Time-Resolved APXPS with Chemical Potential Perturbations: Recent Developments at the MAX IV Laboratory

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Introduction

Heterogeneous systems made up of gas-solid interfaces are common in nature and in industrial processes. They play a critical role in heterogeneous catalysis, formation of weather patterns, atmospheric phenomena, and corrosion. For many of these systems, the activity and structure of the interface are intimately related and rapidly responding to changes in the gas phase composition. To understand such activity-structure relationships, correlated measurements of activity and interfacial structure and composition are required. Often, studies of heterogeneous systems focus on experiments under steady-state conditions. Under such conditions, however, the acquisition of correlated data is often complicated by the dynamic nature of the heterogeneous processes and their complexity [1]. For example, under steady-state conditions only the slowest reaction steps and most abundant intermediates are characterized. It is only when the system is driven away from its steady state and allowed to relax that the true time evolution of its key features becomes observable. The literature often discusses that such transient methods result in a better mechanistic understanding of surface reactions than steady-state experiments [2]. The general scheme for a time-resolved experiment thus should follow the classical pump-probe scheme: the transient conditions are created on demand by driving the system away from the steady state via an external perturbation (the pump). Among the multitude of methods to excite/perturb the system, chemical potential perturbations are desirable for investigating activity-structure relationship and can be implemented via changes in gas composition above the solid surface. The structural/compositional response is then measured (the probe) during subsequent relaxation of the system into the previous (for reversible processes) or new (for non-reversible processes) resting state (Figure 1) [3].

The simplest way to perform a time-resolved measurement is to decrease the acquisition time for a measurement. However, the signal-to-noise ratio required for extraction of meaningful information sets the lower limit achievable in this approach. The analysis of a consequent series of such measurements allows extraction of the time evolution of the signal. During such an experiment, the measurements of the sample response occur in real time, which gives the advantage of studying non-reversible processes as well as spontaneously oscillating reactions. It thus becomes possible to precisely match composition data with the activity characteristics. Both the perturbation and measurement must occur on a much shorter time scale than the subsequent relaxation to provide meaningful data.

During the past two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has developed to become one of the most popular and powerful experimental techniques for studying gas-solid interfaces under realistic conditions. Currently, the time resolution of XPS experiments with chemical perturbations is limited to a few hundred milliseconds when performed at modern synchrotron facilities; reaching a time resolution far better than this is currently a challenge, due to the relatively low efficiency of the collection of photoelectrons and the presence of the gas phase at few mbars. To overcome this issue and achieve a breakthrough in the time resolution of the APXPS experiment, it must be combined with an averaging approach in which the same process is repeated multiple times and the data are summed/averaged to improve the signal-to-noise ratio.

In the following examples, we demonstrate the current state-of-the-art time-resolved in situ APXPS measurements performed at the SPE-
CIES and HIPPIE beamlines of MAX IV Laboratory with and without the help of event-averaging. Experimental methodologies for data collections and analysis, advantages of each approach, their limitations, and the best achieved time resolutions will be discussed.

**Case study: Reaction mechanisms of ALD unfold with time-resolved APXPS**

Atomic layer deposition (ALD) is a technique for accurately growing highly uniform and conformal ultrathin layers of material with high aspect ratio on both flat and structured substrates [4]. The technique relies on cyclically exposing the substrate to gas phase precursors that react with the active parts of the surface in a self-limiting fashion. Characterization of the deposited layers is often carried out using XPS [5, 6]. Ex situ XPS measurements, while providing an excellent characterization tool of the grown layers after a few or several ALD cycles, do not result in any deeper insight into the surface chemistry of ALD since they do not carry information on, e.g., transient surface species and kinetics. True in situ measurements, carried out during the ALD, are required to provide such insight, but are difficult to perform due to the complexity of the ALD process and vapor pressure and temperature requirements. As an in situ technique, APXPS is an excellent match to ALD, as the ALD pressure and temperature regimes are very close to those achievable with current APXPS sample environments [7, 8].

Here, we present an example of the ALD of the high-κ oxide HfO₂ on thermal and native oxide-covered InAs substrates from the tetrakis(dimethylamido) hafnium (TDMAHf) and water precursors [9]. In the first half-cycle, TDMAHf was dosed onto the InAs surface at a pressure of approximately 10⁻³ mbar (Figure 2). During the dosing, X-ray photoelectron (XP) spectra of the In 4d and Hf 4f as well as the As 3d core levels were acquired at a repetition rate of about 0.1 Hz to obtain the image plots shown in Figure 2a and b. The In 4d/Hf 4f image plot clearly shows that a new doublet appears upon exposure of the InAs substrate to TDMAHf. Its binding energy is consistent with that of HfOₓ. At the same time, the oxide covering the InAs surface is reduced, as is visible from the disappearance of the oxide components in the As 3d XP spectrum at around 44.0 eV binding energy. A deeper analysis from the in situ study highlights that the amount of available oxide from the InAs surface limits the deposition of TDMAHf complexes. Indeed, the thickness of the HfOₓ overlayer that is formed is determined by the thickness of the oxide on the InAs surface prior to the deposition [10]. These results show how the time-resolved in situ APXPS measurements allow us to understand the gap between ideal

![Figure 2: (a) InAs oxide removal and (b) HfOₓ formation during the first half cycle of HfO₂ ALD on InAs. Reprinted with permission from ref 11. © 2020 American Chemical Society.](image-url)
and real reaction mechanisms in ALD by being able to record valuable chemical information from the surface as the surface chemical reaction is on-going [11].

**Well-defined gas perturbations synchronized with time-resolved XPS at SPECIES**

Temporal Analysis of Products (TAP) is an example of a powerful time-resolved analytic technique that relies on the ability to impose well-defined perturbations of the gas composition. The technique makes use of the spatial and temporal distribution of the gas molecules scattered from the surface of a solid sample, which is characteristic of its structure and the nature of the solid-gas interaction. This, combined with use of a robust model of the gas transport through the reactor device, gives TAP its key advantage—the possibility to precisely quantify the reaction kinetics of the investigated surface chemical reaction. When combined with tr-APXPS measurements, the TAP experimental/modelling approach can enable full reconciliation of the spectroscopic and kinetic data at sub-second temporal resolution [12]. The required well-defined fast perturbations of the gas phase composition must be digitally synchronized with XPS data acquisition, which has been challenging to achieve in practice. At the SPECIES beamline, we have recently developed a hardware/software interface for performing well-defined and fully automated gas perturbations fully synchronized with time-resolved XPS data acquisition, paving the way for kinetically well-defined APXPS experiments [13].

In proof-of-principle experiments based on the injection of nitrogen gas pulses over a gold foil [11], the delay line detector (DLD) of the tr-APXPS analyzer was triggered by a TTL signal generated by a home-built Raspberry Pi 3 unit and controlled by a custom-made Python software. The same unit triggered the operation of the fast-acting valve on the gas feed system. In addition, the composition of the gas effluent of the cell was probed by a quadrupole mass spectrometer (QMS). All measurements were obtained using the X-rays from a Mg K$_\alpha$ X-ray anode.

**Figure 3** shows the N 1s and Au 4f transient signals. They are visible already for 1s valve opening time, but become significantly more prominent as the valve opening time is increased to 10 s. Each data point corresponds to a single spectrum measured with a dwell time of 100 ms.

We have estimated the number of gas molecules injected per pulse to be in the order of $10^{-9}$ mol, similar to a typical TAP experiment. This establishes a semi-quantitative compatibility of our setup with laboratory-based TAP measurements in terms of accessible pressure, temperature, pulse intensity, and temporal resolution. The reproducibility and temporal characteristics of the perturbations were confirmed by conducting a series of 80 pulses into the AP cell at constant conditions.

We have also demonstrated that well-defined sequences of gas pulses can be used to gradually alter/prepare the chemical state of surfaces in APXPS experiments in a titration-like manner [11]. Eventually, the kinetic information from both the gas and surface phases will be reconciled for a more in-depth understanding of the surface-activity relationships underlying catalysis by complex materials.

**Following undercover catalysis with time-resolved APXPS**

Intercalation of atoms and molecules under 2D materials has been extensively studied in the past both under ultrahigh vacuum conditions and in the mbar regime [14]. Some studies report improved catalytic properties for transition metal surfaces covered by 2D materials [15]. However, a detailed understanding of undercover reaction mechanism including gas exchange kinetics is still missing.

At the MAX IV Laboratory, we have used gas-composition pulses created with mass flow controllers as a tool to study H$_2$ and CO oxidation below flakes of graphene. From our prior experience with intercalated surface structures of CO [16], H-atoms [17], and O-atoms [18] on G/Ir(111), it has become apparent that the core-level spectra of the 2D material can be used as an indirect probe to exclusively follow the catalysis taking place below the flake. For graphene, the sharp and intense C 1s signal gives a highly sensitive signal ideally suited for

![Figure 3: Transient signals from different valve opening times as seen in the XPS signal of (a) gas phase N 1s core level and (b) gold foil surface Au 4f core level. (c) Corresponding responses from the QMS placed on the outlet of the cell.](image-url)
time-resolved studies with short acquisition time for each spectrum. In fact, the C 1s signal is often better suited for following the undercover catalysis than the core levels associated with the reactant or product molecules.

Figure 4 compares O 1s and C 1s image plots acquired in situ with a frequency of 1 Hz and 4.2 Hz, respectively, on a Ir(111) surface half covered by graphene and held at 370 K. During acquisition, the total pressure was 1 mbar, the total flow 10 sccm, and the gas composition was oscillated between pure oxygen and 9:1 flow ratio of H2:O2 (marked H2 pulse the figure). Clearly, the O 1s image plot is very noisy, making quantitative analysis difficult. Also, the O 1s spectra are complicated by overlapping information about the surface chemistry on Ir(111) both without and with the graphene. In contrast, the C 1s spectra selectively probe the chemistry under the flakes. Also, the strong C 1s signal allows for performing a quantitative analysis without the need to bin the data, thus allowing us to study how water is formed undercover and replenished by intercalated oxygen without losing time resolution. Figure 4c shows the evolution of intensities for various C 1s components as a function of time. The time resolution achieved in this measurement was 240 ms. From the figure, it is clear that the water formation happens very rapidly. This is due to hydrogen mixing into the intercalated oxygen structure and resulting in subsequent undercover water formation. As the undercover water phases are very dense [19], the water becomes trapped and the graphene flakes partly re-laminate to the Ir(111) surface. This makes oxygen intercalation after the H2-rich pulse difficult and results in significant larger time-scale for this process.

Event-averaged measurements with internal synchronization signal

As discussed in the introduction, an increased time resolution of the measurement requires that the pulse-probe process be repeated multiple times and subsequently event-averaged. The key requirement enabling averaging is the synchronization of each cycle. In the following, we discuss a case study in which the synchronization signal is extracted from the data itself by post-processing the time-resolved data [20].
In the experiments, a Pd(100) crystal was kept at 550 K and exposed to a mixture of CO:O2 at 3.2 mbar total pressure. The composition was alternated between 2.7:1 (45 s duration) and 1.2:7 (145 s duration) mixing ratios. The change in composition caused the surface structure to oscillate between a so-called √5 surface oxide (Figure 5a, left) and a CO-covered Pd surface (Figure 5a, right). Raw spectra measured during a single cycle are shown in panel b of the same figure. Clearly, curve-fitting and a quantitative analysis of these spectra without time binning are impossible.

To maintain the time resolution, we have developed a method to bin the data on an event basis. The method is based on searching in the raw data for a locking signal (any feature in the image plot can potentially be used for this) that defines the transition events from the √5 surface oxide to the CO-covered surface and vice versa. Examples of such signals are shown in Figure 5b with the two small, dotted squares. The algorithm loops over the multiple cycles and searches for the best match between these stamp signals in all (58 cycles) pulse sequences. Hereby, the absolute time of the transition in every cycle is determined and the final event-averaged image can be constructed using these internal time stamps. The result of the final event-averaged image plot is shown in Figure 5c. Clearly, this dramatically improves the signal-to-noise ratio, and a quantitative analysis becomes possible at a preserved 148 ms time resolution (Figure 5d).

This way of event-averaging has the advantage of using a synchronization signal originating from the structural or compositional changes on the surface or in the gas phase just above it. Such a signal is independent of the external conditions, such as stability of the gas flows or the repeatability of the individual cycles. Finally, the use of an internal synchronization signal also opens the door to time-resolved studies of non-periodic processes such as, e.g., spontaneous surface oscillations [21].

**Event-averaged measurements with external synchronization**

When the acquisition time of a single spectrum reaches a few microseconds, the total electron count becomes limited to a few dozens. This is insufficient to extract any stamp signal from the raw data. Therefore, the events must be synchronized externally to ensure sorting of the obtained data into correct time bins.

An experimental setup allowing for such synchronization was built at the HIPPIE beamline of the MAX IV Laboratory [22]. In the setup, a sample can be exposed to short gas pulses with mbar internal pressures created by a fast piezo valve [23]. The time-resolved spectra are then measured by the APXPS electron energy analyzer equipped with a camera capable of acquiring data with 20 µs resolution. Both the valve and camera shutter are controlled by a delay generator, providing external synchronization to the setup. Figure 6a shows the evolution of the N 1s gas phase and Pt 4f surface signals during pulsing N2 gas onto the surface of the Pt sample. Panel b of the same figure shows the evolution of the peak areas and internal gas pressure calculated from the scattering of the Pt 4f signal [20]. Clearly, it is possible to generate and measure pulses with the internal pressure of 1 mbar that are a few hundred µs long and with less than 100 µs rising edge.

When a second gas is introduced into the chamber (either via a second pulse valve or a leak valve), one can study chemical reactions between the two reagents while oscillating the composition of the gas mixture. Figure 6c shows O 1s spectra measured while pulsing CO into a constant stream of O2 onto a Pt(111) surface held at ~400°C. Observation of both the O 1s gas phase (signals with a binding energy larger than 535 eV) and surface (binding energy smaller than 535 eV) components in the same spectra allows for correlation of the catalyst’s activity and its surface chemical composition. Thus, from the evolution of the gas phase peaks in Figure 6c, a clear transient nature of both CO pulse and O2 flow is seen. This is due to a complete replacement of oxygen by carbon monoxide during the CO pulse. The analysis of the surface peaks shows that the Pt surface is covered with a mixture of surface oxide and chemisorbed oxygen before the CO pulse (spectra corresponding to 700–775 µs). These surface species get consumed by the CO pulse simultaneously but are
still present on the surface when the surface is highly active (spectra at 800 µs and 825 µs). The inset of Figure 6c shows measurement of a gas phase at 800 µs delay, which corresponds to the maximum CO₂ production rate as discussed in [20]. Finally, after complete oxygen replacement by CO (spectra at 859 µs and 900 µs), the Pt surface becomes covered by CO species, and it is no longer catalytically active for CO oxidation.

Conclusions and outlook

To summarize, we have discussed and exemplified how we use time-resolved APXPS combined with gas-composition pulses as a tool to study surface processes. In particular, we have discussed how the time resolution can be increased by using a specific spectroscopic probe, such as a 2D material or by event-averaging the data either using an internal or external synchronization signal. Event averaging over many events requires a high repetition frequency of the gas-composition pulsing. To achieve this, a small reactor volume and/or directional dosing of reactant molecules onto the sample surface are needed. This will be realized in the improved cell designs, which will combine the fast gas-composition pulsing with our transferrable sample holders and ultra-high vacuum systems at the SPECIES and HIPPIE beamlines at the MAX IV Laboratory.

When the time resolution of measurement approaches microseconds, its efficiency falls dramatically in case only a single time delay is recorded per cycle. Thus, in an experiment with 100 µs time resolution and 100 Hz repetition rate (10 ms period cycle), the detector idles for 99% of the time. Long relaxation time might be necessary to pump away injected gas. In such cases, fast detectors capable of continuous data readout such as delayline detectors (DLD) become essential for acquisition of spectra with high time-resolution.
We hope that this article can inspire other synchrotron light sources to initiate work with time-resolved measurements using chemical perturbations such as gas composition pulses within the APXPS field but certainly also outside it.

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