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J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/jp312706s • Publication Date (Web): 08 Feb 2013

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Design and Performance Aspects of a Custom Built Ambient Pressure Photoelectron Spectrometer Towards Bridging the Pressure Gap: Oxidation of Cu, Ag, and Au Surfaces at 1 mbar O₂ Pressure

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Abstract: The critical features of a custom built laboratory version ambient pressure photoelectron spectrometer (Lab-APPES) are presented. A double front cone differential pumping arrangement and an aperture free design employed in the electrostatic lens regime improves the data collection and data quality. In contrast to the conventional x-ray photoelectron spectrometers (XPS) operating at ultra high vacuum (UHV), it is possible to explore the electronic structure of solid surfaces under working conditions or closer to working conditions with Lab-APPES. Especially surface dependent phenomena can be explored up to 1 mbar pressure and up to 873 K by conventional heating methods and up to 1273 K by a laser heating method. Simultaneous XPS and reaction kinetic measurements on solid surfaces make the Lab-APPES an important tool to measure the dynamic electronic structure changes on material surfaces under reaction conditions. The interaction of O₂ with polycrystalline foils of Cu, Ag, and Au from UHV to 1 mbar and up to 773 K has been studied.

Keywords: XPS, APPES, 1 mbar, electronic structure, surface science, heterogeneous catalysis
1. Introduction

X-ray photoelectron spectroscopy (XPS) has been available since the mid 1960’s and has been an indispensable tool to chemists and physicists in unraveling the electronic structure of many compounds and materials of interest\(^1\). XPS works on the photoelectric effect; by shining UV/X-ray photons on a solid surface, electrons are ejected from the valence and core levels. Energy conservation is governed by the fundamental equation (Eq. 1). The binding energy (BE) is the energy required to excite an electron from any occupied level to the Fermi level (\(E_F\)), and the additional energy required to remove an electron from \(E_F\) into vacuum is the work function (\(\phi\)) of the solid, and the remaining energy is associated with the ejected electron in the form of kinetic energy (KE), which depends on the photon energy (Eq. 1). Electrons that are ejected into the vacuum should

\[
h\nu = BE + KE + \phi \quad [1]
\]

reach the detector, without any inelastic collision with any other atoms/molecules within the solid surface layers or in vacuum; due to this stringent requirement ultra high vacuum (UHV) (\(\leq 10^{-9}\) mbar) is maintained in XPS spectrometers.

Although XPS gives a wealth of information about the electronic structure of material surfaces, there is always a question asked about the applicability/reliability of the information derived from this technique. This is primarily due to the pressure difference that exists between the XPS measurement condition, which is UHV, and the actual working condition of the material, which is usually the ambient condition. Indeed, the above pressure difference is more critical for materials that are involved largely in surface dependent phenomena/activities, such as, adsorption, catalysis, electrochemistry, and nanomaterials. For example, industrial catalysis
occurs at atmospheric or high pressures as well as at high temperatures; however the electronic structure information derived on catalysts in XPS was under UHV conditions, and correlation among them could only be established for limited systems.\textsuperscript{2-3} The above pressure difference between UHV measurement conditions in XPS and the actual working conditions of the materials was often considered as a reason for the above disconnect, and it is known as “pressure gap” in surface science.\textsuperscript{4} The last decade has seen a real impetus in developing new tools for probing materials at realistic conditions or closer towards that.\textsuperscript{5} The demanding needs of environmental and catalysis science have driven the advancement of photoelectron spectroscopy to function at higher pressures. For instance, rational design of new functional materials, whose properties are solely dependent on surface or subsurface phenomena, needs to be understood at the molecular level under in-situ conditions as well as in a time resolved manner. The time resolved fast XPS results using synchrotron radiation were helpful to elucidate the reaction mechanisms of several industrially relevant catalytic problems.\textsuperscript{6} The high brilliance of synchrotron radiation available worldwide has also aided in developing and creating facilities for doing APPES.\textsuperscript{7}

It is worth mentioning that the new generation of APPES evolved due to the constant efforts by several groups around the globe who contributed to the development of APPES. In the late 1970’s, M. W. Roberts, Cardiff Univ., attempted to bridge the above pressure gap, but with limited success.\textsuperscript{8} Nonetheless, it was successfully attempted by Robert Schlögl’s group at Fritz-Haber Institute, Berlin and Miquel Salmeron’s group at Univ. California, Berkeley during the last decade.\textsuperscript{9} Of course there are few other groups who also built their own Lab-APPES\textsuperscript{10-11} and, notably H-P. Steinrück, Univ. Erlangen-Nürnberg is one among them.\textsuperscript{10} Indeed, the APPES measurements could be carried out with either laboratory x-ray sources or with synchrotron
radiation. The popularity of this technique among the researchers is evident from the commissioning of Lab-APPES by a few other groups.\textsuperscript{12-13} Recently, a custom-built Lab-APPES unit was commissioned at National Chemical Laboratory (NCL), Pune (Figure 1). Basic design features were provided by NCL, Pune and the system was supplied by Prevac, Poland; XPS/UPS measurements can be made up to 1 mbar pressure and up to 1273 K on the solid surfaces in the above Lab-APPES system. The details of the setup are given in the following section.

![Figure 1. Photograph of the recently installed Lab-APPES at CSIR-NCL, Pune.](image)

2. Experimental section

General features that are common for APPES can be found in detail in the earlier literature reports\textsuperscript{7-11} and they are not mentioned in this section. Those aspects that are relevant and special to our APPES system are described in detail. Following major advancements in the instrumentation, particularly, contributed to the development of APPES around the world. Over the last decade, an advanced electrostatic lens regime (ELR) with effective electrostatic focusing has been developed. In the conventional (UHV) XPS units, electrons that are collected from the
sample surface into the ELR undergo divergence, and hence the number of electrons decreases when they pass through each aperture. However, in APPES this cannot be affordable, since the number of electrons collected into the ELR at high pressure is significantly lower. This is simply due to more inelastic collisions that occur at high pressures, say 1 mbar. Hence, to retain the electrons that are collected into the ELR, three important parameters are adapted in the analyzer (VG Scienta R3000HP) of the Lab-APPES at NCL, Pune (Figure 2). First, the sample surface is kept very close to the tip of the cone attached to the ELR (effective differential pumping starts here), mainly to minimize the loss of electrons due to inelastic collisions at 1 mbar. The above distance is typically 0.5-1 mm in our Lab-APPES system. Electrons with a KE of 400 eV in 1 mbar O\textsubscript{2} atmosphere can survive up to 4 mm; before they undergo inelastic collisions.\textsuperscript{9} It underscores the necessity of decreasing the distance between the sample surface and the tip of the ELR. Once electrons enter into the ELR, two main factors contribute to obtain high quality spectral data, namely, effective differential pumping and the converging of electrons in the ELR. Effective differential pumping creates a better vacuum in the ELR. At 1 mbar N\textsubscript{2} pressure, a vacuum of \(5 \times 10^{-4}, 10^{-6}\) and \(10^{-7}-10^{-8}\) mbar is maintained in the first, and second differential pumping sections in the ELR, and in the third differential pumping in the electron energy analyzer (EEA), respectively. First, second and third differential pumping regimes are pumped down by a combination of 400, 300 and 400 l/s turbo molecular pumps, backed by rotary pumps. The area pumped increases gradually from first to second ELR to EEA. Further, a special design of a double front cone pumping arrangement (Figure 2) is available in the ELR. Both cone regions are shown in different colors. The main advantage with this design is a fast decrease in pressure with a steep pressure gradient from the bottom of the cone (which is very close to the sample surface) to the EEA. This helps to minimize inelastic scattering in the ELR. Another
critical factor that minimizes the loss of electrons in the ELR is the utilization of the advanced concept of electron converging in the ELR. In contrast to the conventional ELR,\textsuperscript{9} electrostatic voltages in the R3000HP model analyzer are applied in such a way that they converge all the electrons.\textsuperscript{14} Further, unlike other high pressure electron analyzers,\textsuperscript{9} R3000HP employs an aperture free ELR (Fig. 2b). This design enables the study of angle resolved XPS and fast data acquisition under 1 mbar conditions. Fundamentally, an electrostatic lens in the APPES unit refocuses the electron trajectory in such a way that electrons are converged due to the applied potential; more details are available in ref. 14.
Apart from the above advancement in the ELR, a few other critical design aspects are also incorporated. (a) An exchangeable cone with different apertures (0.3 to 5 mm) can be fitted to the tip of the ELR. Currently, a 0.8 mm aperture is fitted in the APPES system for high pressure XPS measurements and the data reported in this communication is obtained with the above aperture. Indeed, this cone separates the ELR and EEA regions through effective differential pumping to maintain increasingly better vacuum from the high pressure region on the sample surface in the analysis chamber. (b) The highest resolution achieved is $0.42 \pm 0.02 \text{ eV}$ with 50 eV pass energy at a (analyzer entrance) slit width of 0.2 mm, and it is in good agreement with that reported for the R3000HP by Mangolini et al.; however, the resolution measured is $0.6 \pm 0.02 \text{ eV}$ with the maximum slit width of 3.0 mm of the analyzer.

Apart from the R3000HP analyzer, our Lab-APPES system has several distinctive features for analysis and experimentation. These are discussed in the following sections. A bird’s eye view of the analysis chamber of the APPES viewed from the analyzer side (but without the analyzer) is shown in Figure 3. The instrument carries two excitation sources for carrying out XPS. One is a conventional dual anode (Al K\(\alpha\) and Mg K\(\alpha\)) which can work up to a maximum power of 600 and 400 W, respectively. The other excitation source is an Al K\(\alpha\) monochromator MX 650 from VG Scienta. The X-rays work with an acceleration voltage of a maximum of 15 kV with a maximum output power of 650 W. The X-ray monochromator is isolated from the analysis chamber by a thin aluminium window (5 \(\mu\)m) mounted in a ring and inserted into the port separating analysis chamber and monochromator through a 150CF axis port. The aluminum window efficiently seals the monochromator region, and hence the analysis chamber could be held at 1 mbar during high pressure experiments with a stable monochromatic X-ray generation.
by the MX650. Easily a vacuum level of $10^{-6}$ mbar is maintained in the X-ray monochromator regime, when the analysis chamber pressure is at 1 mbar. This effectively minimizes x-ray absorption by gas phase molecules to a negligible level in the monochromator regime. Apart from Al and Si$_3$N$_4$, graphene oxide has been reported recently to be effective for X-ray transmission under high pressure conditions.$^{15}$

The analysis chamber is also equipped with a UV source which can give stable He I and He II UV radiation for doing valence band photoelectron spectroscopy (UVPES) under UHV as well as 1 mbar conditions. The water cooled UV source is mounted on a CF40 flange which can give an emission current up to 100 mA for He I and 200 mA for He II. Reference metal surfaces spectra recorded with UVPES at 1 mbar N$_2$ pressure demonstrate the distinctive feature of the survival of low KE electrons at high pressure. Data obtained from XPS and UVPES at high pressure would be complementary, since valence band features from different elements can be identified. An electron flood source operating between 0-500 eV for charge compensation during XPS operation is attached to the analysis chamber. This is not only useful for analyzing insulating or semi-conducting materials with XPS, but also under 1 mbar conditions. A major advancement in our Lab-APPES setup is the ability for carrying out photoemission at 1 mbar pressure. The gas manifold is equipped with three mass flow controllers and useful to mix three different gases to a required composition to generate gas mixtures to simulate catalysis reactions. The gas manifold is connected to the gas doser via a z-axis manipulator in the analysis chamber. The capillary of the gas doser inside the analysis chamber can be extended very close to the sample holder. Further, this gas doser can be heated up to 873 K, mainly to heat the input gas for the experiments that are to be carried out at high temperatures. High temperature on the sample surface can be maintained better, when the input gas is also heated to that temperature. This is
especially critical at high pressure, where the heat dissipation is expected to be more due to convection as well as conduction.\textsuperscript{9}

One of the critical aspects of any high pressure experiments is the accurate measurement of the pressure near the reaction zone, which is the sample surface. This is achieved using a CTR gauge connected to the analysis chamber through a CF35 flange and extending all the way close to the sample surface (Figure 3). This arrangement makes sure that the pressure achieved and

**Figure 3.** A bird’s eye view of the main chamber viewed from the analysis chamber side and without the analyzer. The inset shows an expanded view of the analysis spot to illustrate the pressure measurement with a CTR gauge and the gas dosing arrangements.
reported in our in-situ studies are accurate. Lab-APPES measurements can be complemented by quadrupole mass spectral (QMS) measurements. This is achieved by interconnecting the analysis chamber to the QMS placed in the preparation chamber through a bellow and a leak valve kept close to the QMS. This arrangement allows simultaneous spectral and kinetic measurements and there is no time lag between them. A similar arrangement is available between the QMS and the first differential pumping of the analyzer stage. This is similar to the previously reported APPES design by Somorjai and co-workers.\(^{16}\) Since the cone of the analyser is held very close to the sample surface (0.5 mm) the arrangement like this makes sure that the gas analysis is from the outcome of the reactions from the sample surface and not from the residual reactivity from other parts of the chamber. Thus, the setup acts like a sniffer assembly for studying the reactivity of surfaces. Another fine leak capillary, which is connected directly from the analysis chamber to the QMS, can also be used for product analysis and also to compare the results obtained from the first differential pumping stage mass spectral data.

Special sample holders, which can be heated resistively and also using electron bombardment, can withstand the sample temperature up to 2273 K in UHV. Often heating the samples under high pressure reactive gases (1 mbar) is not practical because of the issues related with the stability of the heating filaments. To overcome this problem laser heating is employed where the sample surface can be heated up to 1273 K using a near IR laser \((h\nu = 920 \text{ nm})\) with 120 W power. The whole assembly is mounted outside on a special optical window where the laser power can be controlled and collimated and allowed to fall on the sample thereby achieving precise heating.
High resolution Pd 3d core level spectra measured under different O$_2$ partial pressures at ambient temperature are shown in Figure 4a. The same spectra, recorded in fixed or fast data acquisition mode in 1 s, are shown in Fig. 4b. Only a marginal change in intensity and count rate is observed for high resolution spectra between UHV and 10$^{-2}$ mbar. However, at 1 mbar the count rate decreases to about 45% of that of UHV conditions. We attribute the above quality results to effective differential pumping in the ELR regime, which minimizes the inelastic scattering. Hardly any change in BE (335 eV for Pd 3d$_{5/2}$) is observed, indicating that the Pd

![Figure 4](image-url)

**Figure 4:** Lab-APPES measurements recorded for Pd-foil at ambient temperature for Pd 3d core levels at (a) different O$_2$ partial pressure, and (b) spectra acquired in 1 s at different O$_2$ partial pressure. The dashed line is a guide to the eye. 1 s spectra acquired indicate the possibility of measuring transient kinetic aspects and reaction dynamics on catalysts under 1 mbar conditions.
remains in the metallic state.\textsuperscript{17} Fig. 4b gives an idea of the quality of data collection possible in 1 s by fixed mode. This is similar to a snapshot recorded for fast movement by high resolution cameras. It is to be noted that the same basic features, such as BE, FWHM, as those at high resolution are very well observed in the 1 s spectra. Although the signal/noise (S/N) is around 6 for a spectrum recorded at 1 mbar, it is higher for the spectrum recorded at lower pressure. This feature demonstrates the possibility of following the reaction dynamics for some of the reactions.

3. Results and Discussions:

The first set of experiments has been carried out on the interaction of oxygen with polycrystalline coinage metal (group 11) surfaces using APPES and explained in the following section. The knowledge accumulated over the years from studies on clean solid surfaces had great impact on our understanding in areas like corrosion, catalysis, semiconductor technology and biomedical sciences.\textsuperscript{18-19} Interaction of oxygen with transition metal surfaces and catalytic oxidation reactions has been an area intensely pursued by surface scientists due to technological and industrial importance. From the perspective of catalysis, the interaction of oxygen with late transition metals, especially Cu, Ag, and Au, has been studied by several surface science techniques for its applications related to methanol synthesis and its oxidation, steam reforming of alcohols, epoxide formation, CO oxidation, and several other industrially important reactions.\textsuperscript{20} Systematic surface science studies, where XPS and UPS were employed for studying these three surfaces, were reported by Evans and co-workers as early as 1974.\textsuperscript{21} Thus, initial stages of the oxidation of these metal surfaces, the dynamic evolution of oxide phases on the metal, and the sub surface diffusion of the oxygen and its consequences on surface electronic modification have had a huge impact on the understanding of catalysis phenomena.\textsuperscript{22} The recent developments in the APPES have led to re-visiting some of the fundamental surface science problems like
oxidation of metal surfaces under near ambient conditions. Especially Pd- surfaces has been employed, and the results are reported in detail.\textsuperscript{23}

Many other metal surfaces are yet to be studied by APPES, including Cu, Ag, and Au. In this regard we have carried out the in-situ studies up to 850 K and 1 mbar on the interaction of oxygen with polycrystalline foils of Cu, Ag, and Au using APPES in our laboratory. Specifically, polycrystalline surfaces have been employed, as the surface characteristics are similar to that of catalytically active metal surfaces in supported metal catalysts. Further, this would also bridge the material gap\textsuperscript{2} to a significant extent. Au, Ag, and Cu metal foils, obtained from MaTeck GmbH, Germany, were cleaned in the preparation chamber by repeated cycles of Ar\textsuperscript{+} sputtering and annealing. The cleanliness was checked by XP spectra. The O\textsubscript{2} gas (99.99\%) controlled by flow controller was introduced up to 1 mbar by a variable leak valve. We confirmed that there are no detectable gas impurities by mass spectroscopy. XP spectra were measured using monochromatic Al K\textalpha{} (1486.6 eV) unless otherwise stated.

Curve fitting was performed by the software CasaXPS, using asymmetric Lorentzian–Gaussian sum-type line-shapes, preceded by a subtraction of the Shirley background. Gas-phase peaks from O\textsubscript{2} under ambient-pressure conditions were observed at 538 eV and they do not overlap with the peaks from the sample surface. As for the XPS intensity, it is noted that the intensities taken under different conditions cannot be directly compared, because the presence of the ambient-pressure gas affects the photoelectron intensity, and therefore the intensity was normalized.

3a. O\textsubscript{2} at 1 mbar on Au surfaces:

Surface science studies on the adsorption of oxygen on bulk gold surfaces are rarely attempted largely due to the low heats of adsorption of O\textsubscript{2} on Au surfaces.\textsuperscript{24-25} One of the earlier
works by Madix and co-workers demonstrated this by showing no adsorption under vacuum conditions ($10^{-4}$ Torr). The adsorption was in turn induced by generating atomic oxygen through a hot platinum filament. The enormous interest that nanogold has generated for various oxidation reactions prompted us to re-investigate the metal surface under APPES. The O 1s and Au 4f core level spectra recorded at 1 mbar and at various temperatures are shown in Figure 5. It is very clear from the O 1s spectrum that from room temperature to 600 K and at 1 mbar O$_2$ the surface showed no evidence for oxygen adsorption. Interestingly, a weak and broad feature started to develop above 600 K which transforms into a solid peak centered around 529.9 eV (arrow in Fig. 5a). Earlier literature related to XPS studies on the Au oxidation and oxides of gold shows that the O 1s in Au(III) oxide exhibits a BE feature at 530 eV. The remarkable closeness of the O 1s feature observed in Lab-APPES with the values reported in literature is worth looking at in more detail in the future. Presumably these features could possibly originate from the oxidation of the under-coordinated Au atoms present on the polycrystalline gold foil. O 1s features from gas phase molecular oxygen appear between 538 and 540 eV. Au 4f core level spectra recorded from RT to 850 K in 1mbar O$_2$ hardly show any change. The Au 4f$_{7/2}$ core level appears at 84.1 eV, a typical BE reported for metallic Au. Indeed it reiterates the highly inert nature of bulk gold, in spite of surface defects on polycrystalline gold.

3b. O$_2$ at 1 mbar on Ag surfaces:

Figure 6 shows the Ag 3d core level data collected from Lab-APPES at 1 mbar O$_2$ at different temperatures on a Ag foil. Indeed, complementary experiments from UHV to 1 mbar at different temperatures have been measured; since the changes observed are from significant to maximum level at 1 mbar, we restrict our discussion to the same. A sputter-cleaned Ag metal surface under
Figure 5: Core level spectra measured while exposing 1 mbar of O$_2$ on a polycrystalline Au foil at various temperatures. (a) O 1s, and (b) Au 4f$_{7/2}$. O 1s features from gas phase molecular oxygen appear between 538 and 540 eV. Arrows are a guide to the eye.

UHV conditions at RT shows the Ag 3d$_{5/2}$ peak at 368.0 eV (dashed arrow) which is in agreement with the literature values. No feature due to common impurities like C, O, or Si was observed, indicating the atomically clean surface nature. After the above measurements, O$_2$ was allowed in the analysis chamber, and the O$_2$ partial pressure was increased gradually to 1 mbar. Once the pressure stabilizes at 1 mbar, XPS measurements were carried out at RT and higher temperatures. There are no significant changes observed, either in terms of shift in BE or FWHM of the Ag 3d features at RT. In fact, no O 1s feature was observed as well. The above observations underscore the inert nature of the Ag-surface, similar to gold, to O$_2$ at ambient temperatures. The Ag 3d$_{5/2}$ spectrum obtained at various temperatures at 1 mbar O$_2$ pressure showed an increased broadening and asymmetry on the lower BE side. It is to be noted that the Ag 3d$_{5/2}$ peak maximum occurs at the same BE irrespective of 1 mbar oxygen treatment at different temperatures up to 600 K. Broadening of the Ag 3d$_{5/2}$ peak observed at low BE is due
Figure 6. Ag 3d$_{5/2}$ spectra at 1 mbar O$_2$ pressure collected at different temperatures. Intensity is normalized to the UHV-RT spectrum. Difference spectra obtained by subtracting UHV-RT from 1 mbar - 600 K is given at bottom in yellow color demonstrate the presence of Ag$_2$O like feature. Inset shows the deconvolution of Ag 3d$_{5/2}$ spectrum measured at 1 mbar O$_2$ pressure and 600 K. Black and red color for experimental and sum of the fitted peaks, respectively. Green and grey color for metallic Ag and precursor to Ag$_2$O peaks, respectively. Background subtraction trace is given in pink color.

to gradually increasing interaction between the Ag surface and O atoms. Indeed the difference spectra obtained between 1 mbar -600 K and UHV-RT spectra shows the feature at 367.5 eV, due to Ag$_2$O like feature. The inset in Fig. 6 shows the deconvolution of the Ag 3d$_{5/2}$ core level recorded at 1 mbar O$_2$ pressure and at 600 K. The feature at 367.5 eV is similar to that of Ag$_2$O. However, the predominant Ag- feature suggests that either the interaction with oxygen is weak or there might be other processes, like migration of atomic oxygen to subsurface layers and/or bulk.

Figure 7 shows the O 1s spectrum measured at different temperatures and at 1 mbar O$_2$ pressure on Ag surfaces. Unlike gold surfaces, silver interacts with oxygen, and it is evident from
the results given below. It can be clearly seen that adsorption of O$_2$ at 1 mbar at 300 K results in the formation of a feature at 530.5 eV (dashed arrow) in the O 1s core level spectrum. The intensity of the 530.5 eV peak increases as the temperature increases to 400 K. An increase in the S/N ratio underscores the oxygen interaction with Ag at increasing temperature. The spectrum recorded at 500 K and 1 mbar O$_2$ is considerably broader, and shifted towards higher BE indicating the presence of multiple peaks. This spectrum is deconvoluted with two different peaks at BE values of 531.2 eV (solid arrow) and 530.5 eV. Interestingly, the area under the 530.5 eV peak is lower compared to the spectrum obtained at 400 K suggesting that the higher BE peak is possibly growing at the expense of this peak. The O 1s spectrum obtained at 600 K is considerably sharper and exhibits only the presence of the feature at 531.2 eV peak. Rocha et al recently reported a detailed APPES work on the O-Ag system$^{22}$ and the feature at 530.5 eV is attributed to O$\alpha$ species which represents atomic oxygen adsorbed on the Ag surface. The atomic oxygen transforms to oxidic oxygen at 531.2 eV (O$\beta$) at temperatures above 400 K. This has been assigned by Rocha and co-workers as oxygen in an octahedral site below the Ag surface.$^{22}$ A detailed look at the literature suggests that the formation of a more stable oxide on the Ag surface is demonstrated by the appearance of an O 1s peak at 529.6 eV. It is understandable that we did not observe such a stable oxide feature in the present study as the feature, which is denoted in literature as O$_{\gamma}$$^{33-34}$, starts to appear at higher temperatures ($\geq$ 773K). Interestingly, we observe the formation of atomic oxygen on the surface and its transformation to subsurface oxygen, which is considered a precursor to the formation of the bulk oxide. The presence of a considerable amount of defects on the polycrystalline foil also facilitates the diffusion of oxygen into the subsurface in the present case. In spite of the heat treatment at 600 K in 1 mbar O$_2$,
Figure 7. O 1s spectra at 1 mbar O_2 pressure collected at different temperatures on Ag-foil. Polycrystalline Ag seems to be resistive to stable oxide formation, and Ag metal features are dominantly observed. Indeed, this could be the reason for the less significant changes in the Ag 3d feature; however, the low BE feature is attributed to the Ag atoms interacting with the above mentioned subsurface oxygen which is identified to be the precursor for stable oxides.

It is also to be mentioned here that the electron escape depth is few nanometers in the present analysis, since AlKα can penetrate deeper at normal incidence angle due to high photon energy (1486.6 eV). However, the KE involved with Ag 3d (~1115 eV) and O 1s (~955 eV) are not too different, and hence the depth of surface layers analyzed can be assumed to be approximately the same in the present communication. Nonetheless, core level analysis using incident photon energy around 410 and 575 eV (in any synchrotron radiation center) for Ag 3d and O 1s, respectively, and/or angle resolved spectral measurements would give more information on the surface sensitivity aspects. This is especially required if oxidation is limited
to top surface layer. A simple calculation\textsuperscript{35} mainly based on the KE of Ag 3d and O 1s core levels shows an electron escape depth of about 2.4 nm, suggesting the diffusion of oxygen atoms, at least to that depth.

3c. \( \text{O}_2 \) at 1 mbar on Cu surfaces:

The surface chemistry of oxygen with Cu is richer compared to Ag and Au, because of the much higher reactivity of Cu compared to the other two. Indeed 3d transition metals are known to be pyrophoric and easily get oxidized. The Cu 2p, and Cu LMM Auger spectra obtained in the presence 1 mbar \( \text{O}_2 \) from RT to 675 K are shown in Figures 8a and b, respectively. The Cu 2p spectrum from a clean Cu surface obtained under UHV conditions and at RT immediately after \( \text{Ar}^+ \) sputtering and annealing is shown for reference (Figure 8a). The Cu 2p\textsubscript{3/2} core level spectrum centered at 932.8 eV (grey solid arrow) which is characteristic of metallic Cu remains unchanged until 425 K indicating that the metallic nature of Cu surface is retained until this temperature.

The spectrum obtained at 500 K is clearly distinct from the one at 425 K by the shift in the peak maximum towards the lower BE side. The peak maximum in this case is at 932.4 eV (dashed arrow) which is characteristic of Cu(I) in the XPS literature.\textsuperscript{36-37} However it is to be noted that only from the core level shift in BE, it is difficult to ascertain the change in oxidation state, and Auger spectral measurements are also necessary to confirm the change in oxidation state, especially on Cu-based materials. This aspect will be discussed later. The characteristics of the peak at 932.4 eV remain the same until 600 K, indicating the stability of the Cu(I) species on the surface. Onset of oxidation of \( \text{Cu}_2\text{O} \) to \( \text{CuO} \) occurs between 500 and 600 K, and it is fully oxidized to \( \text{CuO} \) >600 K; it is evident from the observation of the following new features: (a) The high BE feature at 933.5 eV (dotted arrow) suggests typical Cu\textsuperscript{2+} species and indicates the
coexistence of Cu\(^+\) and Cu\(^{2+}\) species at 600 K. Deconvolution of the Cu 2p\(_{3/2}\) feature demonstrates the coexistence of Cu(I) and Cu(II) species at 600 K. (b) Evidence for the presence of CuO also comes from the well-developed Cu\(^{2+}\) satellite between 939 and 945 eV corresponding to the Cu 2p\(^5\)3d\(^9\) final state configuration\(^{37}\) from 600 K and above. (c) Cu 2p spectra at 625 and 675 K are broad (FWHM= 3.6 eV) exhibiting the presence of exclusive bulk CuO. No feature due to Cu\(_2\)O or Cu was observed at higher temperatures demonstrating the onset of bulk oxidation of Cu to CuO. (d) Charge transfer (\(\Delta\)) from the oxygen ligand to Cu\(^{2+}\) occurs, leading to a Cu 3d\(^{10}\) – O 2p\(^5\) configuration in the initial (ground) state.\(^{37,38}\) Indeed, this configuration is at higher energy due to charge transfer, compared to the Cu 3d\(^9\)- O 2p\(^6\) initial state. However on photoelectron emission from the Cu 2p core level, energy reversal occurs in the final state due to better shielding of core hole in Cu 2p\(^5\)3d\(^{10}\) compared to Cu 2p\(^5\)3d\(^9\), and this leads to the main line at 934 eV and satellites between 939-945 eV, respectively.\(^{38,39}\) Above energy reversal occurs due to attractive energy between Cu 2p core hole and valence electron in 3d, and the same is denoted as Q. Indeed the satellite feature is unique for the 3d\(^9\) configuration and observed easily. Energy associated with different configurations in the ground state and final states are shown schematically in Figure 9 for illustration.

It is well known that the different oxide phases of Cu are better discernable in the LMM Auger spectrum of Cu. The X-ray initiated Auger spectrum obtained at different temperatures at 1 mbar oxygen pressure is shown in Figure 8b. The UHV RT spectrum shows the characteristic Cu LMM Auger peak at 918.9 eV for clean Cu metal (grey arrow). In addition to the above metallic Cu feature, a new peak starts to emerge at 916.1 eV from 375 K onwards, indicating the growth of the Cu(I) phase (dashed arrow) on the surface. Upon increasing the temperature up to
Figure 8: Core level spectra measured while exposing a polycrystalline Cu foil to 1 mbar O₂ at various temperatures. (a) Cu 2p, and (b) Cu LMM.
Figure 9: Schematic energy level to show charge transfer (Δ) in the ground state and energy reversal in the final state configuration (due to Q), corresponding to main line. Energy of satellite feature due to Cu 3d⁹ configuration is relatively unaffected due to photoelectron emission.

500 K, the Cu(I) oxide phase at 916.7 eV increases at the expense of metallic Cu. On further increasing the temperature to 500 K, the fully developed Cu₂O feature is observed at 916.8 eV at the expense of the metallic Cu feature. This indicates the complete surface oxidation of Cu to Cu₂O at 500 K and 1 mbar O₂. In fact, the above complete oxidation to Cu₂O was observed better with Auger spectral changes than with Cu 2p core level changes. On increasing the temperature to 600 K the spectrum becomes broad, indicating the formation of a third type of species, Cu²⁺, on the surface. The Cu²⁺ LMM Auger peak at 918.1 eV (dotted arrow) obtained in the present case is in agreement with several literature reports. The growth of Cu²⁺ is much more evident in the 625 and 675 K spectra where the peak maximum is centered around 918 eV. Oxidation of Cu₂O to CuO is equally evident from Cu 2p core level and Auger spectral changes and they are in agreement with each other. Indeed, different KEs observed for different oxidation states lead to different Auger parameter values, and this reiterates the changes in oxidation state.

O 1s spectra acquired at different temperatures and at 1 mbar pressure are shown in Figure 10. An increase in temperature to 375 K at 1 mbar O₂ pressure is accompanied by a broad peak centered at 530.4 eV (dotted arrow). The feature at 530.4 eV in the O 1s spectrum is attributed to oxygen in Cu₂O. Along with the predominant 530.4 eV feature, the presence of a 532 eV species is observed in both the 375 and the 425 K spectra. The O 1s feature at 532 eV has been attributed to OH species in the past, but it could also be attributed to oxygen bound to residual impurities on the Cu surface. The O 1s feature at 530.4 eV grows in intensity, and other features disappear on increasing the temperature from 375 to 500 K. The O 1s spectrum at 500 K is mostly dominated by oxygen from Cu₂O species with the emergence of a new feature at
529.6 eV (dashed arrow). This feature is characteristic of CuO surfaces. Nonetheless, the spectrum measured at 600 K is dominated by 529.6 eV species, at the expense of Cu$_2$O, and demonstrates the oxidation of the Cu(I) to the Cu(II) state on the surface. Interestingly, we could find the presence of another species at around 531.3 eV which is attributed to the suboxide species.$^{41,43}$ The suboxide species is only stable under oxygen pressure and decomposes once the high pressure regime is reverted to UHV (data not shown). Oxygen from Cu$_2$O at 530.4 eV completely disappears >600 K indicating the complete oxidation of the surface layers to CuO.

Figure 10: O 1s core level spectra measured while exposing a Cu foil to 1 mbar O$_2$ at various temperatures. O 1s spectra were deconvoluted to show the systematic changes from Cu metal to CuO through Cu$_2$O.
Changes observed in the core level XPS reflect very well in the valence band (VB) spectra of Cu-surfaces (Figure 11) at 1 mbar O₂ pressure at different temperatures. UHV-RT spectra show the 3d₁₀ feature of Cu-metal surfaces. Onset of a new feature at 1.4 eV (dashed arrow) is observed on O₂ treatment at 375 K. This particular feature grows in intensity up to 500 K, and then it decreases. This feature is attributed to the Cu₂O formation on the surface. A characteristic narrowing of the 3d band at 3.2 eV occurs at 500 K, compared to the spectra recorded at lower temperatures; it is attributed to the complete oxidation of Cu⁰ to Cu₂O.³⁸ By utilizing the photoionization cross section values, it is easy to identify the origin of peaks from the regions of O 2p or Cu 3d by spectral weight. The photoionization cross-section (σ) of O 2p and Cu 3d is 2.4x10⁻⁴ and 1.2x10⁻² Mb, respectively, at hv = 1486.6 eV.⁴⁴ Indeed, the Cu 3d spectral weight is primarily observed in the VB for both Cu₂O and CuO and it is fully supported by the larger σ of Cu 3d, by 1.5 order of magnitude. A weak and broad feature observed between 5 and 8 eV is due to O 2p derived spectral features, and it is observed at 500 K. This underscores the ~3.5 eV energy gap between the peak maximum of Cu 3d and O 2p derived features for Cu₂O due to weak hybridization between fully filled Cu 3d₁₀ and O 2p⁶ orbitals. Indeed, our results are in excellent agreement with those reported by Ghijsen et al.³⁸

A major change occurs in the VB spectrum on further increasing the temperature to 600 K; the VB broadens between 1 and 13.5 eV, and the same features are observed at higher temperatures up to 675 K. The typical feature for Cu₂O at 1.4 eV decreases in intensity ≥ 600 K. Further, a broad feature is observed between 8 and 12.5 eV (dotted arrow). Indeed, this feature is characteristic for CuO and attributed to a satellite due to the 3d⁸ final state configuration. Photoionization of the 3d⁹ ground state configuration leads to the above satellite. This feature is very similar to the high BE satellite observed for CuO in core level XPS. A high BE shoulder is
Figure 11: High pressure valence band spectra recorded at 1 mbar O$_2$ and at different temperatures. Systematic conversion of Cu metal at UHV-RT to Cu$_2$O (at 500 K) and CuO above 500 K is observed in 1 mbar O$_2$.

observed between 4 and 8 eV with the main VB peak at 3.5 eV (solid arrow) at 600 K and above.

The above broad feature is attributed to the strong hybridization of Cu and O in CuO, which is typical for cuprates.$^{3,45}$ In comparison to the energy gap (~3.5 eV) observed between O 2p and Cu 3d derived spectral weights in the VB spectra recorded between 375 and 500 K, the overlapping shoulder with the main VB at ≥600 K demonstrates the formation of CuO due to
strong hybridization. A feature observed at 21 eV (dash-dot arrow) is attributed to the O 2s shallow core level.

4. Conclusions

Special features available with Lab-APPES have been described in detail. Especially, a better vacuum is maintained in the electrostatic lens column under 1 mbar pressure conditions in the analysis chamber, and the aperture free lens regime provides better quality data collection with simple laboratory x-ray sources. Using Lab-APPES at 1 mbar oxygen pressure various stages of silver, copper, and gold oxidation have been probed. With Lab-APPES available at NCL, Pune, it is possible to simulate the catalysis reaction conditions on solid surfaces, in terms of pressure up to 1 mbar and temperatures, at least, up to 1273 K.

ASSOCIATED CONTENT

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Acknowledgements:

We thank Dr. S. Sivaram (Ex-Director, NCL, Pune), and Dr. S. Pal (Director, NCL, Pune) for supporting the Lab-APPES unit, and for establishment of the Center of Excellence on Surface Science at CSIR-NCL, Pune. CSG gratefully acknowledges the helpful discussions with Prof. Jörg Libuda, Univ. Erlangen-Nürnberg, and Dr. Axel Knop Gericke, FHI-MPI, Berlin, during the Humboldt Kolleg at Goa on Nov. 2011. CSG thanks Dr. J. Michael Gottfried for some helpful discussion on design aspects of Lab-APPES during a visit to Univ. Erlangen-Nürnberg on June 2009. We thank Mr. P. M. Suryavanshi for many practical discussions on some design aspects. VG Scienta, Sweden and Prevac, Poland is acknowledged for supplying Figures 2 and 3, respectively, and providing details of the same. We also acknowledge Prevac, Poland for fabricating the Lab-APPES system with many safety features. KR thank CSIR, New Delhi for senior research fellowship. Funding for Lab-APPES from CSIR, New Delhi is gratefully acknowledged. Partial financial support from CSIR under 12th FYP (CSC0404) for the presented work in the manuscript is acknowledged.
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Design and Performance Aspects of a Custom Built Ambient Pressure Photoelectron Spectrometer Towards Bridging the Pressure Gap: Oxidation of Cu, Ag, and Au Surfaces at 1 mbar O₂ Pressure

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