

Toward the Origins of Binding Energy Shifts and “Satellites” Formation During Plasma-XPS Measurements

Running title: Binding Energy Shifts in Plasma-XPS

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In-plasma X-ray photoelectron spectroscopy (plasma-XPS) emerges as a powerful platform for real-time, *in situ* chemical analysis under conditions relevant to semiconductor processing and other plasma-enabled technologies. This study investigates the origins of binding energy (BE) shifts and the formation of “satellite” peaks observed during plasma-XPS measurements across conductive, dielectric, and gas-phase systems. Using a standard laboratory-based ambient pressure XPS apparatus coupled with an alternating current (AC)-driven capacitively coupled plasma source, we demonstrate that metastable surface species, such as transient Au oxides, can be detected during plasma exposure, revealing chemical states that are hardly accessible using conventional ultrahigh vacuum (UHV) XPS. In dielectric samples (e.g., undoped diamond, sapphire), we observe pressure- and plasma-type-dependent BE shifts of more than 50 eV, attributed to X-ray-induced and plasma-mediated surface charging. These shifts are mitigated at higher pressures/plasmas or in electronegative plasmas (e.g., O₂), the latter due to enhanced charge

compensation mechanisms involving slow negative ions. For gas-phase species, AC-plasma excitation leads to spectral broadening and the emergence of “satellite” peaks with energy separations of a few eV, linked to oscillating local plasma potentials in the probing volume. These findings highlight the complex and important interplay between plasma parameters, surface charging, and local electric fields in shaping XPS spectra. Overall, plasma-XPS emerges as a critical metrological tool for probing transient surface chemistry, with implications for semiconductor processing, material synthesis, and plasma diagnostics.

I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is one of the most surface-sensitive, informative, and well-established electron spectroscopy techniques for analyzing surface chemical states, and therefore it is routinely used for wafer analysis in the semiconductor industry. However, due to standard XPS's ultra-high vacuum (UHV) requirements, the wafer fabrication process has to be interrupted, and the sample has to be (in-vacuo) transferred from the plasma reaction chamber for XPS analysis.^{1, 2} On the other hand, real-time analysis of the chemical composition of the interfaces with sub-monolayer precision is an attractive opportunity for plasma-assisted process control and development in modern semiconductor fabrication technology. These processes typically operate at pressures ranging from 10^{-1} Pa to 10^3 Pa under a plasma environment, making them difficult to interface with standard UHV surface science analytical equipment. The application of electron spectroscopies such as UV laser-induced electron photoemission for *operando* plasma etching endpoint detection,^{3, 4} or plasma-enhanced chemical vapor deposition (PECVD) film growth⁵ has been reported already in the 1980s. However, the chemical specificity of these techniques was rather limited, which precludes the identification of the process-specific short-lived reactive intermediates. Many of the challenges have been neatly resolved by the

Donnelly group using the spinning wall approach,⁶ where the fast-rotating surface of interest can be analyzed in high vacuum using Auger electron spectroscopy⁷ as fast as a millisecond after plasma exposure. The adaptation of this method for planar samples, such as Si-wafers, has yet to be realized. Alternatively, the through-the-membrane XPS method^{8,9} has been proposed to probe the interfaces at elevated pressures, but the method's applicability for plasma XPS studies and the longevity of ultrathin membranes in plasmas have yet to be proven.^{10,11}

On the other hand, modern ambient pressure XPS (APXPS, also known as near ambient pressure (NAP) XPS) instrumentation covers the pressure range used in standard plasma applications, and its application space can easily be extended to the plasma environment in this regard. Recently, we¹² and others^{13,14,17} demonstrated that high-quality XPS data can be collected during plasma-induced oxidation-reduction reactions, at least under quasi-remote plasma conditions. We also demonstrated the influence of plasma chamber wall reactions on sample surface chemistry, as well as the capability of plasma-XPS to analyze plasma chemistry in the gas phase.¹⁶ Moreover, the electron spectrometer's capacity to measure the electron energy distribution even without X-ray excitation¹⁷ demonstrates the potential of APXPS for plasma diagnostics.

Dielectric materials and coatings are prevalent in real-world samples and devices. Although the charging and charge neutralization mechanisms of poorly conducting samples during XPS, both in vacuum and at elevated pressures, are well-documented, the charge-induced binding energy (BE) shifts under plasma conditions have not been studied yet. On the other hand, plasma-induced charging and damage of wafers with an insulating layer are well-known semiconductor fabrication challenges.^{18,19} Thus, plasma-XPS metrology can be a useful tool for better diagnostics and mitigation of the latter effects.

Here, in addition to the Au oxidation example, we test plasma-XPS metrology in applications to dielectric and gas-phase samples. We observe plasma condition-dependent anomalous XPS binding energy shifts due to sample charging and propose mechanisms responsible for this. We also observe and discuss the plasma-induced BE shifts, broadening, and “satellite” formations when measuring plasma gas phase XPS.

II. EXPERIMENTAL

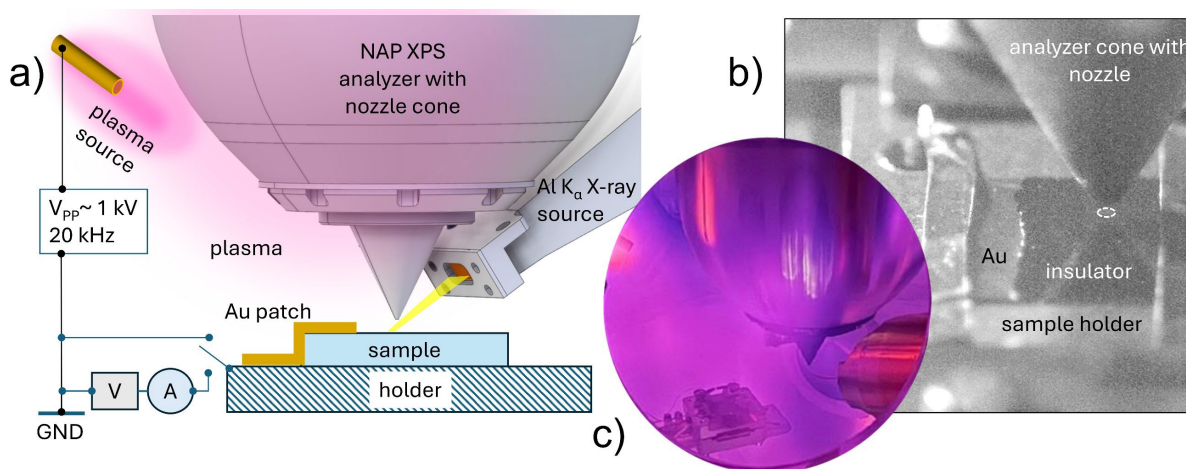


Figure 1. The experimental setup (a) of the plasma-XPS setup and (b) corresponding optical image analyzer cone, sample holder and X-ray source. (c) The optical image of the experimental setup under the plasma ON conditions. See the text for details.

Plasma-XPS experiments were conducted at the Center for Functional Nanomaterials at Brookhaven National Laboratory, which houses a lab-based APXPS system. Further details about the experimental setup and its capabilities can be found elsewhere.^{12,15,16} The APXPS instrument (Figure 1) features a reaction chamber with a base pressure of $<5 \times 10^{-7}$ Pa and the capability to backfill the chamber with the gas of interest during data collection. The reaction chamber is separated from the multi-stage, differentially pumped electrostatic focusing lens system of the APXPS electron energy analyzer by a 300 μm diameter cone aperture, enabling XPS data

collection at pressures up to 200 Pa. A monochromatized Al K α X-ray source ($h\nu = 1487$ eV), focused to a spot size of about 300 μm and fixed at a 30° angle from the sample normal, was used for photoemission excitation. The sample-to-nozzle distance was adjusted to the focal point of the X-rays, which is approximately 600 μm away from the aperture, by optimizing the intensity of a photoemission peak. Gas-phase XPS spectra were collected with the sample retracted centimeters away from the focus of both the X-ray source and analyzer. The sample, an undoped 5 mm \times 5 mm \times 0.5 mm diamond or 7 mm \times 7 mm \times 1 mm sapphire dielectric with approximately one-quarter of its surface area coated with a 200 nm Au film, was attached to a sample holder with Ta strips via spot welds and loaded into the APXPS chamber. This Au patch (Figure 1), electrically connected to the sample holder, served as a reference material for XPS spectra. For the plasma-induced oxidation experiment, a polycrystalline 99.95 % 100 μm thick Au foil was used. Prior to oxidation, the foil was first exposed to H₂ plasma to remove surface carbon and then annealed to 400 K in UHV and then in O₂ to further remove adventitious carbon species. The sample holder can be either grounded or biased and used to monitor the photoemission current or the plasma-induced current. To measure the current, the ground connector on the manipulator was connected to an electrometer. Typically, the photoemission current for a well-focused X-ray source is within the range of 100 pA \pm 10 pA, and the measured plasma-induced current is in the range 0 μA to 100 μA , depending on discharge and sample bias parameters (see also SI). The holder can be heated *in situ* to up to approximately 700 K in a gaseous environment.

Plasma was ignited in the APXPS by backfilling the analysis chamber with 5 Pa to 200 Pa of the gas of interest (H₂, He, O₂, or N₂) and applying high AC voltage (22 kHz, up to a one keV peak-to-peak (pk-pk)) to a copper wire driving electrode mounted on a high-voltage feedthrough (Figure 1), located approximately 10 cm from the analyzer's focal point. The high-voltage power

supply is set to output from 12 % to 40 % of its nominal power in our experiments, which approximately peaks to up to a few watts of discharge power (see SI). Langmuir probe measurements, plasma potentials, and ion energy distributions were measured for representative plasma conditions in a separate plasma diagnostic vacuum chamber. The exact plasma power numbers (as well as many other plasma parameters such as plasma potential, floating potential, electron or ion densities, and temperatures) strongly depend on the gas type and pressure used, but for the purposes of this paper, we will refer to the percentage power output of the current setup since the true discharge power scales with those. Some of the results reported below use the pressure excursions under the plasma ON condition. It is important to note that due to the inherent entanglement of many plasma parameters, the discharge emission intensity and its spatial distribution (see SI) respond sensitively to gas pressure changes, which results in significant alteration of the ions, electrons, photons, and neutrals fluxes at the sample surface.

C 1s and Au 4f spectra were collected with a 20 eV pass energy, a 250 ms dwell time, a 50 meV step size, and multiple sweeps for improved signal-to-noise ratio. For data collected at elevated pressure, the number of sweeps was doubled. XPS spectra were collected as a function of gas pressure, plasma power, and composition, temperature, and sampling point location.

III. RESULTS AND DISCUSSION

A. Peak “satellites” observed on electrically conducting samples

The plasma-induced chemical shifts observed thus far during operando plasma-XPS^{12-14, 16, 17} closely resemble those measured in previous reduction, oxidation, or etching experiments conducted using the “before-and-after” approach. The value of plasma-XPS metrology compared to its standard UHV before-and-after realization is in accessing metastable interfaces, transient or short-living reactive intermediates that vanish immediately after plasma termination. An

industrially important example of the metastable interface is Au oxide, which can be formed by exposing a clean Au surface to oxygen under UV light, ozone, or oxygen plasma, but is unstable in UHV and at elevated temperatures above 400 K ²⁰⁻²⁶.

Figure 2a presents a series of XPS spectra of gold collected under different plasma conditions. The bottom spectrum is taken at 10 Pa, showing a typical Au 4f XPS peaks. Note, the latter retains the same shape both at 200 Pa of oxygen and UHV condition with appropriately attenuated intensity due to electron scattering. The middle spectrum is collected at 7 Pa under oxygen plasma conditions, revealing an appearance of an additional peak (shoulder) indicative of a metastable gold oxide formation. The top spectrum is obtained under UHV conditions after plasma exposure and does not show the Au-O band, as the oxide did not remain after plasma quenching.

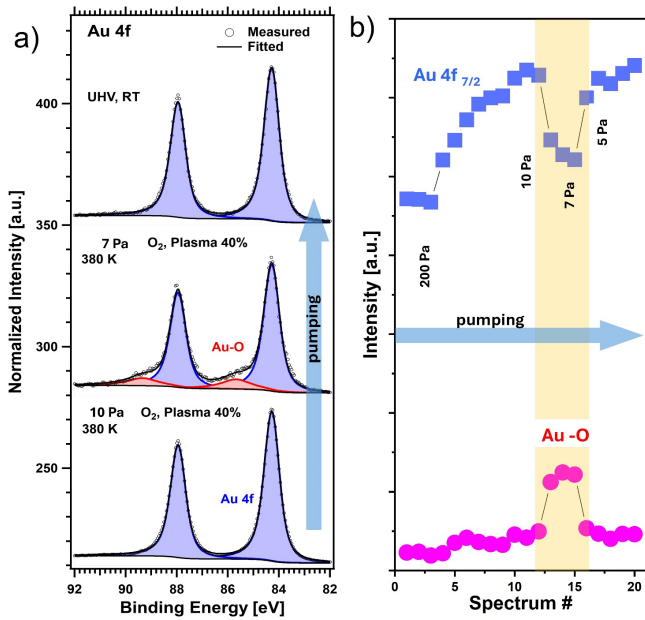


Figure 2. a) The appearance of the Au-O component in Au 4f spectra from Au foil at approximately 7 Pa upon exposure to oxygen plasma at 380 K. b) The evolutions of intensities of the main Au 4f_{7/2} peak and corresponding Au-O “shoulder” during slow pumping of the chamber while under plasma ON conditions (until 5 Pa). The highlighted region (spectra 12 through 17) indicates the conditions under which Au oxide was stable.

Figure 2b summarizes 20 sequential spectra collected under plasma ON conditions as the oxygen pressure is gradually reduced from 200 Pa down to ultra-high vacuum. The top curve shows the intensity of the main metallic Au 4f_{7/2} peak, which increases as the pressure decreases due to

reduced attenuation of photoelectrons by the background gas. The bottom curve indicates the intensity in the “shoulder” region of the expected gold oxide “satellite” around 85.5 eV BE, which grows suddenly within the 10 Pa to 5 Pa pressure range and then disappears as the pressure is further reduced. Note that the intensity of the main Au 4f_{7/2} peak is reduced concomitantly at this particular pressure range. We attribute this effect to the formation of the Au-oxide at the surface and concomitant attenuation of the Au 4f_{7/2} photoelectrons by the newly formed oxide layer. This experiment corroborates with the prior observations²⁰⁻²⁶ of the metastability of the gold oxide under high vacuum conditions and elevated temperatures. In our case, the narrow window of the plasma parameters near the sample exists during the pressure decrease, where the dynamic equilibrium of the incoming oxygen radicals responsible for Au oxide formation overwhelms the O₂ desorption rate, and as a result Au-oxide can be detected at the surface.

B. BE shifts observed on insulator samples

We have studied the plasma-induced charge accumulation and neutralization during XPS

measurements. The standard experiment routine includes sequential XPS on the reference Au

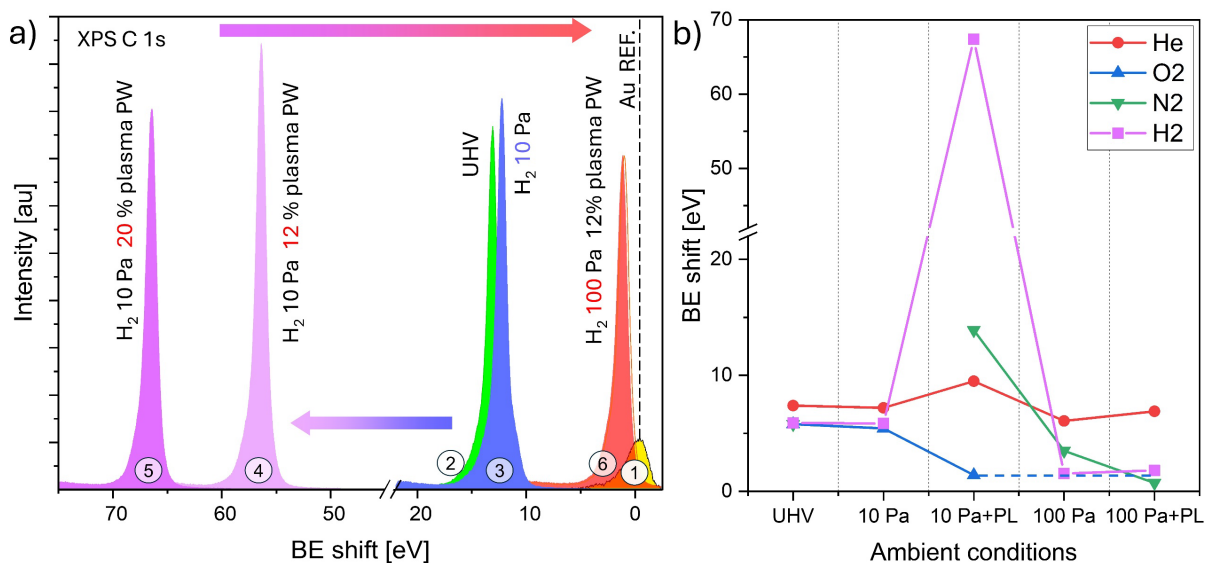


Figure 3. The evolution of the C 1s spectra (a) of undoped diamond relative to adventitious carbon on grounded Au film upon exposure to different H₂ plasma conditions. Note 100 Pa spectrum significantly overlaps with the corresponding plasma spectrum and is not shown here. (b) Binding Energy (BE) shifts values observed during different plasma conditions and gas environments. PL notation here implies plasma ON condition at the corresponding gas pressure

patch area (spectrum 1 in the Figure 3a) and dielectric sample center under UHV conditions (spectrum 2), followed by similar measurements at 10 Pa of H₂ (spectrum 3). After that, XPS under 12 % and 20 % of the output plasma power were collected (spectra 4 and 5 correspondingly). The plasma was then turned off, and the pressure in the chamber was increased to 100 Pa of the gas of interest. XPS spectra were collected again (overlaps with spectrum 6, not shown), followed by corresponding in-plasma measurements (spectrum 6). The chamber was then evacuated to UHV, and reference spectra from the grounded Au patch were checked again.

Figure 3a depicts the typical evolution of the C 1s XPS peak position collected from the middle of the single crystal undoped diamond under the different hydrogen gas and plasma environments. As can be seen, the C 1s spectrum collected in a vacuum is shifted approximately 14 eV toward higher BE in our experimental settings, which reflects the local positive charging of the X-ray irradiated spot of the dielectric up to the surface potential value until outgoing photoemission, Auger, and secondary electron fluxes become compensated through multiple charge neutralization channels^{27,28} such as sample surface/bulk leakage current, photoemission from surrounding parts, and recapture of the low-energy secondary electrons. Note that leakage current in dielectrics and diamond in particular also includes X-ray-induced photocurrent.

The admission of 10 Pa of hydrogen induces a slight reverse shift of the C 1s peak to the lower binding energy due to the appearance of an additional charge neutralization channel via ionization of the nearby ambient gas by the primary X-ray beam and by outgoing photo-emitted and energetic secondary electrons.²⁹ The increase in pressure to 100 Pa makes this charge neutralization mechanism dominate and leads to nearly complete surface charge compensation (see below), which has also been observed in multiple APXPS reports.³⁰⁻³⁴

The ignition of the plasma at 10 Pa results in a significant (> 50 eV) additional shift toward higher binding energy. Increasing the plasma power to 20 % enhances the effect even further (> 65 V, see Figure 3a, compare spectra 4 and 5). This drastic plasma-induced BE shift can be almost completely nullified if the hydrogen pressure is increased to 100 Pa while the plasma is still on. Note that in our settings, the absolute values of the BE shift strongly depend on the experiment geometry, plasma type/conditions, sample type (diamond or sapphire), temperature, and even irradiation spot location on the same sample. However, the pressure results are reproducible for

the same sample with an error bar of approximately 3 eV provided all other experimental parameters are locked.

Figure 3b summarizes the BE shift results for undoped diamonds under different conditions and plasma gas types. Overall, the trend for all studied plasmas (He, H₂, N₂) and also for the sapphire sample (see SI) is qualitatively the same: lower pressure 10 Pa plasmas cause significant plasma-induced surface positive charging, while a pressure increases to 100 Pa, with or without plasma,

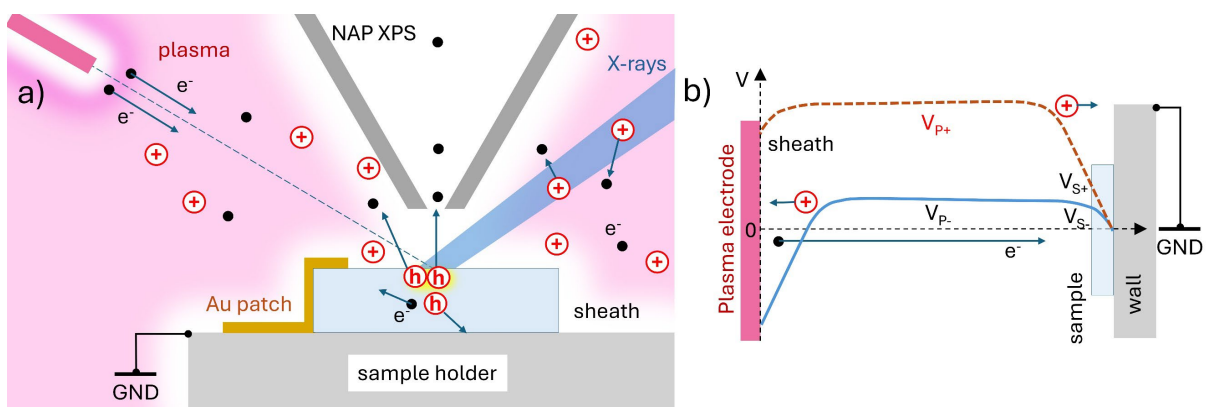


Figure 4. a) The possible charge formation and compensation mechanisms during X-ray photoemission and plasma exposure of dielectric samples. An electropositive plasma case is shown. b) The schematics of the potential distribution between the AC plasma driving electrode and one side grounded dielectric sample (wall). Negative (bottom curve) and positive (top curve) half-cycles are shown. See details in the text.

significantly compensates surface charge. The oxygen plasma, however, deviates significantly from the above trend: no plasma-induced charging can be observed, and instead, even 10 Pa O₂ plasma compensates for surface positive charge almost completely.

A few mechanisms can be invoked to explain qualitatively the appreciable (10 V to 100 V) additional to X-ray positive charging of the dielectric sample in a plasma environment in our experimental settings (Figure 4 a, b).

The (vacuum) ultraviolet ((V)UV) plasma emission can constitute a noticeable partition of the energy flux to the sample^{35,36}, induce the measurable photoemission from the sample and therefore its charging, if not compensated. However, the observed values of plasma-induced BE shifts significantly exceed the most extreme UV radiation energies of the used plasmas, and therefore, the (V)UV photoemission-induced charging mechanism can be ruled out. On the contrary, VUV light sources are often used in industry for charge compensation in insulating samples in vacuum via (V)UV-induced photoconductivity (leakage current) and secondary electron emission (and/or residual gas ionization) of the sample surroundings³⁷.

The alternative explanation relies on the fact that the plasma potential is always positive with respect to the grounded walls and sample holder, regardless of the positive or negative driving potential of the driving electrode (see the diagram in Figure 4b). Moreover, the estimated plasma frequencies in our settings are at least an order of magnitude larger compared to the driving frequency (see SI, section F), and we may safely conclude that, to a first approximation, our plasma can be treated as a plasma of a DC glow discharge, where the plasma-generating electrode acts as a cathode or anode. The thin dielectric sample rests on the other grounded electrode, and its surface potential is floating. When the plasma-generating electrode acts as the anode, the floating potential of the plasma bulk (“positive column”) V_{p+} is at the highest positive potential with respect to the chamber wall and sample holder (top curve in the Fig. 4b). The maximum value of this potential is even higher than the amplitude of the applied voltage (which is up to 1 kV). At the same time, on the chamber wall, there is a thick cathode sheath with a distributed space charge, whose main function is to provide high-energy ions for the generation of secondary electrons from the metal cathode through bombardment, thereby maintaining gas ionization and allowing the passage of electric current through the gas. The surface of a dielectric sample resting on such a cathode is

generally charged positively due to secondary electron emission as a result of ionic bombardment. The steady-state potential on the dielectric surface (V_{S+}) will acquire a value necessary to stop ionic bombardment and secondary electron emission since almost no current flows through the dielectric. On the other half of the cycle, when the plasma-generating electrode acts as the cathode (bottom curve in Fig. 4b), the floating potential of the plasma bulk (V_{P-}) remains positive, albeit relatively small, above the zero potential of the chamber wall acting as the anode. Since the charge relaxation time of the dielectric surface is usually much longer than the period of the voltage oscillations, the average potential acquired by the dielectric surface is positive with a steady state value depending on the properties of the plasma sheath, which are, in turn, function of type of the gas, gas pressure, value of the applied voltage, and the current density in the plasma. It can be expected that at 10 Pa, the positive potential on the dielectric surface will be highest for the plasma with the lowest resistance, which is hydrogen in our case, and indeed has been observed. Overall, the surface of the dielectric becomes charged to the local floating plasma potential, thereby establishing a dynamic equilibrium with the plasma. Measurement of the local plasma potential near the dielectric surface with the use of a Langmuir probe yielded values comparable to the BE peak shifts observed in the XPS measurement. It's important to note that no significant broadening of the XPS peak's Full Width at Half Maximum (FWHM) is seen, suggesting the potential is not fluctuating nor is the sample differentially charging across the probed spot.

Another factor favoring the formation of a high positive potential at the sample surface is the emission of ballistic high-energy electrons from the driving electrode during its cathode half-cycle. Indeed, at low pressure (10 Pa), the mean free path for a few hundred eV electrons is in the order of ten centimeters, and a significant fraction of the electrons generated at a cathode can gain up to 1 keV energy before impinging on the sample (anode). Similarly, at the most positive

potential at the driving electrode, the significant fraction of ions impinges on the sample with V_{P+} potential (Fig. 4b). Given the fact that the dielectric samples have secondary electron yield well above 1 for few hundreds eV primary electrons but significantly low ion-induced secondary electron emission coefficients, the above mechanism will sponsor a positive potential accumulation at the dielectric surface with its steady state value depending on secondary electron emission, leakage and (photo-)currents.

At high pressure, the current density is generally unevenly distributed over the electrode's surface, and correspondingly, the sheath structure and plasma parameters in the sheath are not even along the electrode surface. If the current density in the plasma around the dielectric is small, which is most likely true for our experiments, the dielectric surface will be near the potential of the sample holder. Similarly, with the pressure increasing to 100 Pa, all ballistic mechanisms vanish because of the multiple scattering effects, and the sample surface charge becomes effectively neutralized. The unusual behavior of the surface charge under oxygen plasma (see Fig.3 b) can also be explained in the same terms, taking into consideration the plasma's electronegativity. Even at 10 Pa, the number of free electrons is significantly reduced in favor of the formation of negative ions. These charged species effectively neutralize the surface charge at any point during the AC cycle.

Another alternative explanation also relies on the positive plasma potential around the sample as a major factor responsible for the observed surface charging. However, different from the above scenario, the major ionization source remains X-ray excitation. At lower plasma pressures, the presence of a positive plasma potential, coupled with a large electron mean free path, reduces the recapture of photoemitted and slow secondary electrons, leading to the observed positive sample charging. As in the prior scenario, the increase in pressure leads to an increase in

the electron scattering phenomena and near-surface gas ionization, resulting in effective charge neutralization.

Overall, the observed dielectric sample charging is a complex phenomenon that can be explained via multiple mechanisms. Due to the inherent entanglement of multiple plasma parameters, a more detailed and thorough study (e.g., plasma frequency dependence) is required to discriminate between them.

C. Gas phase BE shifts

We also observed the dramatic effect of plasma on X-ray photoemission from the gaseous species. To explore the influence of the plasma conditions on gas phase XPS, the gas phase spectra with plasma ON and OFF APXPS data were collected sequentially with the sample holder retracted from the analyzer/X-ray source focal spot to avoid ground and/or sample charging interference. Argon plasma was used as a model system. It was found that gas pressure and plasma excitation parameters have a dramatic effect on the intensity, broadness, and binding energy (BE) positions of the XPS peaks.

Figure 5 depicts Ar 2p, 3s, and 3p spectra collected with and without 10 % AC (1 kV pk-pk, 22 kHz) 500 Pa plasma in our experiment geometry settings. Table I summarizes the peak fitting parameters.

The plasma ignition results in:

- (i) Appreciable reduction of the intensity of the main peaks (note the scaling ratio)
- (ii) Slight shift of the main peaks position toward the higher BE
- (iii) Slight broadening of the main peaks and

- (iv) The most pronounced effect is the appearance of prominent, broad “satellite” peaks at higher binding energies.

An important observation is that the energy shift between the “satellites” and corresponding main peaks remains constant across the entire XPS spectrum (approximately 2 eV in our case), including Auger band(s) (compare the peak-satellite shifts in Ar 2p, 3s, 2p spectra). Moreover, the cumulative photoelectron yield calculated as the total area of the main peak (when the plasma is OFF) and the main peak plus corresponding “satellite” (when the plasma is ON) remains nearly

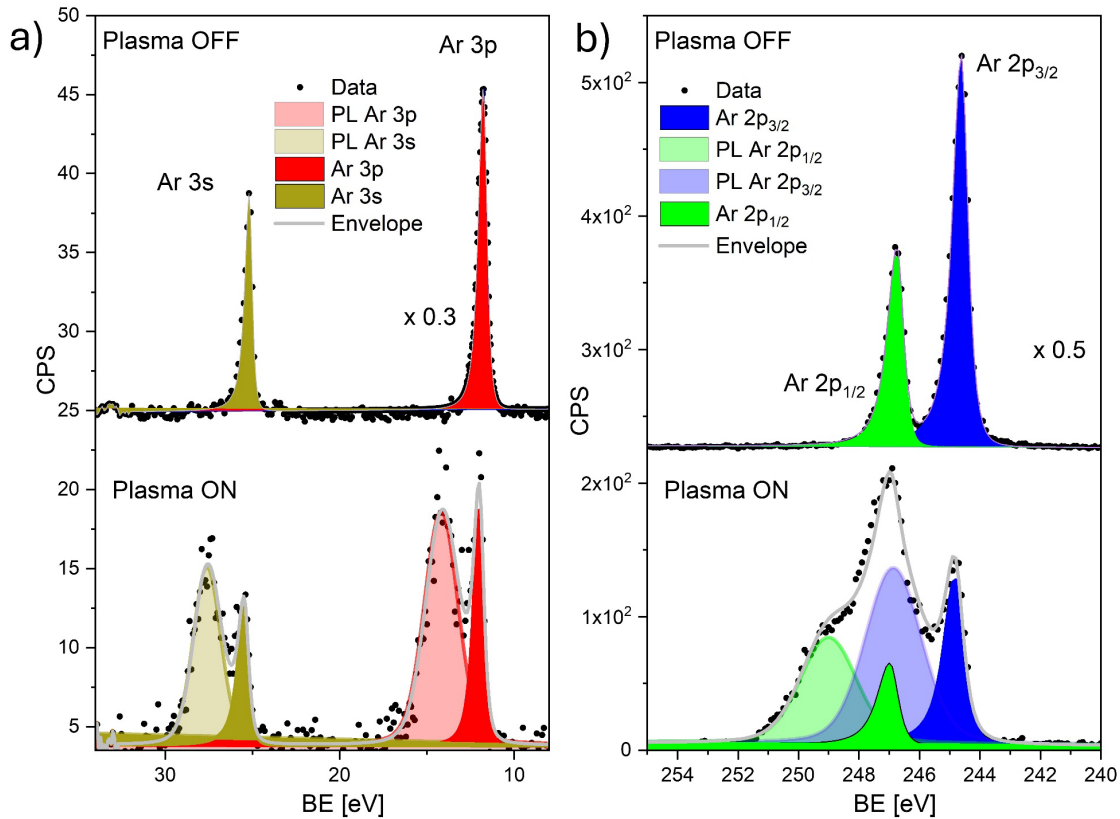


Figure 5. a) Ar 3p, 3s, and b) Ar 2p spectra collected with plasma ON (bottom curves) and plasma OFF (top curves) conditions. Plasma conditions: 10 % power, AC (1 kV pk-pk, 22 kHz) 500 Pa. BE denotes “Binding Energy” here.

the same. The latter indicates that the transmission of electrons to the analyzer lens is not

significantly affected by our plasma conditions, and instead, the partitioning of electrons from the main peak to the “satellite” peak occurs.

The observed effects can be explained by the presence of relatively small (a few electron volt) and oscillating local plasma potential in the X-ray probed volume near the analyzer's focal point (similar to the sample floating potential $V_{S+/-}$ in Figure 4b). It always has a positive value with respect to the ground independently of negative or positive oscillation half-cycle, and its value depends on multiple parameters (geometry and areal ratio between driving electrode and chamber walls, including the analyzer cone, pressure, gas type, driving voltage, etc.)³⁸. This explains why the spectra intensity drops upon plasma ignition in favor of the corresponding “satellite” peak, and “satellite” BE is shifted to higher binding energy. Note that this plasma potential oscillates around the mean value with a frequency equal to that of the driving source, 22 kHz. This leads to the observed significant “satellite” lines broadening, which is evident in all the spectra.

Table I: Major Ar 2p, 3p, and 3s XPS peak parameters retrieved after the fitting without plasma (left half) and with (shadowed half) plasma ON. Note that despite the BE positions of the main peaks can be measured and fitted with uncertainty of approximately 50 mV in this study, the “satellite’s” intensity, BE shifts, and peaks broadness sensitively depend on the geometry of the experimental setup and plasma parameters.

Peak assignment	BE [eV] 500 Pa Ar	FWHM [eV] 500 Pa Ar	Area under the peak [CPSxeV]	BE [eV] at 500 Pa Ar + 10 % plasma	FWHM [eV] 500 Pa Ar + 10 % plasma	Area
Ar 3p	11.8	0.5	52.2	12.0	0.6	13.8
Ar 3p sat	-	-	-	14.1 $\Delta=2.1$	2.2	37.7
Ar 3s	25.2	0.4	32.4 $\Sigma=84.6$	25.5	0.6	8.6
Ar 3s sat	-	-		27.6 $\Delta=2.1$	1.8	23.4 $\Sigma=83.5$

Ar 2p _{3/2}	244.6	0.5	480	244.8	0.7	127.8
Ar 2p _{3/2} sat	-	-	-	246.8 $\Delta=1.97$	2.2	332.2
Ar 2p _{1/2}	246.8	0.5	240 $\Sigma=720$	247.0	0.7	63.9
Ar 2p _{1/2} sat				249.0 $\Delta=2.0$	2.2	199.4 $\Sigma=723.3$

Such XPS peak splitting/broadening is commonly observed in AC-biased substates where the excitation frequency is comparable to or higher than the spectrum acquisition rate (see, for example, ref. ³⁹ and references therein).

IV. SUMMARY AND CONCLUSIONS

The observed formation and decay of the Au-oxide at the surface of Au foil during oxygen plasma exposure demonstrates the unique capability of plasma-XPS metrology to detect transient chemical states that might not be visible in conventional UHV XPS measurements. The latter is a valuable metrological advancement highly relevant to current needs in semiconductor fabrication, where the instant chemical composition of the interfaces is imperative for process control.

We also checked the plasma's ability to neutralize the X-ray-induced charging of practically important poorly conducting samples. This initial BE shift in vacuum is routinely observed during XPS on dielectric samples and is attributed to the spot's local positive charging due to X-ray-induced photoemission, Auger processes, and secondary electron emission. The degree of the BE shift under steady-state conditions is defined by the equilibrium between the photoemitted electron flux and charge compensation electron/hole flows in the solid. In a vacuum, the latter is defined by surface and bulk conductance, including photoconductance. Adding the gas to the chamber

results in the appearance of a new charge compensation channel through the ionization of the gas in front of the sample by X-rays and the emission of secondary or photoemitted electrons.

We observed that the plasma environment can lead to both charge neutralization and significant positive charging, depending on (i) pressure and (ii) whether electronegative or electropositive low-pressure plasma is used. At low pressure, the positive plasma potential surrounding the sample and the large electron mean free path promote photoemission, reducing the recapture of slow secondary electrons, which leads to the observed positive sample charging. The increase in pressure leads to an increase in the electron scattering and, following effective charge neutralization. In electronegative plasmas, such as oxygen in our case, the effective formation and capture of slow negative ions promote the neutralization of positive charge, even at low pressures.

We also demonstrate that the gas-phase XPS spectra can be significantly affected by the AC plasma, depending on the plasma conditions. Plasma-induced “satellites” with few eV BE shifts and large peaks broadening appear due to the presence of the positive oscillating plasma potential at the probing volume. To verify the aforementioned proposed hypothesis, more systematic comparative studies are required under DC and RF plasmas.

Overall, plasma XPS metrology is a new, powerful analytical capability that excels in measuring metastable surface states that are impossible or difficult to detect under traditional ultra-high vacuum conditions using the before-and-after approach. It’s particularly valuable in fields such as semiconductor fabrication, biomedical treatments, aerospace applications, and the synthesis of new materials. Ongoing research into the effects of various electromagnetic fields present in plasma on the formation of XPS spectra will further refine our ability to interpret these complex surface chemistries and can contribute to plasma diagnostic metrologies.

SUPPLEMENTARY MATERIAL

Supplementary material is available, which contains optical and electrical characterization of the discharges used in this research, as well as the data fitting protocol.

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AUTHOR DECLARATIONS

The authors declare no conflicts of interest.

AUTHOR CONTRIBUTIONS

J. Trey Diulus: Data collection and analysis (lead); Investigation (lead); Writing (supporting). Ashley Head: Data collection (lead), Formal analysis (supporting); Investigation (supporting); Writing (supporting); Jorge Anibal Boscoboinik: Data collection (lead), Formal analysis (supporting); Investigation (supporting); Writing (supporting), Carles Corbella Roca: Data collection (lead); Investigation (supporting); Writing (supporting). Alexander Tselev: Investigation (supporting); Writing (supporting). Andrei Kolmakov: Conceptualization (lead); Data analysis (lead); Investigation (equal); Supervision (lead); Writing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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