. SPELEEM

Most of the results in photoelectron spectroscopy using a PEEM published so far have been obtained with electrostatic hemispherical analyzers. A schematic drawing of such an instrument is shown in Fig. 6. It is a commercial LEEM system with an energy filter, based on a design by Veneklasen and Bauer, and has been named spectroscopic photoemission and low energy electron microscope (SPELEEM). Such instruments are operational in Elettra,\textsuperscript{6} the Swiss Light Source,\textsuperscript{31} and SPring-8,\textsuperscript{32} and several other synchrotron light sources are preparing to install a SPELEEM, as well. The SPELEEM is a LEEM/PEEM with full spectromicroscopic capabilities. The analyzer has a radius of 100 mm and is operated with a pass energy of approximately 900 V. Besides LEEM and LEED, the use of an electron gun and an energy analyzer allows measurement of the energy distribution of the electrons (electron energy loss spectroscopy (EELS)) from a micrometer spot on the sample. In complete analogy to this, three modes of operation are available when working with photons: Imaging PEEM (spectromicroscopy), dispersive plane imaging (microspectroscopy), and diffraction mode (photoelectron diffraction (PED)).\textsuperscript{6}

In the imaging PEEM mode, the photoelectrons from the sample are collected, selected in energy, and projected on a phosphorous screen where a magnified image of the sample surface is displayed and recorded by a CCD camera. The best lateral and energy resolution are 22 nm and 250 meV, respectively.\textsuperscript{6, 30} In each image the intensity represents the photoelectron yield at a fixed kinetic energy relative to that specific location. For each pixel it is possible to plot the intensity as a function of energy, thereby obtaining local photoemission spectra. The images are isochromatic within 0.1 eV, i.e. within 0.1 eV each pixel of the image corresponds to the same energy.\textsuperscript{30} The spectra shown in Fig. 3 have been obtained in this way.

In dispersive plane imaging, all the photoelectrons originating from a micrometric region of the sample are collected and dispersed in energy by the hemispherical analyzer. Electrons with different energies are then projected on different regions of the phosphorous screen along a line. The intensity along the projected line corresponds to the photoemission spectrum. A best energy resolution of 150 meV has been achieved in this mode.\textsuperscript{30} The dispersive plane mode, although at the expense of lateral resolution, has the advantage of faster acquisition times (of the order of seconds for a complete spectrum) which allows a fast time resolved analysis. To illustrate this point, Fig. 7 shows a time-resolved series of dispersive plane spectra from the As 3d core level of a GaAs sample which was measured at a photon energy of 130 eV. The component in the spectra at lower kinetic energy

![Fig. 6. Schematic drawing of the SPELEEM instrument.](image-url)
Fig. 7. As 3d core level spectra, taken in dispersive plane mode, from the native oxide of a GaAs sample, as a function of exposure time to X-rays of 130 eV.

corresponds to emission from As-oxides in the native oxide of the sample, while the component at higher kinetic energy corresponds to bulk GaAs from the substrate. Due to exposure to X-rays, the native oxide partially desorbs, which results in a decrease in the intensity of the oxide component and a corresponding increase in the intensity of the substrate component. For details, see Ref. 33.

8. Aberration Correction

While all methods to improve the lateral resolution of the PEEM discussed so far did not eliminate the aberrations of the lenses but reduced their influence on the expense of transmission of the microscope, the ideal solution would be to build an optical system without aberrations. However, in contrast to light optics in the visible where aberrations can be corrected by a lens combination (achromat), Scherzer demonstrated already in 1936 that all conventional electron lenses have aberrations of the same sign, and therefore it would be impossible to construct an electron-optical achromat with conventional electron lenses.

Several methods have been proposed to overcome this limitation and to build aberration corrected electron microscopes. The moving focus method improves the lateral resolution of the electron microscope by a superposition of images taken at different focus values. The time-of-flight technique reduces chromatic aberrations with a fast switching lens field. Electrons with different energies (which give rise to chromatic aberrations) have different velocities and pass therefore the corrector at different times. If the corrector is fast enough, it can change the focal properties of the lens so that all energies are focused in the same point. A correction of spherical aberrations with this approach, however, seems much more complex. Multipole lenses are already successfully employed in scanning and transmission electron microscopes, and sub-Å resolution has been demonstrated. A similar approach, using a multipole Wien filter, is now under development for PEEM. Finally, the use of an electron mirror has been proposed for aberration correction in PEEM and LEEM. While all conventional electron lenses have aberrations of the same sign, an electron mirror (like the multipole lenses) produces aberrations of the opposite sign and allows therefore to compensate for the aberrations of the lenses.

A new generation of aberration-corrected PEEMs is under construction: the SMART project at BESSY-II and the PEEM 3 project at the ALS. Both instruments will use an electron mirror for aberration correction. For the SMART microscope, a best lateral resolution of 0.5 nm has been calculated. Alternatively, at a lateral resolution of 10 nm the calculated transmission of the SMART will be 3,000 times higher than that of an uncorrected PEEM with the same resolution. For the PEEM 3, the highest resolution predicted is 5 nm at 2 % transmission, while a transmission of ≈ 30 % has been calculated at a resolution of 20 nm. This has to be compared to a transmission of 1 % for the uncorrected PEEM 2 at its resolution limit of 20 nm.

9. Summary

PEEM is now an established technique for X-ray spectroscopy with high lateral resolution and for the imaging of magnetic domains. PEEM systems with energy filter are already commercially available. Soon the first aberration corrected PEEM systems will be operational, and fs-PEEM in combination with XFEL sources will become a standard technique for the imaging of fast dynamic processes at surfaces with some 10 nm-resolution.

Acknowledgements


References


