Near ambient pressure photoelectron spectro-microscopy: from gas–solid interface to operando devices

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Abstract
Near ambient pressure scanning photoelectron microscopy adds to the widely used photoemission spectroscopy and its chemically selective capability two key features: (1) the possibility to chemically analyse samples in a more realistic gas pressure condition and (2) the capability to investigate a system at the relevant spatial scale. To achieve these goals the approach developed at the ESCA Microscopy beamline at the Elettra Synchrotron facility combines the submicron lateral resolution of a Scanning Photoelectron Microscope with a custom designed Near Ambient Pressure Cell where a gas pressure up to 0.1 mbar can be achieved. In this manuscript a review of experiments performed with this unique setup will be presented to illustrate its potentiality in both fundamental and applicative research such as the oxidation reactivity and gas sensitivity of metal oxides and semiconductors. In particular, the capability to perform operando experiments with this setup opens the possibility to study operating devices and to properly address the real nature of the studied systems, because if microscopy and spectroscopy are simultaneously combined in a single technique it can yield to more conclusive results.

Keywords: photoemission, near ambient pressure XPS, photoelectron spectromicroscopy, SPEM, oxidation, 2D materials, gas-solid interfaces

(Some figures may appear in colour only in the online journal)

1. Introduction
The investigation of solid/gas interfaces requires dedicated techniques, and x-ray photoelectron spectroscopy (XPS) is among the most important one thanks its surface and chemical
Due to technical limitations, XPS instruments were originally developed to investigate homogeneous samples in ultra-high vacuum (UHV) conditions. At the same time, functional materials found in catalytic systems or working devices exhibit a wide range of heterogeneity, complex structures, morphologies, and interfaces ranging over different spatial scales and often require more realistic higher pressures environments to be properly studied. These discrepancies are known as the material and pressure gaps, respectively.

For instance one of the most studied model catalysts, the Ru(0001) surface, has been investigated for decades with UHV-based techniques exploring its attitude to oxidize CO. Only when more realistic pressure environments could be established during the characterization, it was found that the low-pressure surface oxide phases previously investigated in UHV were not the main players in the real catalytic conditions where other phases are formed [2, 3]. In addition, modern technologies for the production and deposition of catalysts and functional materials do not lead to, in general, homogeneous samples, but rather composite ones often in the form of micro- or nano-sized particles/clusters with specific structures [4, 5]. The characterization of such material requires spatially resolved experimental approaches. Therefore revealing the complexity of the processes occurring at the surface/gas interfaces under working conditions, i.e. in-situ or operando, and at the relevant scale is of paramount importance to understand and optimize the involved processes.

To fully exploit the potentials of XPS, the aforementioned material and pressure gaps have to be addressed by: (i) adding the possibility of sub-micron spatial resolution and (ii) extending the measurement conditions to pressures range higher than UHV. In the past decades solutions to separately address these limitations have been developed, but the design and realization of technologies capable of simultaneously overcoming both is extremely challenging.

The synchrotron-based Scanning PhotoEmission Microscopy (SPEM) combines XPS with spatial resolution, it is a powerful technique to image and probe chemical and electronic properties of micro- and nano-structured samples [6, 7]. SPEM uses a direct approach to characterize materials at the submicron scale, i.e. to illuminate samples with a submicrometric x-ray probe while raster-scanning the sample with respect to it. The SPEM hosted at the ESCA Microscopy beamline at the Elettra synchrotron research laboratory [8] has been operated since 1996, performing experiments on various types of nanostructured surfaces and interfaces, shedding light on the related phenomena occurring at mesoscopic length scales [9].

The need for a UHV environment in conventional XPS setups is mainly due to the short mean free path of the photoelectrons with kinetic energies below 1500 eV at high gas pressure. These electrons, indeed, suffer from scattering by the molecules in the gas environment (for instance, photoelectrons with a kinetic energy of 100 eV travelling in 1 mbar of molecular oxygen have a mean free path of about 1 mm). Another reason resides in the presence of high voltages in the electron detector setup which may generate discharges at higher pressures. The state of the art approach to perform XPS at the mbar range, defined as near ambient pressure XPS (NAP-XPS), consists in confining the high pressure only at the sample region, shortening as much as possible the path of photoelectrons in the high pressure region. All these conditions are satisfied in the so called differentially pumped Hemispherical Electron Analyzers (HEA) by placing the electron analyser nozzle close to the sample area, such distance being typically lower than 1 mm, and differentially pumping the electron analyser lenses stages to create a high vacuum regime not affecting anymore the travel of the photoelectrons [10–14].

The implementation of differentially pumped HEA in SPEM is not straightforward, mainly, because both the analyser and the x-ray optics setup must be positioned at short distance in front of the sample surface occupying the same space simultaneously. The near ambient pressure cell (NAP-cell) developed at the ESCA Microscopy beamline [15–17] encapsulates the sample within a closed volume and keeps the high pressure environment locally confined. Such decoupling allows using conventional electron analyser and x-ray optics systems as in a conventional UHV setups and thereby offering an alternative solution to the classical near-ambient arrangement.

In the following we will present, together with a detailed description of the SPEM (section 2) and the NAP-cell (section 3), some recent results obtained by using the combination of NAP-cell and SPEM, in order to provide an overview of the capability of this approach in the analysis of gas/solid interfaces and highlight the possibilities in understanding phenomena at the submicron scale in in-situ and operando conditions.

The studies we propose in this paper will be presented with a progressive increase in the setup complexity to better introduce the different possibility of the combination of SPEM and NAP-Cell in different field. The examples consists of:

(a) fundamental oxidation studies of polycrystalline Ni and Cu foils (sections 4 and 5 respectively), where the activity of specific structures will be addressed;
(b) a more complex system consisting of graphene on copper (section 6) where the oxidation propagation underneath the graphene flakes will be studied;
(c) gas sensors active devices based on semiconducting metal oxides (section 7) and a single 2D MoS
flake (section 8) where inside the NAP-Cell not only sample temperature and gas pressure were controlled, but also potentials were applied to the systems and electrical responses were recorded during measurements, i.e. close to operando in NAP-Cell more realistic conditions.

Each example will be presented with a brief introduction to the corresponding research field and topic.

2. Scanning photoemission microscopy basic concepts

To produce a sub-micrometric probe the incoming x-ray beam is focused by means of lithographically made Fresnel Zone
Plate (ZP) [18], which generate a large number of diffracted orders each one having a specific intensity and focal position. In the SPEM only one order must be used to create the focused x-ray spot. To do so, the first diffraction order is selected and the higher ones are blocked by an additional pinhole, the so called Order Selecting Aperture (OSA). The straight radiation passing through the rings, defined as the zeroth order, is stopped by a metallic x-ray absorbing layer, called central stopper, lithographically grown on the ZP center.

The typical set-up used at ESCA Microscopy consists of a 200–250 μm diameter ZP lens with 50–100 nm outermost ring and an 80 μm central stopper, and a 75 μm wide OSA. With the photon energies available at the beamline, in the 400–1200 eV range, this focusing system is capable to demagnify the photon beam down to a spot of 130–180 nm diameter providing a focal length in the 5–15 mm range, with both the spot dimension and focal length being function of the photon energy [18].

As sketched in figure 1, samples are placed in the focal point of the optics, the latter working in normal x-ray incidence. Samples are then raster scanned, in the plane orthogonal to the beam, by two sets of motors. The first one consists of stepper motors designed for large movements, up to several mm, with a minimum step movement of 1 μm, while the second one is a piezoelectric stage capable of 100 × 100 μm scanning range with a minimum step movement of 5 nm for high spatial resolution imaging of samples.

Due to the geometric restrictions imposed by the short focal length, the photoelectrons detectable by the HEA have a take-off-angle with respect to the sample surface of 30°, figure 1(a), and the HEA maximum acceptance angle is ±10°. This configuration strongly enhances the surface sensitivity of the instrument. The HEA is equipped with a delay line electron detector that is binned to 48-channels [19].

The SPEM can operate in two modes: (1) imaging spectroscopy and (2) micro-spot spectroscopy. The imaging mode maps the lateral distribution of elements or chemical states by collecting photoelectrons within a selected kinetic energy window while scanning the specimen with respect to the microprobe. The micro-spot mode is identical to conventional XPS spectra, but it is measured from selected submicron spots on the sample.

Figure 1(b) reports an example of a photoemission image, acquired on a partially oxidized nickel foil using the Ni 2p core level signal. The grey scale is proportional to the photoelectron intensity recorded by the HEA in that particular point. The contrast in the image is mainly generated by surface topography rather than by chemical variations, with the intensity in each point reflecting its orientation with respect to the HEA, where a region oriented toward the HEA appears

Figure 1. (a) Sketch of the SPEM setup. (b) Raw photoelectron image acquired at Ni 2p binding energy, 854 eV, with an energy window of ±4 eV. (c) Reference Ni 2p photoelectron spectra for metallic and oxidized nickel. The colored bars in (c) represent the energy window used for the acquisition of map (b). (d) Chemical map extracted from (b) by dividing the two sub maps obtained by selecting the two energy regions showed in (c) by the coloured bars. Brighter points correspond to a higher content of metallic Ni.
Figure 2. (a) Sketch of the NAP-Cell setup. (b) Photography of the NAP-Cell with all four electrical feedthroughs and the x-ray pinhole highlighted. (c) Comparison between a SPEM image, on the left, and optical image, on the right, of the field of view available for SPEM measurements on the sample.

brighter due to more normal emission. Nevertheless, the 48 channels electron detector allows to highlight the lateral distribution of the different chemical states in the image and to remove the topographic contributions. At each scanned position the corresponding 48 points XPS spectrum, defined by the selected window energy, is stored, thereby generating an array of 48 maps each one showing the distribution of specific photoelectron energy. By properly choosing the map acquisition energy and analysing each of these spectra it is possible to create maps corresponding to specific spectra features. For example in figure 1(c) two Ni spectra are reported, indicating a non-uniform chemical sample composition. One spectrum is mostly metallic, but a larger width compared to the standard for metallic nickel [20, 21] indicates the presence of residual oxides; the broad width of the second spectrum suggests the presence of a mixture of different oxidation states. Accordingly, two binding energy regions, centred at 850–854 and 854–858 eV, corresponding to the mostly metallic states and the high oxygen content oxides respectively have been highlighted. The point by point ratio of the integrals of the 48 points spectra from these two energy regions generates the map showed in figure 1(d). Here, the greyscale represents the metal to oxide ratio and thus identifies local chemical differences. In addition, the topography contribution is removed [19].

3. Near ambient pressure cell

Higher pressures at the sample can be achieved by a special designed cell, which contains the sample and decouples the sample environment from the rest of the analysis chamber [15–17]. The top plate of the NAP-cell contains two 450–500 µm diameter pinholes whose impedance to gas flow establishes the needed pressure drop between the inside volume of the cell and the rest of the analysis chamber. One pinhole is perpendicular to the sample and is used by the incoming focused x-ray beam. The second pinhole for the emitted photoelectrons is oriented at 30° with respect to the sample surface and has a conical shape to properly fit the HEA acceptance angle. The sample inside the NAP-cell (figures 2(a) and (b)) is located 650 µm far away from the surface of the inner body of the cell. This position allows the sample to be at the intersection point of the axis of the two pinholes. A flexible pumping/dosing line is connected to the cell to control the environment without affecting any sample movement.

The compact design of the NAP-cell allows to mount it on a standard SPEM sample holder and to fit in the limited space between the sample and the focusing optics, making feasible to operate the SPEM in the same operation modes described above. The pressure inside the cell can be raised up to 0.1 mbar while the pressure in the main chamber remains below 1 × 10⁻⁵ mbar, which is the safety operating limit for the SPEM system without the necessity of any differential pumping unit applied to the electron analyser.

A ceramic heater is located below the sample for controlling its temperature in the range 300–1073 K. Samples are electrically insulated from the body of the cell, having four independent electrical contacts for potential and current applications or for sample grounding, see figure 2(b).

With this design a 450 µm wide sample field of view can be achieved, as shown in figure 2(c). Moreover, the gas composition of a chemical reaction can be determined by a mass spectrometer located in the analysis chamber.

4. Oxidation of polycrystalline nickel

Catalysts used in heterogenous catalysis are typically complex structures of active materials dispersed on a support and with addition of promotors [22, 23]. This complexity often entails a chemical inhomogeneity that could only be tackled
by spatially resolved techniques [23]. In addition, these investigations need to be performed under *in situ operando* conditions since the phase of interest may not exist in initial or post mortem studies [23]. Up to now there are only a few techniques that fulfil these requirements [15, 24–26]. In this chapter we will provide a fundamental oxidation study of a polycrystalline Ni foil highlighting the capabilities of spatially resolved NAP-XPS measurements.

The investigations were performed using a 0.25 mm thick polycrystalline nickel foil (Advent Research Materials Ltd, purity 99.99%). After mechanical polishing the sample was cleaned by repeated cycles of sputtering (1.5 keV, 30–60 min) and annealing (∼820 °C, 60–90 min). After transferring the Ni foil into the NAP-cell and right before the experiment, additional cleaning cycles of oxidation (360 °C, 0.07 mbar O₂) and reduction (420 °C, 0.18 mbar H₂) were performed. The photon energy was set to 974.5 eV.

### 4.1 Results and discussion

At first, the morphology of the polycrystalline Ni-foil was investigated using the imaging capabilities of SPEM. A representative image acquired from this sample using the O 1s core level signal is shown in figure 3(b). As described in sections 2 and 3, the XPS maps acquired by SPEM are a superimposition of chemical and topographic information, while in the present case topography is dominating. According to topography, the shown region can be divided into several parts. At the left side of the image the surface is mostly flat with only small ripples that are typical of rolled metal foils. On the other hand, on the right side of the map a strong contrast is present with pronounced, bright lines. To the right of each bright line an additional faint black line can be observed. Due to the grazing analyser position these adjacent lines can be identified as trenches. The origin of these trenches is most likely attributable to bulk grain boundaries that result in a strong curvature of the material when reaching the surface. Thus, the right image part can be interpreted as the result of the presence of many small grains with the size of a few micrometres separated by grain boundaries. Therefore, the bright features will be called grain boundaries in the following.

These variations in topography may strongly affect the local chemistry of the nickel foil. To probe that the oxidation of the Ni was chosen and its progress was monitored at selected regions, such as at single grains, at flat regions, or at the strong curvature of the grain boundaries. To do so, 0.08 mbar of oxygen was introduced and the sample temperature was stepwise increased from 315 °C to 430 °C. At each temperature step, spectra at selected points of interest were acquired. The map shown in figure 1(b) was taken from this oxidation series. Ni LMM Auger spectra series acquired on the flat region and on one of the grain boundaries are provided in figures 3(a) and (c), respectively. In both series, a strong change in the Auger peak shape was detected between 315 °C and 380 °C. Since the Auger peak shape is highly sensitive to the Ni oxidation state [27], this can be attributed to a transition from mostly metallic to oxidized Ni. A closer look at the data reveals that the change in the peak shape at the grain boundary occurs at lower temperatures compared to the flat Ni, this is particularly clear in the spectra acquired at 350 °C (highlighted in light blue). For a quantitative analysis of the Ni oxidation state, the latter was extracted from the Auger spectra by a linear combination fitting using reference peak shapes. The results are provided in figure 4 and confirm the differences in Ni oxidation states in the different regions. In both cases, an almost linear increase of the fraction of oxidized nickel is observed between 315 °C and 370 °C. The complete oxidation is finally reached around 380 °C. The corresponding curve for the grain boundaries is shifted by about 20 °C towards lower temperatures compared to the flat regions, i.e. the oxidation of grains boundaries occurs at a 20 °C lower temperature. This implies a higher reactivity of the grain boundaries towards oxidation compared to the flat region, which is in line with their expected behaviour [25, 28, 29] due to their high number of defects, high atomic step density, and the fact that grain boundaries can act as a diffusion path of adsorbed oxygen into the bulk [30]. Although the density and spatial dimension of the grain boundaries are quite high in the shown region, the

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Figure 3. Oxidation of a polycrystalline Ni foil. The Ni LMM spectra were taken (a) at flat Ni regions and (c) localized at a grain boundary. The spectra acquired at 350 °C (marked in light blue) show the largest deviation in peak shape. (b) The map taken at the O 1s core level shows the investigated area (BE centred at 530.5 eV; PE = 40 eV).
bright lines contribute only about 7% to the area of the shown map. Therefore, any effect of the grain boundaries would be hardly visible using averaging techniques rather than spatially resolved ones.

This preliminary study shows the feasibility to direct address the surface chemistry at selected topographic features using the combination of SPEM and NAP conditions. The next step will be to proceed with a heterogeneously catalysed reaction and investigate these topographic features of the catalyst under operando conditions which is very difficult with other techniques. These features could be active sites of the catalysts and therefore investigating their local chemistry would help to understand their working principle [22, 25, 28, 29].

5. Formation of metastable phases during oxidation of polycrystalline copper

Metal oxidation is an interesting topic, considering its importance in high temperature corrosion, as well as general solid-state surface reactivity. The knowledge of bulk phase diagrams for oxidation products is highly developed. However, the formation of meta-stable, sub-stoichiometric phases that might only exist at the nano-scale, and for only short durations, is much less understood. Nonetheless, these phases are important for the kinetics of the oxidation. There is certainly substantial evidence of the formation of defective, sub-stoichiometric, meta-stable oxides formed during oxidation, but the lack of knowledge in this field is because experimental observation of such phenomena is technically very challenging. In-situ photoemission spectro-microscopy methods have recently made great progress in this direction.

Investigations on sub-stoichiometric and meta-stable phases greatly benefit from the ability to detect signals representative of chemical state, from spatial domains at the nanometre scale. The reason why this is important, is that sub-stoichiometry as well as metal coordination geometry influences photoelectron signals, such as XPS. Thus, evidence of sub-stoichiometry can generally be found in electron spectra. However, when meta-stable states are minority species, present simultaneously with the majority bulk thermodynamically stable species, the signal from the meta-stable species can hardly be discerned. For this reason, being able to spatially isolate the signal from the meta-stable species is a great asset to such investigations.

A polycrystalline copper foil of 0.1 mm thickness and 99.998% purity from Advent Research Materials Ltd was used for this experiment. Prior to the measurements, copper samples were cleaned using cycles of Ar⁺ ion bombardment polishing followed by annealing in 0.2 mbar high purity (99.999%) H₂ at 700 °C–800 °C. The result was a fully reduced surface.

A combination of in-situ SEM and in-situ SPEM was used to examine the oxidation of the Cu foils and in particular the oxide phase transition that is not accessible using traditional UHV spectroscopic methods. The oxidation was performed by exposing the Cu foils at 0.1 mbar O₂ at 300 °C. The transition of Cu₂O to CuO, that typically occurring during atmospheric oxidation of Cu, is not accessible at very low O₂ pressures. However, using spectro-microscopic methods in the mbar pressure range, one can observe this transition live, and with chemical detail. The SEM image in figure 5(a) shows that some sort of intermediate morphology forms during the onset of the phase transformation from Cu₂O to CuO. This intermediate morphology is represented by the light grey feature spreading across the dark-grey surface. The dark grey is CuO. The cauliflower-like morphology is CuO (as determined by post-reaction analysis not shown here). However, the middle grey morphology is unknown from SEM images and does not remain after cooling the sample down and moving to air, preventing post-reaction analysis.

This interesting morphology is somehow related to the initial formation of CuO, and could potentially represent a meta-stable, sub-stoichiometric oxide phase. However, to determine its identity, one requires in-situ spatially resolved spectroscopic methods that can characterize chemical states. To this end, in-situ SPEM was applied. The photoemission map in figure 5(c) shows the Cu²⁺/Cu⁺ contrast; despite the lower spatial resolution regions with similar morphologies as in figure 5(a) can be found. Panel (b) in figure 5 shows the Cu 2pₓᵧ₂ point spectra from the points A and B indicated in figure 5(c). Spectrum A was measured directly at the edge of a growing CuO front and shows the growth front containing a superposition of Cu²⁺ and Cu⁺ spectra. The Cu²⁺ component is identified by the satellite peaks between 940 eV and 945 eV, as well as the main peak at 934 eV, whereas the Cu⁺ component consists of only a main peak at 932.5 eV. Point B was measured in the middle of a Cu₂O phase and shows only evidence of Cu₂O.
The ability to have chemical identification on the nanoscopic scale, and under in-situ conditions, is very powerful in that it can yield more conclusive results when microscopy and spectroscopy are combined.

6. Graphene barrier towards Cu oxidation

The study and development of anticorrosive coatings is of high technological interest and strategic industrial importance due to the high costs that metal corrosion implicates [31]. Oxidation is an example of high-temperature corrosion that happens when a metal is exposed to an oxidizing atmosphere at elevated temperatures. For instance this is a typical environment in gas turbines, engines, or furnaces. Oxygen and nitrogen dioxide are typical aggressive gases that can enter in contact with metal parts. O$_2$ is naturally present in air, while NO$_2$ is a common air pollutant, contributing to the formation of smog and acid rain and a product of combustion in car engines. Graphene, an intrinsic 2D material, is impermeable to any molecule and inert to most chemicals [32]. It acts as a barrier for the supporting substrate, being a promising candidate as an anticorrosive coating for metals [33–36]. The case of copper, in particular, is being recently studied in deep since it is a common substrate for graphene growth, other than for its wide use in everyday life. It was shown that the protection offered by graphene is very effective in different reactive environments, as high relative humidity [37, 38], hydrogen peroxide [39] high temperature in oxidizing gases [33, 34, 40]: when the exposed metal areas were already corroded, the region protected by graphene were still unaffected.

SPEM has revealed to be an useful tool to study supported and suspended graphene [41–46], opening the possibility to follow the different kinetics involved in this process at a single flake level.

In this experiment, we studied the oxidation of copper protected by graphene flakes in different gas environments (O$_2$ and NO$_2$ at 0.1 mbar) and at a variable temperature. The graphene flakes are not covering the whole copper surface, thus having available under the same field of view both unprotected Cu areas and graphene-covered Cu. The flakes are mostly single layer of about 20 µm in side, with few multilayer areas. In figure 6, the 72 × 72 µm$^2$ C 1s map at 300 °C clearly shows graphene flakes with a well-defined hexagonal shape, the darker spot on the top of the map indicated the presence of a multilayer region, while the brightest part is the bare Cu substrate. The corresponding map of copper is acquired on the Cu LMM Auger window (centred at a kinetic energy of 918 eV) and the chemical analysis by making the ratio of fingerprint distribution of these C moieties is shown in figure 6. Contextual to the intercalation is the starting of oxidation of the metallic copper underneath. The etching of graphene, however, does not happen at the same time of copper oxidation which indeed is an undercover reaction [33, 47].

When the temperature is increased to 340 °C, the oxygen molecules start to intercalate under the graphene mostly from flakes’ edges, as shown in the zoomed 38 × 38 µm$^2$ map in figure 6. Contextual to the intercalation is the starting of oxidation of the metallic copper underneath. The etching of graphene, however, does not happen at the same time of copper oxidation which indeed is an undercover reaction [33, 47].

C 1s spectra (not shown here) measured in different areas are centred at two different binding energies (BE): 284.1 eV as the nominal position for Gr [41] and shifted to lower binding energy of about 0.4 eV, in agreement with oxygen-intercalated graphene where the graphene is lifted from the substrate and the interaction is therefore reduced [48]. The spatial distribution of these C moieties is shown in figure 7(a) corresponding to the 360 °C condition. Zone A (dark blue) corresponds to areas where the C 1s peak is centred at its original position, zone B (light blue/green) to areas with the shifted peak and zone C (yellow/red) indicates the absence of carbon signal.

When the temperature is further increased beyond 380 °C the single-layer graphene is etched away. Only small multilayer regions are still present and under them the copper maintains its metallic character: they are visible in the upper part of the maps at 380 °C in figure 6. The etching of graphene happens through combustion with the oxidizing gas and it is facilitated by the change of the copper morphology which, at

Figure 5. (a) In-situ SEM image of Cu$_2$O while heated in 0.3 mbar O$_2$ at 300 °C, showing the initial formation of CuO. The dark grey area is Cu$_2$O, the middle grey area is an intermediate morphology that precedes bulk CuO formation, the bright cauliflower-like morphology is bulk CuO. (b) In-situ microspot Cu 2p$_{3/2}$ XPS spectra measured from the growth front of an the CuO phase transition (red) and from the Cu$_2$O phase (blue), as indicated in the Cu 2p$_{3/2}$ Cu$^{2+}$/Cu$^{+}$ SPEM map in panel (c); the intensities of the two spectra have been normalized with respect to the peak at 934 eV for clarity. The conditions for the SPEM measurements were 0.1 mbar O$_2$ at 300 °C.
Figure 6. O 1s (top row), C 1s (middle row) and Cu LMM (bottom row) photoemission maps of graphene/Cu foil at different temperatures. The red dotted square in the $72 \times 72 \, \mu m^2$ C 1s map represents the zoom-in of the following $38 \times 38 \, \mu m^2$ maps. The Cu LMM Auger maps are have been processed in order to distinguish the contribution of metallic copper and Cu$_2$O indicated with different colour in the images.

this stage of oxidation, creates protuberances on the surfaces [33, 49]. This is evident in the O 1s map in figure 6 where the topographical contribution was intentionally not corrected and shows the presence of regions with different height on the sample, represented by sharp dark/bright edges.

When NO$_2$ instead of O$_2$ is used, a higher and faster aggressiveness of the oxidation process is noticed [50]. The formation of the second oxide of copper, CuO, is one of these effects. The lineshape of the Cu LMM Auger spectrum is the best fingerprint to disentangle the different Cu phases [34, 47]. Thanks to the different kinetic energy of the main peak, the chemical contrast maps in figure 6 were obtained. In figure 7(b) the Cu LMM Auger spectra recorded at different temperature and gas composition on the graphene/Cu sample are reported. At 200 °C in NO$_2$ atmosphere, the copper protected by graphene is still in its metallic phase (red spectrum) with the main peak at 918.3 eV, while the bare Cu surface is oxidized to CuO (green spectrum, main peak at 917.9 eV). On the contrary, while exposing to O$_2$, at 250 °C the copper still shows sign of metallic phase together with the formation of Cu$_2$O at 916.6 eV (blue spectrum). The formation of CuO in oxygen atmosphere is subsequent to the formation of Cu$_2$O and evolves with the temperature [34].

Figure 7. (a) $38 \times 38 \, \mu m^2$ C 1s photoemission map at 360 °C obtained by making the ratio of shifted and pristine C 1s fingerprint regions in the energy window. The different regions correspond to pristine (A) and O-intercalated (B) graphene and carbon free areas (C). (b) Cu LMM Auger spectra at three different conditions.

In summary, with NAP-SPEM we were able to follow the oxygen intercalation and undercover copper oxidation beneath graphene and contextually to establish the mechanism of graphene protection towards copper oxidation in different
aggressive environments, namely O\textsubscript{2} and NO\textsubscript{2} atmosphere, at high temperature.

7. Characterization of LaFeO\textsubscript{3} based gas sensors

Semiconducting metal oxides are the basis for the majority of chemoresistive gas sensors that are used in many applications such as detection of flammable and hazardous gases, indoor air quality management, or industrial process control [51–54]. While widely used oxides such as SnO\textsubscript{2}, WO\textsubscript{3}, or ZnO respond to many target gases, gas sensors based on LaFeO\textsubscript{3} (LFO) with perovskite structure exhibit a high sensitivity towards acetylene and ethylene and, more interesting, reveal an intrinsic temperature dependent selectivity to these target gases [55, 56]. In order to investigate the detailed mechanisms of the gas/solid interaction, research is mainly focused on \textit{operando} techniques where the sensor’s surface can be studied in conditions similar to the intended future application. In this study, local variations at the LFO based gas sensors surface were identified under realistic operating conditions via spatially-resolved elemental maps obtained using SPEM. Even if the maximum pressure of 0.1 mbar available in this setup is significantly lower than atmospheric pressure, its effect on the chemistry of the sensor surface is still detectable.

7.1. Experimental

The LFO based material was synthesized by a sol-gel process starting from La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O and Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O as described in a previous publication [55]. The obtained gel was calcined at 600 °C for 2 h. The sensing device consists of an alumina platelet (4 × 7 mm\textsuperscript{2}) with interdigitated Pt electrodes at the surface (electrode gap: 300 μm). The sensitive layer is deposited onto the substrate via screen printing with a thickness of approximately 50 μm (see inset of figure 8). The sensor was heated to 300 °C using the resistive heater of the NAP-cell. The atmosphere in the cell consists of dry synthetic air (20.5% O\textsubscript{2}, 79.5% N\textsubscript{2}) and a pass energy of 20 eV. The sensor was heated to 300 °C using the resistive heater of the NAP-cell. The atmosphere in the cell consists of dry synthetic air (20.5% O\textsubscript{2}, 79.5% N\textsubscript{2}) and a pass energy of 20 eV. The sensor was heated to 300 °C using the resistive heater of the NAP-cell. The atmosphere in the cell consists of dry synthetic air (20.5% O\textsubscript{2}, 79.5% N\textsubscript{2}) and a pass energy of 20 eV.

7.2. Results and discussion

Even though the response of the sensor to acetylene and ethylene is significantly higher at 250 °C or 200 °C, respectively, the study was carried out at 300 °C to avoid the deposition of carbon at the surface during the experiment (due to the gas triggered displacement of contaminants unavoidably present on the NAP-cell walls). In order to compensate for the lower signal, a rather high concentration of hydrocarbons of 1 vol.% was chosen. The results of the DC resistance measurements are shown in figure 8. As expected for a p-type semiconductor, the extent of the hole accumulation layer decreases and, hence, the resistance of LFO increases during the exposure to reducing gases such as ethylene and acetylene [57, 58]. The obvious decrease in resistance around 31 and 45 h, respectively, is due to heating the sample above the temperature of operation in order to remove carbon that was adsorbed at the sample surface while the sharp increase in resistance around 32 h of operation is due to a decrease of the gas pressure within the NAP-cell. The sensor response to acetylene is significantly higher than for ethylene which is in line with previous \textit{operando} investigations [55].

The characterization of the surface chemical composition was performed using SPEM, acquiring the Fe 2p and 3p, La 3d and 4d, O 1s, and C 1s core level peaks at a constant photon energy of 975 eV. The maps at La 4d and Fe 3p core level signals are reported in figures 9(a) and (b) respectively. The contrast is dominated by the topography of the sample. As the contrast is identical in both maps, the material showed excellent homogeneity in terms of elemental composition and no obvious areas with an excess of La or Fe or even separate phases could be identified. As described in section 2, the topography can be removed by making ratios of properly chosen regions of the energy window, and an example for the Fe 3p map is shown in figure 9(c). This normalized map was generated by dividing the spectra region in half and taking the corresponding ratio between this two half. The areas around the spots labelled as A and B were identified to be promising candidates for locally recording XPS spectra.

A comparison of the metal spectra, especially their oxidation states and multiplet splitting, did not reveal any differences neither between points A and B nor in different environmental conditions. The introduction of gases however has a remarkably different effect on the binding energy (BE) recorded on points A and B. For point B the shift in BEs between different conditions is less than 0.3 eV. In contrast, a positive BE shift, on the order of several eV, is observed for the core levels recorded on point A. In figure 10 all shifts are plotted relative to the BE recorded on point B in dry air. Spectra recorded without the focusing optics, thus averaging over a 75 μm diameter area (not shown here) show the same BEs as...
point B and hence the latter are taken as a reference for the shifts observed in dry air reported in figure 10. We ascribe the BE shifts observed on spot A to a local sample charging. For the latter to happen, in addition to the charge carrier concentration decrease induced by the reaction with acetylene and ethylene (which occurs everywhere on the sample), a loose electrical contact between the particular volume under investigation and the rest of the sample has to be considered. The decreased conductivity at the grain boundaries together with the loose contact could make the area around spot A electrically more isolated, thereby enhancing local charging. From the resistance data it is evident that the effect of acetylene on the conductivity is higher than the one of ethylene and the same can be observed for the BE shift.

Interestingly, the peak shift in dry air, recorded after the exposure to acetylene, is higher than in the presence of ethylene. These findings as well as the spectra of the O 1s region indicate a non-reversible change in the surface of the sensing layer. Deconvolution of the O 1s spectra was possible using three components with the main one representing the bulk oxygen (green line at lowest binding energy in figure 11). The second component ($\Delta BE = 1.4–1.5$ eV) can either assigned to hydroxyl groups or formate species at the surface, while the third peak can be attributed to highly-oxidized adsorbates such as carbonates ($\Delta BE \geq 2.4$ eV) [59–61]. Unfortunately the interpretation of C 1s spectra could not provide additional information on the origin of these components, since the charging and the generally decreased amount of carbon species on point A do not allow a direct comparison with point B. Moreover, the microspot XPS of O 1s on location A reveal an increased contribution of oxygen containing surface species compared to the bulk component in the spectra recorded subsequent to the ones in ethylene. To a lesser extent the same can be observed on spot B. Since La and Fe did not reveal any changes in their oxidation states and the O 1s and C 1s spectra between points A and B differ, we can conclude that organic surface components formed by the exposure to the target gases play a key role in the reception of the gas sensing process, most likely influencing the adsorption strength and geometry of the target gas itself. The identification of these species requires additional spectroscopic investigations and may finally be required to explain the inhomogeneous behaviour of the surface and the origin of the significant BE shifts.

In this study, NAP-SPEM was successfully applied to a gas sensitive material. Although the sample surface was chemically homogeneous, sites with different reactivity towards the target gases ethylene and acetylene were identified. These findings, crucial for an applied device, would not have been revealed with averaging spectroscopic techniques. Further studies of non-homogeneous samples, e.g. heterostructures or materials with additive clusters, will be performed in the future using the same approach delineated here.

8. MoS2 monolayers as gas sensors: an operando study

Two dimensional (2D) layered nanomaterials are promising candidates for ultra-sensitive gas sensors due to their high surface to volume ratio, high carrier mobilities and tuneable
bandgaps [62, 63]. For field effect transistors (FETs) based on 2D layered molybdenum disulphide (MoS\(_2\)), sensitivities down to parts-per-billion towards NO\(_2\) have been demonstrated [62, 64–66]. The sensing mechanism is believed to be based on a charge transfer process [67, 68] where oxidizing (reducing) gases accept (donate) electrons from the channel upon adsorption, leading to an increase (reduction) in the resistance.

8.1. Methods

8.1.1. Device fabrication process. Dry transfer technique was used to place mechanically exfoliated MoS\(_2\) monolayers on pre-prepared hBN flakes. Electron-beam lithography (EBL) followed by reactive ion etching was used to pattern the MoS\(_2\) channel. Electrodes were realized by EBL and e-beam evaporation and lift-off of Ti/Au (5 nm/110 nm) metals.

8.1.2. SPEM characterization. The x-ray beam energy used for these measurements was set to 701.3 eV. A mixture of Argon and NO\(_x\) (1.7 ppm mol NO and 1.9 ppm mol NO\(_2\)) was introduced to the NAP-cell, at a pressure of 8.2 \(\times\) 10\(^{-4}\) mbar. The maps were centred around KE 473 eV, corresponding to the Mo 3d\(_{5/2}\) region. To extract local BE peak positions the data were first filtered by applying a 3 \(\times\) 3 averaging filter to reduce the noise. Using an automated routine, peak deconvolution was performed at every pixel. New maps were created containing the total area of the deconvolution Mo 3d\(_{5/2}\) component for every pixel.

8.1.3. Electrical characterization. Electrical transport properties were characterized using two-point configuration with a Keithley 2440 source meter. The gate voltage was applied using a Keithley 2450 instrument. All data were recorded by a purpose made LabVIEW program.

8.2. Results

The MoS\(_2\)-based FET was mounted into the NAP-cell with three independent electrical contacts for gate (\(V_G\)), source (\(V_S\)) and drain (\(V_D\)). Figure 12(a) shows an optical image of the device, while figure 12(b) show SPEM maps centred at the Mo 3d\(_{5/2}\)/S 2s signal, acquired before (left) and during exposure to NO\(_x\) gas (right). In both maps, a bright spot can be
seen close to the left side contact. This was caused by beam damage during preliminary focused beam measurements. Due to this beam damage, the current measured in UHV prior to gas detection was rather low. Nevertheless, the gas sensing device was still functioning, and a drop to zero conductivity was observed when NO$_2$ was introduced in the NAP-cell. Representative electrical transport properties of the device without local damage due to beam exposure can be found in [66].

The effect of the gas can be clearly seen as a decrease in intensity in the middle of the MoS$_2$ channel shown in figure 12(b) right. To investigate in detail the effect of NO$_2$ gas on the MoS$_2$ channel, each spectrum contained in the SPEM maps was peak deconvoluted with an automated routine. Figure 12(c) show the total area of the fitted Mo 3d$_{5/2}$ component, presented as maps. In UHV (left), the MoS$_2$ channel and the excess MoS$_2$ flake in the top right corner can be clearly distinguished from the parts of the device not containing MoS$_2$ (purple). By contrast, in the presence of NO$_2$ (right), the Mo 3d$_{5/2}$ component seems vanished from the middle of the MoS$_2$ channel and can only be found in the regions closest to the Au contacts. This is a result of the drop in conductivity induced by the gas, which cause the Mo 3d$_{5/2}$ component in the middle of the channel to be shifted out of the energy window of the SPEM map due to sample charging. Only the regions in close proximity to the Au contacts avoid sample charging at such high gas pressures. Figure 12(d) shows XPS spectra extracted from the same area of the MoS$_2$ channel in UHV and NO$_2$ gas, illustrated in figure 12(c) by black and red boxes, respectively. In UHV, the Mo 3d$_{5/2}$ component can be observed, while in NO$_2$ gas, it is no longer present and detailed spectra, not reported here, showed no indication of Mo oxide formation.

In summary, we have demonstrated how SPEM and NAP-cell can be employed to investigate both operando chemical and electrical properties of 2D-materials based devices. The richness of the data offered by the chemical maps open the future possibility to investigate in detail the sensing mechanism of a single MoS$_2$ micrometric flake in a working gas sensor prototype.

9. Conclusion

With the studies presented in this paper, we demonstrate the wide flexibility offered by the unique combination of SPEM and NAP-cell in a variety of different case studies and setups. We showed the possibilities offered by this approach in fundamental study, like metal oxidation dynamics, where reactions on a specific sub-micrometric structure can be addressed, or following the intercalation of oxygen underneath a graphene coating, and also in more applicative research where the behaviour of the active sensing material, in a working prototype of gas sensor, can be highlighted in realistic condition and at the relevant scale.

For research in fundamental and applied surface science, microscopic and spectroscopic methods are a mainstay. The ability to have chemical identification at sub-micrometric scale, under in-situ and operando conditions, is very powerful in that it can yield more conclusive results when microscopy and spectroscopy are simultaneously combined in a single technique.

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