



2332

School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

19 - 30 March 2012

Additional information lecture Dr. M. Kiskinova

M. Kiskinova Sincrotone, Trieste



Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research A

journal homepage: www.elsevier.com/locate/nima

Synchrotron-based photoelectron microscopy

Alexei Barinov, Pavel Dudin, Luca Gregoratti, Andrea Locatelli, Tevfik Onur Menteş, Miquel Ángel Niño, Maya Kiskinova *

Sincrotrone Trieste, Area Science Park, Trieste 34012, Italy

ARTICLE INFO

Available online 3 January 2009

Keywords: X-ray photoemission electron microscopy Scanning photoelectron microscopy Surfaces Interfaces Surface reactions Nanostructures

ABSTRACT

The paper is a brief overview of the operation principles and the potentials of the scanning photoelectron microscopes (SPEM) and X-ray photoemission electron microscopes (XPEEM) operating at synchrotron facilities. Selected results will illustrate the impact of high spatial resolution for micro-characterization of the surface composition and electronic structure, a key issue for analysis of technologically relevant materials and for fundamental understanding of many unexplored surface phenomena.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

X-ray photoelectron spectroscopy (XPS), born more than a half century ago in Uppsala and recognized with the Nobel prize in physics granted to Kai Siegbahn in 1981 [1], has remained the best method for probing the composition and electronic structure of solid surfaces and interfaces. Using conventional X-ray tubes the yield of the photoelectrons emitted from the atomic electron levels is relatively low, which has imposed severe limitations on the spatial resolution of the laboratory XPS machines [2]. This major obstacle in development of the XPS microscopy has been overcome with the construction of the third generation synchrotron facilities. They provide ultra-bright and tunable photon beams, which is of fundamental importance to push the XPS lateral resolution into submicrometer length scales, maintaining a sufficient signal level and an acceptable acquisition time [3].

In the modern XPS microscopes operating at the synchrotron facilities the high spatial resolution is achieved by either, magnifying the image of the irradiated surface area or demagnifying the incident photon beam. The instruments using a suitable electron optical imaging system for magnification and projection of the emitted electrons are called X-ray photoemission electron microscopes (XPEEM). The instruments using X-ray photon optics for demagnifying the photon beam to submicrometer dimensions are called scanning photoelectron microscopes (SPEM), because the images are formed by scanning the sample with respect to the focused beam. These microscopes use the power of the surface sensitive photoelectron spectroscopy to obtain chemical characterization of the systems under investigation with submicron spatial resolution and probing depth up to a few tens Å. The scientific and technological impact of the synchrotron-based XPS microscopes derives from their ability to study surfaces, interfaces and thin films as well as complex surface phenomena at or below the micron scale.

In the present article after a brief overview of the operation principles, advantages and limitations of the two types of XPS microscopes, we will demonstrate their possible applications and illustrate the achieved performance level using selected case studies.

2. Operation principles of synchrotron-based XPS microscopes

2.1. X-ray photoemission electron microscopy—XPEEM

The emergence of third generation synchrotron sources determined the renaissance of photoelectron emission microscopy (PEEM), whose invention dates from the early 1930s [4]. XPEEM combines the photoemission microscope with the use of soft X-ray synchrotron radiation. Compared to laboratory PEEM, which uses UV sources and images spatial variations in the work function, XPEEM provides a true chemical sensitivity by employing the intense and tunable soft X-ray sources. This has been achieved by implementing laterally resolved versions of X-ray absorption and photoelectron spectroscopy (XAS and XPS). XAS-PEEM is finding use in an increasing number of applications ranging from material science to geology and biology. Since it measures the secondary electron yield as a function of the photon energy, the experimental set-up is relatively simple and energy filter is not needed. Making use of the polarization of the synchrotron light, X-ray magnetic circular and linear dichroism

^{*}Corresponding author. Tel.: +390403758549; fax: +390403758565. *E-mail address:* maya.kiskinova@elettra.trieste.it (M. Kiskinova).

^{0168-9002/\$ -} see front matter \circledcirc 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.nima.2008.12.157

(XMCD and XMLD) have become one of the most required methods for probing the magnetic state of surfaces and interfaces with elemental sensitivity and submicrometer resolution [5,6]. On the other hand the implementation of an energy filter is required for performing XPS microscopy at constant photon energy [7–9]. The presence of the energy filter also reduces the chromatic aberrations in the electron optics [10]. This improves the spatial resolution allowing chemical imaging with a lateral resolution of a few tens nm. Important applications of XPEEM have been described in several reviews, to which we address the reader who is interested in more details [5,6,11,14].

In the more advanced instruments, PEEM can be coupled with complementary low energy electron microscopy (LEEM) and micro-spot low energy electron diffraction (LEED), thus enabling structural sensitivity [12,13].

Fig. 1 shows the principle construction of an XPEEM microscope with XPS and LEEM capabilities. The microscope uses a combination of electrostatic and magnetic lenses to image a specimen illuminated with X-rays. The magnified image of the sample is projected onto a phosphorus screen, where it is converted to visible light and finally collected by a CCD camera. The lens system in front of the electron energy filter (hemispherical in this case) allows selection of the operation mode, described in details in Ref. [7]. By focusing onto the image plane at the beam separator both LEEM and energy-filtered XPEEM imaging modes are possible, depending whether electrons or photons are used as probe. XPEEM can reach an energy resolution of 0.3 eV, and lateral resolution of few tens nm [9]. The same optical system can also image the diffraction pattern at the objective back-focal plane. This operation mode allows LEED, photoelectron diffraction (PhD) and angle-resolved photoelectron spectroscopy (ARPES), as demonstrated in the last section of this article. All measurements are restricted to an area of a few μm^2 by inserting an area selecting aperture. Another important operation mode is micro-spectroscopy. Here, the dispersive plane of the analyzer is imaged while the column focuses the aperture at the beam separator. In this mode the spectral resolution is higher (0.2 eV) than in the energy filtered mode, at the expense of the relatively modest spatial resolution.

2.2. Scanning PhotoElectron Microscopy (SPEM)

In the scanning approach the X-ray photon optics demagnifies the incident photon beam to a small spot onto the sample, and an



Fig. 1. Sketch of an instrument combining LEEM and energy-filtered PEEM. Reproduced with copyright permission from Ref. [14].

image is acquired by detecting the photon or electron signal while rastering the sample. The microprobe in the scanning X-ray microscopes is formed using reflective (glancing or near-normalincidence mirror systems) or diffractive optical elements (zone plates) [3,15,16]. No 'universal' focusing optics exists and a proper choice has to be made considering the application, the required spatial resolution and the photon energy and flux in the microprobe. Since the microprobe is a strong function of the source size, pushing the microproprobe sizes below a micrometer has become possible using the collimated photon beams, provided by the insertion devices at the synchrotron facilities. For the soft X-ray range used by the surface sensitive XPS microscopy, a Schwarzschild spherical mirror objectives, coated with multi-layers optimized for a selected wavelength [3,17-19] or zone plate diffractive lenses are most commonly used ones [3,8]. The Schwarzschild objectives, being normal incidence mirrors are suitable only for longer wave lengths (phonon energy below 100 eV). The zone plates offer the best compromise of spatial resolution and flux in the focal spot. The basic relationship describing the zone plate performance is $f=D\Delta r/\lambda \approx D\Delta r/1240$ E(eV), where f is the focal distance for the first order diffraction, D is the diameter of the zone plate, Δr is the width of the outmost zone, which determines the size of the microprobe, λ and *E* are the photon wavelength and energy, respectively. The requirement for sufficient working distance between the optical system and the sample (more than a few mm) in order not to obstruct the path of the emitted photoelectrons to the analyzer, imposes wavelength limitations for the zone-plate XPS microscopes-they work usually at photon energies above 250 eV [3,8]. In brief, SPEMs using Schwarzschield objectives and zone plates are complementary: the first one is very well suited for probing valence band and shallow electron levels, whereas the second one is excellent for probing deeper core electron levels. The relaxed working distance in SPEM with Schwarzschild optics allows implementation of a second analyzer for angular resolved valence band photoelectron microscopy. It should be noted that SPEM with zone plates can work also in total electron yield, adding complementary XANES, but this needs implementing a synchronized moving of the optic system to keep the sample in focus.

Fig. 2 shows a schematic drawing of a SPEM microscope. The main difference compared to classical XPS instruments is that the sample has fixed normal incidence geometry, imposed by the use of focusing optics, and grazing acceptance angle (usually 55 ± 5) of the analyzer, which enhances the surface sensitivity. The SPEM has two operation modes, microspot spectroscopy and imaging spectromicroscopy. The microspot mode is identical to the XPS spectroscopy, i.e. energy distribution curves are measured from



Fig. 2. Sketch of SPEM instrument with a hemispherical energy analyzer and zone plate (ZP) optics. The central stop of the ZP and the order sorting aperture (OSA) cut the undesired zero and the diffraction orders higher than one.

the selected micro-spot area. The great advantage of the photon tunability is that one can optimize the photoelectron yield, considering the elements contained in the sample. The imaging mode maps the lateral distribution of elements by collecting photoelectrons with a selected energy while scanning the specimen with respect to the microprobe. The potential and efficiency of the SPEM instruments have been significantly improved by implementation of multi-channel electron detectors, where each channel measures electrons with specific kinetic energy, defined by the selected energy window [20]. This has allowed simultaneous collection of images equal to the number of the channels and adds a spectro-imaging option, i.e. the reconstruction of the spectrum corresponding to the covered energy window from a selected micro-area.

2.3. Comparison of the performance of XPEEM and SPEM

Both XPEEM and SPEM map energy and intensity variations in the emission from core or valence levels. Such spectral imaging reveals the local composition, along with the chemical or electronic state of the specimen under consideration. Depending on sample-analyzer and illumination geometries, the topography of the surface can also contribute to the intensity of the emitted electrons due to enhancement and shadowing effects. These topographic artifacts can be removed by processing procedures involving subtraction and division by the secondary electron background [21]. However, useful information on the specimen is often provided by correlating topographic and chemical images.

XPEEM and SPEM have their respective advantages and limitations. In SPEM the lateral resolution is determined only by the focusing optics. Achieving lateral resolution better than 50 nm is still a big challenge, mainly due to signal and working distance constraints [21]. The lateral resolution of SPEM is the same in imaging and micro-spot spectroscopy modes, which are separate measurements. This allows independent optimization of each mode concerning energy resolution and acquisition time. The lateral resolution of XPEEM is limited by the spherical and chromatic aberrations of the electron optics, and at the state of art reaches few tens nm [13]. Such figures are obtained by reducing the angular acceptance of the microscope, i.e. limiting considerably its transmission. The imminent introduction of microscopes implementing aberration correction will offer simultaneous improvement of the transmission and lateral resolution, reaching only few nm.

From the practical point of view, SPEM is insensitive to the sample size and topography. On the contrary, XPEEM requires reasonably flat surfaces and the absence of field emitters and tips, which may produce discharges due to high voltage bias between sample and objective lens (in the range 10–20 kV).

An advantage of SPEM over PEEM is that the scanning approach allows different detection modes, e.g. measuring sample current or adding X-ray detectors for monitoring transmitted or emitted photons. SPEM experiments where external potentials are applied in situ to the samples are also feasible [22–24].

The strength of instruments combining XPEEM with LEEM is that it is possible to implement a real multi-method approach to the study of surfaces, adding structure sensitivity to the PEEM [10]. These instruments, incorporating parallel image acquisition of the full field, provide an excellent tool for investigation of dynamic processes in real time. On the other hand, due to sequential detection, scanning instruments can image only slow processes.

In brief, the complementary capabilities in terms of spectroscopy, spatial and time resolution of XPEEM and SPEM have already been used for various multi-disciplinary studies at the synchrotron facilities. The next section illustrates the recent achievements using these instruments.

3. Application examples

3.1. Morphologically complex metal/semiconductor interfaces

Semiconductor interfaces make up an important class of systems, in which lateral inhomogeneity in the morphology and/ or composition can exert spatial variations in their electronic properties (e.g. Schottky barrier heights), mass transport phenomena etc. A great number of SPEM studies have been dedicated on the interfacial chemistry, electronic properties, as well as super-imposed effects of temperature and electric fields on the surface diffusion. In many studies we prepared confined metal films of sizes of tens to hundreds μm , deposited through appropriate masks. Using the unique potential of photoelectron spectromicroscopy to probe selectively the evolution of the regions inside and outside the deposited patch one has always the reference of the atomically clean semiconductor surface. Exploring the area across the edge of the confined films, which usually expand over a few µm, we were able to follow the evolution of the interfacial composition and band-bending as a function of metal coverage and the mass transport phenomena after processing at different temperatures or applying external potentials.

3.1.1. Ni/Si interfaces

The first example concerns investigations focused exclusively on identifying the lateral distribution and composition of different phases formed during interfacial reactions at various temperatures and metal coverage. The Ni/Si interface is a typical example of the occurrence of different silicide phases growing nearly epitaxially on the Si substrate [25]. The desired phase is NiSi₂, since its resistance is preserved with shrinking dimensions of the interconnect line width [26]. According to earlier structural analyses with electron microscopy and chemical analysis with laterally resolved X-ray spectroscopy and scanning Auger electron spectroscopy, a few nm thick NiSi2 islands and a diluted two dimensional (2D) phase with Ni coverage less than 0.15 ML form after annealing of deposited thin Ni films [27]. The applied chemical methods, being limited in surface and/or chemical sensitivity, were not able to distinguish the intermediate NiSi phase, since it is structurally similar to the equilibrium NiSi, one. SPEM results have identified the coexistence of metastable intermediate NiSi islands, since they showed distinctly different Si 2p and valence band spectra [28,29].

Fig. 3 shows large and small area Ni 3p chemical maps taken after annealing of a 2 ML Ni film deposited on a Si(111)-7 \times 7 surface. The reaction at the temperature range 700-800 °C results in formation of silicide islands surrounded by a dominant a (1×1) -RC 2D structure, consisting of alternating nm rings of 0.04-0.14 ML Ni adsorbed on Si and Ni-free Si (not resolved by our spatial resolution) [30]. As can be seen in Fig. 3 the 2D phase dominates the surface and the variations in the Ni content are reflected by the variations in the contrast level of the Ni 3p maps. The brightest elongated and round features in the Ni 3p map are the Ni-rich silicide islands. The elongated ones are oriented exclusively in the $\langle 110 \rangle$ direction and according to the concentration profiles they contain less Ni. The concentration profiles also show a distinct Ni-depleted zone of $\sim 2 \,\mu m$ around the islands, resulting from the mass transport of Ni atoms dragged to the islands during the interface reaction.

The different composition and consequently electronic structure of the two types of islands have unambiguously been



Fig. 3. (a) 20×20 and $5 \times 8 \mu m^2$ Ni 3p maps and intensity profiles, corresponding to the round, 1, and elongated, 2, islands, respectively. (b) Si 2p and valence band (VB) spectra of round (top), elongated (middle) 3D islands and the 2D phase (bottom). In the deconvoluted Si 2p spectra the grey-filled component corresponds to the non-reacted Si cap on top of the islands or bulk Si for the 2D phase.

confirmed by the Si 2p and valence band spectra shown in Fig. 3(b). As can be seen each of the coexisting phases, NiSi and NiSi₂ islands and the dominant 2D Ni adsorption phase, is characterized by a Si 2p spectrum with a specific lineshape, determined by the Si 2p chemical shifts undergone by the Si atoms bonded to Ni. The Si 2p spectra and the valence band of the elongated islands contain the characteristic features of the NiSi2 phase, namely the components, shifted by -0.55 and 0.3 eV with respect to the Si bulk component and a dominant peak at ~3.1 eV in the valence spectra [31]. The Si 2p spectra and the valence band of the round islands correspond to NiSi, characterized by components shifted by -0.1 and 0.4 eV with respect to the Si bulk component and unresolved double structure at ~ -1.8 and -2.7 eV in the valence band. The assignment of the islands as NiSi and NiSi₂ was also supported by the intensity of the Ni 3p signal (see the profiles in Fig. 3(a)) and the energy shifts of the Ni 3p spectra (not shown) [28]. Comparing the Si 2p spectra from the islands a distinct feature is the high intensity of the bulk Si component in the spectra from the NiSi₂ islands, with its relative weight varying with different islands. This was not the case with the NiSi islands where the weight and variations of Si component were relatively small. Since the islands thickness is larger than the probing depth this Si component is identified as segregated Si capping the islands. This is favored by the much lower surface energy of Si than that of NiSi₂ [25] and apparently the amount of segregated Si depends on the actual size and thickness of the islands. Another important information, contained in the Si 2p spectra is that the Si 2p bulk component of the (1×1) -RC phase is shifted to higher-binding energy by -0.2 eV compared to the Si 2p bulk position in Si(111)-7 \times 7 and NiSi₂. This shift is induced by the band-bending.

3.1.1. Metal/GaN interfaces

Extended studies have been performed with metal/GaN(000 1) interfaces exploring the band-bending shifts as a function of metal coverage and interfacial reactions occurring with increasing temperature. The determination of the Schottky barrier heights is based on the simple mechanism of band bending, which leads to an energy shift of the photoelectron spectrum independent of the transport mechanisms across the barrier [32]. All experiments were performed with films deposited through masks, i.e. always



Fig. 4. (a) Surface plot illustrating the changes in the intensity and energy position of the Ga 3d spectra taken across the edge of a patch of a 3 ML thick Au film (the dark region in the Ga 3d map). (b) Evolution of the Ga 3d spectra after deposition of a 4 ML Ni film at 30 °C and following annealing to 300 °C. The Ga 3d spectra of the GaN substrate outside the patch are shown on the bottom. The dashed line BB indicates the band-bending shift. The filled component corresponds to the reacted Ga, R-Ga.

having the metal-free GaN area as a reference. The selected for these studies interfaces Au–GaN, Ni–GaN and Ti–GaN exhibit different reactivity, i.e. Au and Ni form gallides and the onset of the reaction is at 500° and 300 °C, respectively, whereas Ti forms nitrides, the reaction starting already at room temperature [33–35].

Fig. 4(a) shows a surface plot of the Ga 3d spectra reconstructed from the Ga 3d image centered at the Au patch edge. This plot visualizes the typical trend in the Ga 3d energy position and intensity changes as a function of the metal coverage. The energy shift reflects the Au-induced band-bending (BB), whereas the attenuation of Ga 3d intensity results from screening the Ga 3d emission with increasing metal film thickness. Increasing the temperature results in formation of metal gallides or nitrides. The barrier heights change correspondingly, as illustrated by the spectra for Ni/GaN interface in Fig. 4(b) and the plots in Fig. 5(a). In all cases the best fingerprint for the local reactivity is the amount of the released Ga, which is easily



Fig. 5. (a) Temperature-induced changes in the band-bending measured from the Ga 3d shifts inside the Au/GaN, Ni/GaN and Ti/GaN patches. Filled and open markers show the data from spots on defect and non-defect areas. (b) Ti 2p, N 1 s and R-Ga 4d images in a defect-rich region of the Ti/GaN interface. (c) Ga 3d map, taken in a defect-rich area before Ni deposition, and Ni 3p and R-GaN images after Ni deposition and annealing to 300 °C.

distinguished as a new component, R-Ga, in the Ga 3d spectra (see Fig. 4(b)).

The common feature observed for all three interfaces is the development of lateral heterogeneity in the composition, related to morphological and crystallographic irregularities of the GaN epilayers, e.g. grain boundaries, voids etc, which appear more reactive centers. Selected images in Fig. 5(b, c), measured on Ti/ GaN and Ni/GaN interfaces, show that the metal-enriched regions contain also more R-Ga (and N in the case of Ti) in accordance with the higher local reactivity. One can clearly see the correlation between the presence of defects, appearing as dark holes in the Ga 3d map in Fig. 5(c) taken before Ni deposition, and the Ni-and R-Ga enriched areas developed after annealing to 300 °C. However, contrary to the expectations the lateral chemical heterogeneity exerts negligible influence of the on the local BB, as illustrated by the spectra taken from 'defect' and 'non-defect' areas in Fig. 4(b) and the plots in Fig. 5(a). We have tentatively attributed this insensitivity of the Schottky barrier heights to charge redistribution between the different interfacial regions, which smoothens the potential fluctuations [35].

3.2. Nano-particles and nano-structures

Addressing the surface composition of nano-particles, microparticles and, in general, nano-structured materials is an important chain in understanding their exotic properties. Recently we explored the oxidation of Rh particles with a very broad size distribution and of pure and metal covered multi-walled C nanotubes.

3.2.1. Rh micro- and nano-particles deposited on a support

Comparing the oxidation states of different Rh particles, from a few micrometers to a few nm, attained after the same oxygen exposures and temperatures has unraveled their relevant reactivity. The well established procedures for pulsed laser deposition of Rh on MgO or SiO2 supports allowed reproducible fabrication of samples, containing isolated, randomly distributed Rh microparticles (from ~0.3 to a few μ m), surrounded by areas of dispersed nano-particles with dimensions from a few to a few tens nm. Fig. 6 shows the Rh 3d images of such samples and representative Rh 3d_{5/2} spectra taken from two particles and the area with dispersed nano-particles after mild oxidation. The Rh micro-particles can be distinguished as defined brighter features in the Rh 3d_{5/2} maps, whereas the presence of the nano-particles between them was verified with AFM. Examination of the surface



Fig. 6. (left) Large and small area Rh $3d_{5/2}$ images taken after PLD of Rh on MgO support. The AFM image shows the nano-particles covering the areas between the micro-particles. (Right) Rh $3d_{5/2}$ spectra from the area with nano-particles 1, and from micro-particles 2 and 3, taken after mild oxidation (20 min at 210 °C). The bottom spectrum is taken from metallic nano-particles.

morphology of the micro-particles by SEM revealed that, whereas some of them exposed well defined grains others appear more facetted or rougher [36]. This prompts that the particles may exhibit variable reactivity. Indeed, comparing the oxidation states of different particles after identical oxidation treatments, we observed significant variations in the oxidation state, not correlated to the actual size of the micro-particles. Fingerprints of the oxidation states are the distinct Rh 3d_{5/2} components for the transient 'surface oxide' RhO_x and the two stoichiometric oxides, Rh₂O₃ and RhO₂ [37-39]. The difference in the relative weight of the oxide component in the deconvoluted Rh 3d_{5/2} spectra of the two micro-particles of almost the same size $(\sim 1 \,\mu m)$ clearly illustrates the utmost importance of particle morphology over size. The Rh $3d_{5/2}$ spectra from the nanoparticles show distinct shape and energy differences, both in the oxidized and the reduced state. Size-dependent core level shifts below certain critical particle dimensions, inhomogeneous broadening, since for the relatively large SPEM spot $(\sim 3 \times 10^{-2} \mu m^2)$ probes nano-particles with broad size distribution, and final state effects account for the spectral shape [40]. It should be noted that for the two oxide phases higher BE values were reported for supported Rh nano-particles [41]. For deconvolution of these Rh $3d_{5/2}$ spectra we used two components: a fixed Rh or RhO_x component (analogous to the ones used for the micro-particles), which accounts for nanoparticles larger than the critical size, and a second broad component, which accounts for those with size-dependent binding energy deviations. The actual oxidation state of the nano-particles cannot be exactly defined, since we cannot discriminate the size-induced shift, which is not necessarily the same as for the metallic state. However, comparing with the spectrum of completely reduced metallic nano-particles one can clearly see that the oxidized nano-particles contain no metallic component, supposing that no metallic core has remained.

We were able to monitor heterogeneity in the oxidation state even within the same micro-particle, which we suppose was an aggregate consisting of smaller particles, occasionally observed with AFM and SEM. Fig. 7 shows representative Rh 3d_{5/2} spectra and the Rh 3d_{5/2} images of such micro-particle, explored with sub-micrometer resolution. The Rh 3d_{5/2} spectra of the oxidized



Fig. 7. Rh $3d_{5/2}$ spectra (right panel) after oxidation (30 min at 210 °C), taken in two different areas of the micro-particle, indicated in the Rh $3d_{5/2}$ image (right-bottom). The A and B images correspond to the Rh $3d_{5/2}$ photoelectrons emitted within the narrow energy windows A and B, indicated in the spectra panel. They outline the regions of the higher (A) and the lower (B) oxidation state.

particle, taken in spots 1 and 2 of the Rh $3d_{5/2}$ map clearly evidence that the left-hand side of the particle is in a more advanced oxidation state. This is confirmed by the maps A and B, corresponding to the two narrow Rh $3d_{5/2}$ energy windows, 308.7-309.1 eV, dominated by emission from the RhO₂ phase and 306.8-307.2 eV, dominated by emission from metallic Rh atoms below the oxide layer.

3.2.2. Carbon nano-tubes

Among the recent achievements are the characterization of nano-structured materials, including C- and MoS_x-based nanotubes, SnO₂ nano-wires and nano-belts, GaAs nano-wires etc. [24,42-45]. The high spatial resolution allowed us to visualize individual nano-structures and select the areas for systematic spectroscopic measurements along their axes. An important finding in these studies is the position dependence of the photoemission valence and core level spectra of aligned C and MoS₂ nano-tubes, reflecting the different structural organization along the wall and the tips [42,45]. Recently, we are exploiting the chemical and morphology changes of aligned C nano-tubes, occurring as a result of oxidation at different temperatures. Depending on the oxygen dose and reaction temperature different oxygenated functional groups have been identified and at elevated temperatures gasification and consumption of the C nano-tubes have been observed. We also found that the gasification process is promoted by the presence of metal that was on purpose deposited on the C nano-tubes. Fig. 8(a) shows a typical cross-sectional C1s image of aligned C nano-tubes, grown on a Si substrate with postdeposited Ag. Identical image was observed tuning the analyzer to the Ag 3d_{5/2} emission, which was in accordance with the SEM images showing randomly distributed Ag clusters on the nanotubes surface. The spectra taken from an individual nano-tube and displayed in Fig. 8(c) confirm only the presence of C and Ag. The Ag 3d_{5/2} peak is positioned at a binding energy of 368.4 eV corresponding to metallic Ag. The exposure to oxygen plasma at elevated temperatures results in gradual consumption of the C



Fig. 8. (a) C 1 s image of the C nano-tubes covered with a thin Ag film, taken before exposure to oxygen plasma; (b) Ag $3d_{5/2}$ image taken after gasification and consumption of the C nano-tubes. (c) Ag $3d_{5/2}$, C 1s and O 1s spectra taken on the indicated spots in the images before oxygen exposure, 1, and after gasification, 2.

nano-tubes, the reaction stating from the tips. In the presence of Ag the process is accelerated and occurs at lower temperature as well. As illustrated by the Ag $3d_{5/2}$ image in Fig. 8(b) and the corresponding C 1s, O 1s and Ag $3d_{5/2}$ spectra in Fig. 8(c) the remaining fragments consist of oxidized Ag.

3.3. Reaction-induced spatial redistribution of metal adlayers during surface reactions

Adsorption and reaction studies employing surface sensitive techniques demonstrated that the presence of a small amount of foreign adatoms can alter the physical and chemical properties of the surface [46]. A distinct feature is the dependence of the mobility and bonding of metal adatoms on the surface structure and on the presence of other coadsorbed species. In the case of propagating reaction fronts the 'modifier' adatoms can participate actively in pattern formation processes driven by the presence of a chemical reaction, as documented experimentally by several SPEM and XPEEM studies [47-55]. Most of these studies used the water formation reaction on Rh(110), which is a typical bistable system where the propagation of reaction fronts induce transitions between the O-covered ('oxidised') and clean ('reduced') surface. These reaction-diffusion patterns were influenced by modifying the catalyst surface adding adatoms of another element (K, Cs, Au, Pd, and Ag). The results showed that all investigated 'modifier' adatoms can be transported via the reaction fronts, affecting significantly the front profiles and the front velocity [56]. Compared with continuously traveling chemical waves on a modifier-free surface, the reaction fronts triggering mass transport of the modifier adatoms are transient: their velocity decreases with time until stationary concentration patterns are formed.

These re-organization processes can be followed with SPEM only by setting the reaction conditions to slow down the reaction front velocity [47,48,50,52]. The best choice for these dynamic systems is the combination XPEEM-LEEM, which allows correlating XPEEM chemical with LEEM structural information. This allows exploring in details the ignition and propagation of the reaction fronts, utilizing the faster and better resolved LEEM imaging. Once a stationary pattern is formed the local structures can be verified with micro-LEED and switching to XPEEM complemented with chemical imaging and spectroscopy. This approach is illustrated in Fig. 9. The LEEM images in Fig. 9(a) show the time evolution starting with an Rh(110) surface modified by \sim 0.5 ML of Au. Before the reaction Au is homogeneously



Fig. 9. (a) LEEM images, illustrating the ignition and propagation of reduction (bright) and oxidation fronts (dark), on the initially prepared surface (grey) until a stationary pattern is established after 90 min. (b) Energy filtered Au 4f XPEEM image, where the bright part reflects the accumulation of Au into the reduced areas, and the LEED patterns corresponding to the reduced Au-rich and oxidized Au-depleted regions. (c) Au 4f spectra of the bright and dark areas in (b). Reaction temperature 250 °C, pressure 1×10^{-6} mbar.

distributed and no contrast can be observed in LEEM and XPEEM images even after introducing only one of the reactants in gas phase at reaction temperatures lower than 300 °C. The reaction is ignited after introducing the second reactant, selecting the proper temperature and pressure conditions. The propagation of the reduction fronts leads to the formation of an inhomogeneous surface due to redistribution of Au, which condenses in the O-free areas, as clearly demonstrated by the Au 4f image taken at the stationary state. The local structure measured by LEED shows a streaky $c(2 \times 2)$ pattern involving (1×2) reconstruction of Rh(110) in the O-covered areas, whereas the Au-rich parts preserve the (1×1) structure of the Rh(110) surface. A distinct feature of the Au/Rh(110) surface is that this 'condensation' process is reversible only under reduction conditions, whereas the two distinct spatially separated phases can be frozen in an oxidizing atmosphere [54].

In the case of alkali modifiers (K and Cs) the reorganization of the interface results in a dense mixed alkali+O phase and an alkali-depleted reduced surface, the patterns being dissolvable both in reducing and oxidizing ambient [47–50].

The driving forces leading to the development of such complex surface morphology can be interpreted in terms of mobility and energetic factors. The energetic driving force is determined by the difference in the strength of the adsorption bonds of the metals on the clean Rh and on the O-covered surface, as well as by attractive-repulsive interactions between the adatoms. For the case of Au the O-covered surface is not energetically favored. This drives the reorganization of the interface towards segregated Orich and Au-rich phases, since the energy of the two segregated phases is lower than that of the mixed phase. On the contrary, for alkali adatoms (K and Cs) the O-covered surface is energetically favored and the attractive alkali-oxygen interactions result in formation of segregated mixed phase and a reduced surface with very low alkali coverage. In brief, the observed lateral reorganization of the adsorbed phases through propagating reaction fronts and the formation of stationary structures are not isolated cases, but universal phenomenon. The laterally separated phases exhibit different reactivity and may be viewed as chemical microreactors.

3.4. Photoelectron diffraction and angle resolved photoelectron spectroscopy using XPEEM

As already noted in Section 2.1 an important feature of the XPEEM-LEEM microscopes is that they can image the entire momentum space with energy resolution in the range up to 0.3 eV [7], thus implementing a microscopic approach to angle resolved photoelectron spectroscopy (micro-ARPES) measurements. Similarly, XPEEM-LEEM microscopes enable micro-probe X-ray photoelectron diffraction (micro-XPD), for probing the short range order around the emitter.

Although the feasibility of micro-ARPES and micro-XPD modes with the synchrotron-based XPEEM was demonstrated more than a decade ago, their real exploitation is still in infancy, possibly due to the relatively limited energy resolution of the instruments. However, the current interest in the electronic structure of ultrathin films, such as graphene and other nano-membranes might stimulate further developments and lead to the exploitation of XPEEM as a tool for micro-ARPES. The performance of the



Fig. 10. (a) ARPES of a graphite sample measured at 0.3 eV below Fermi edge; (b) cross-section $\Gamma KM\Gamma$ directions in the k_{jj} space from the same specimen; (c) spectra at the K and M points. Photon energy 90 eV.



XPEEM-LEEM instrument in this respect is illustrated by some recent measurements performed at the Nano-spectroscopy beamline at Elettra. Fig. 10 shows the micro-ARPES measured on a graphite area of $2 \mu m$ in diameter. Fig. 1(a) is an XPEEM image of the diffraction plane at 0.3 eV below the Fermi level. The curves in Fig. 10(b) are cross-sections along the $\Gamma KM\Gamma$ directions in the k_{II} space, obtained from a sequence images acquired at different electron kinetic energies, where the bright areas represent the π bands. The σ bands are weak, barely visible in the lower part of the plot. The curves in Fig. 10(c) are cross-sections of the same ARPES dataset along k_z , i.e. across the directions indicated by the straight lines in (b).

Fig. 11 shows the micro-XPD at the W $4f_{7/2}$ core level measured for a $(1 \times 1 \times 12)$ -O/W(110) surface. The different atomic environments of the bulk-like tungsten atoms and those with oxygen neighbors are evident in the patterns acquired at the bulk and oxide peaks. The atomic positions can be obtained by comparing the photoelectron diffraction patterns to multiple scattering calculations [57].

4. Concluding remarks

Photoelectron spectromicroscopy has undergone a fast development at the third generation synchrotron light sources, becoming a true microscopic tool for probing exotic material properties. The present paper has reviewed recent achievements that have filled the information gap by examining the chemical and electronic properties of complex micro- and nano-structured materials, and identifying local surface processes related to chemical interactions or mass transport. Although the selected results cover only some of the fields where synchrotron-based photoelectron microscopy has become the most desired tool, they demonstrate the high performance level of the instruments.

Some of the near-future upgrades for improving the performance of the photoelectron microscopes are increasing the lateral resolution and time resolution, marching into sub-10 nm and ps range by developing new optical elements and aberration correction systems, and faster and more efficient detection systems.

References

- [1] K. Siegbahn, J. Electron Spect. Relat. Phenom. 51 (1990) 11.
- [2] D. Briggs, M.P. Seah, second ed., Practical Surface Analysis, vol. 1, Wiley, New York, 1996.
- [3] H. Ade, J. Electr. Spectr. Rel. Phenom. 84 (1997) 1 (Special issue on Spectromicroscopy).
- [4] O.H. Griffith, W. Engel, Ultramicroscopy 36 (1991) 1;
- O.H. Griffith, W. Engel, Ultramicroscopy 36 (1991) 262.
- [5] J. Stohr, H.C. Siegmann, Magnetism, Part III, Springer, Berlin, 2006 p. 313. [6] J. Feng, A. Scholl, Photoemission microscopy, in: P.W. Hawkes, J.C.H. Spence
- (Eds.), Science of Microscopy, Springer, Berlin, 2007, p. 657.
- [7] Th. Schmidt, S. Heun, J. Slezak, J. Diaz, et al., Surf. Rev. Lett. 5 (1998) 1287. [8] S. Günther, B. Kaulich, L. Gregoratti, M. Kiskinova, Progr. Surf. Sci. 70 (2002) 187.
- [9] A. Locatelli, L. Aballe, T.O. Mentes, M. Kiskinova, Surf. Int. Anal. 38 (2006) 1554.
- [10] E. Bauer, Rep. Prog. Phys. 57 (1994) 895A.
- [11] E. Bauer, Th. Schmidt, Multi-method high resolution surface analysis with slow electrons, in: F. Ernst, M. Ruehle (Eds.), High Resolution Imaging and Spectroscopy of Materials, Springer, Berlin, 2003, p. 363.
- [12] E. Bauer, M. Mundschau, W. Swiech, W. Telieps, Ultramicroscopy 31 (1989) 49.
- [13] R.M. Tromp, Ultramicroscopy 36 (1991) 99.
- [14] A. Locatelli, E. Bauer, J. Phys.: Condens. Matter 20 (2008) 093002.

- [15] D. Attwood, Soft X-rays and Extreme Ultraviolet Radiation: Principle and Applications, Cambridge University Press, Cambridge, 1999.
- [16] E. Spiller, Soft X-ray Optics, SPIE, Bellingham, 1995.
- [17] F. Cerrina, J. Electron Spectrosc. Relat. Phenom 76 (1995) 9.
- [18] T. Kiyokura, F. Maeda, Y. Watanabe, E. Shigemasa, A. Yagishita, M. Oshima,
- Y. Iketaki, Y. Horikawa, J. Synchrot. Radiat. 5 (1998) 1111. [19] F. Barbo, M. Bertolo, A. Bianco, G. Cautero, S. Fontana, T.K. Johai, S. La Rosa, G. Margaritondo, Rev. Sci. Instr. 71 (2000) 5.
- [20] L. Gregoratti, A. Barinov, E. Benfatto, G. Cautero, C. Fava, P. Lacovig, D. Lonza, M. Kiskinova, R. Tommasini, S. Mähl, W. Heichler, Rev. Sci. Instr. 75 (2004) 64.
- [21] S. Gunther, A. Kolmakov, J. Kovac, M. Kiskinova, Ultramicroscopy 75 (1998) 35.
- [22] B. Lürssen, J. Janek, S. Günther, M. Kiskinova, R. Imbihl, Phys. Chem. Chem. Phys. 4 (2002) 2673.
- [23] P. Melpignano, A. Baron-Toaldo, V. Biondo, S. Priante, R. Zamboni, M. Murgia, S. Caria, L. Gregoratti, A. Barinov, M. Kiskinova, Appl. Phys. Lett. 86 (2005) 41105.
- [24] A. Kolmakov, S. Potluri, A. Barinov, T.O. Mentes, L. Gregoratti, M.A. Niño, A. Locatelli, M. Kiskinova, ACS Nano 2 (2008) 1993.
- [25] H On Kanel Mater Sci Ren 8 (1992) 193
- [26] D.X. Xu, et al., Mater. Res. Soc. Symp. Proc. 402 (1996) 59.
- [27] A.E. Dolbak, B.Z. Olshanetsky, S.I. Stenin, S.A. Teys, T.A. Gavrilova, Surf. Sci. 247 (1991) 32.
- [28] L. Gregoratti, S. Günther, J. Kovac, L. Casalis, M. Marsi, M. Kiskinova, Phys. Rev. B 57 (1998) L2134.
- [29] L. Gregoratti, S. Günther, J. Kovac, M. Marsi, R. Phaneuf, M. Kiskinova, Phys. Rev. B 59 (1999) 2018.
- [30] S.A. Parikh, M.Y. Lee, P.A. Bennett, J. Vac. Sci. Technol. A 13 (1995) 1589;
 S.A. Parikh, M.Y. Lee, P.A. Bennett, Surf. Sci. 356 (1996) 53.
- [31] V. Hinkel, L. Sorba, H. Haak, K. Horn, W. Braun, Appl. Phys. Lett. 50 (1987) 1257
- [32] K. Horn, Appl. Surf. Sci. 166 (2000) 1.
- [33] A. Barinov, L. Casalis, L. Gregoratti, M. Kiskinova, Phys. Rev. B 6308 (2001) 5308.
- [34] A. Barinov, B. Kaulich, L. Gregoratti, M. Kiskinova, A. Rizzi, Appl. Phys. Lett. 79 (2001) 2752.
- [35] A. Barinov, L. Gregoratti, M. Kiskinova, Phys. Rev. B 64 (2001) 201312(R).
- [36] P. Dudin, A. Barinov, L. Gregoratti, D. Sciani, Y.B. He, H. Over, M. Kiskinova,
- J. Phys. Chem. C 112 (2008) 9040.
- [37] S. Zafeiratos, V. Nehasil, S. Ladas, Surf. Sci. 15 (1999) 433;
- S. Zafeiratos, V. Nehasil, S. Ladas, Surf. Sci. (1999) 612.
- [38] NIST database, < http://srdata.nist.gov/xps/>.
- [39] E. Lundgren, A. Mikkelsen, J.N. Andersen, G. Kresse, M. Schmid, P. Varga, J. Phys.: Cond. Matt. 18 (2006) R481.
- [40] H. Hövel, B. Grimm, M. Pollmann, B. Reihl, Phys. Rev. Lett. 81 (1998) 4608.
- [41] Z. Weng-Sieh, R. Gronsky, A.T. Bell, J. Catal. 170 (1997) 62.
- [42] S. Suzuki, Y. Watanabe, T. Ogino, S. Heun, L. Gregoratti, A. Barinov, B. Kaulich, M. Kiskinova, W. Zhu, C. Bower, O. Zhou Phys. Rev. B 66 (2002) 035414.
- [43] S. Suzuki, Y. Watanabe, T. Ogino, Y. Homma, D. Takagi, S. Heun, L. Gregoratti, A. Barinov, M. Kiskinova, Carbon 42 (3) (2004) 559.
- [44] A. Barinov, H. Üstünel, S. Fabris, L. Gregoratti, L. Aballe, P. Dudin, S. Baroni, M. Kiskinova, Phys. Rev. Lett. 99 (2007) 46803
- [45] J. Kovač, A. Zalar, M. Remskar, A. Mrzel, D. Mihailović, L. Gregoratti, M. Kiskinova, Elettra Highlights (2003).
- [46] M. Kiskinova, Poisoning and promotion in catalysis based on surface science concepts and experiments, in: B. Delmon, J.T. Yates (Eds.), Studies in Surface Science and Catalysis, vol. 70, Elsevier, Amsterdam, 1992
- [47] S. Günther, H. Marbach, R. Hoyer, R. Imbihl, L. Gregoratti, M. Kiskinova, J. Electron. Spectrosc. Relat. Phenom. 114 (2001) 989.
- [48] H. Marbach, S. Günther, B. Lürssen, L. Gregoratti, M. Kiskinova, R. Imbihl, Catal. Lett. 83 (2002) 161.
- [49] H. Marbach, G. Lilienkamp, Han Wei, S. Günther, Y. Suchorski, R. Imbihl, Phys. Chem. Chem. Phys. 5 (2003) 2730.
- [50] H. Marbach, S. Gunther, T. Neubrand, R. Imbihl, Chem. Phys. Lett. 395 (2004) 64.
- [51] A. Locatelli, A. Barinov, L. Gregoratti, L. Aballe, S. Heun, M. Kiskinova, Electron. Spectrosc. Rel. Phenom. 144 (2005) 361.
- [52] H. Marbach, S. Günther, T. Neubrand, R. Hoyer, L. Gregoratti, M. Kiskinova, R. Imbihl, J. Phys. Chem. B 108 (2004) 15182.
- [53] Y. De Decker, H. Marbach, M. Hinz, S. Günther, M. Kiskinova, A.S. Mikhailov, R. Imbihl, Phys. Rev. Lett. 92 (2004) 198305.
- [54] A. Locatelli, C. Sbraccia, S. Heun, S. Baroni, M. Kiskinova, J. Am. Chem. Soc. 127 (2005) 2351.
- [55] A. Locatelli, T.O. Mentes, L. Aballe, A. Mikhailov, M. Kiskinova, J. Phys. Chem. B 110 (2006) 19108.
- [56] A. Locatelli, M. Kiskinova, Chem. A Eur. J. 12 (2006) 8890.
- [57] R.X. Ynzunza, R. Denecke, F.J. Palomares, J. Morais, E.D. Tober, Z. Wang, F.J. García de Abajo, J. Liesegang, Z. Hussain, M.A. Van Hove, C.S. Fadley, Surf. Sci. 459 (2000) 69.