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What more can be done with XPS? Highly informative but underused approaches to XPS data collection and analysis **©**

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What more can be done with XPS? Highly informative but underused approaches to XPS data collection and analysis **a**

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ABSTRACT

Because of the importance of surfaces and interfaces in many scientific and technological areas, the use of x-ray photoelectron spectroscopy (XPS) has been growing exponentially. Although XPS is being used to obtain useful information about the surface composition of samples, much more information about materials and their properties can be extracted from XPS data than commonly obtained. This paper describes some of the areas where alternative analysis methods or experimental design can obtain information about the near-surface region of a sample, often information not available in other ways. Experienced XPS analysts are familiar with many of these methods, but they may not be known to new or casual XPS users, and sometimes, they have not been used because of an inappropriately assumed complexity. The information available includes optical, electronic, and electrical properties; nanostructure; expanded chemical information; and enhanced analysis of biological materials and solid/liquid interfaces. Many of these analyses can be conducted on standard laboratory XPS systems, with either no or relatively minor system alterations. Topics discussed include (1) considerations beyond the "traditional" uniform surface layer composition calculation, (2) using the Auger parameter to determine a sample property, (3) use of the D parameter to identify sp² and sp³ carbon information, (4) information from the XPS valence band, (5) using cryocooling to expand range of samples that can be analyzed and minimize damage, and (6) using electrical potential effects on XPS signals to extract chemically resolved electrical measurements including band alignment and electrical property information.

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I. INTRODUCTION

The purpose of this paper is to introduce newer or "casual" x-ray photoelectron spectroscopy (XPS) users to some of the valuable information that can be extracted from XPS by less-common data analysis approaches or specially designed experiments that may be unknown or less often used by those new to XPS. Significant growth in the application of XPS in widely varying research and technology areas has been observed for the past two decades. When using an instrument that has been properly calibrated,^{1–3} XPS is both a reliable and quantitative technique for the measurement of surface chemical composition. Indeed, with careful and considered use, XPS has been demonstrated in multilaboratory studies to provide highly reproducible measurements of surface and near-surface composition in many types of materials systems including, for example, multilay-ered planar structures,⁴ nanoparticle (NP) overlayer thicknesses,⁵ and material compositions.⁶

However, XPS can provide a wider range of information than surface composition as often calculated. In an email note to D.R.B., Martin Seah observed that "[XPS] is very flexible and informative in a very multidimensional way with both chemical and physical data. It is a very data rich method" (quoted in Ref. 7). There remain many opportunities to use XPS to extract untapped information that would be useful for many research and technology applications.

The value of information that can be obtained by using XPS has stimulated the application of the method by new and occasional users less familiar with the method. Accompanying this increased use of XPS and changes in the nature of the user community are (1) an increased number of erroneously analyzed data appearing in the literature,^{8,9} (2) lack of reporting of instrument and analysis parameters needed to assess or reproduce data,¹⁰ and (3) relatively few analysts taking full advantage of the many types of information that can be extracted from well-constructed XPS experiments. Several efforts have been undertaken to provide newer and infrequent XPS users with information to help them avoid common errors, faulty data analysis, and incomplete reporting issues.^{9–16} This paper provides an introduction to some of the ways to extract valuable, and often otherwise unavailable sample information, that deserve to be more widely known and used.

The motivation for this paper was the observation during an examination of XPS in the literature^{8,10} that most publications using XPS ask one or more of three interrelated questions: (1) What elements are present? (2) How much of each element or compound is on the surface? (3) What is the chemical state of the elements present? Only slightly less common are questions involving depth or layer information using either sputter depth profiles or angle resolved determination of depth profiles. These are very appropriate and important uses of XPS and provide essential information for many applications and users, if done correctly and not based on overly simplistic analyses.¹⁶ However, there is a wider range of material and sample information that can be obtained using XPS that enables the technique to be even more powerful with the ability to address multiple types of analysis needs. Specifically relevant is the ability to provide information about sample or system properties, not just the composition, of materials surfaces and nanostructured materials in general. These may involve less traditional methods of data analysis or designing/constructing experiments to obtain the information. Many of these methods are well known to experienced XPS analysts, but they are less known or used by newer or casual XPS users. Sometimes, they are underused because it is assumed, often incorrectly, that the analyses or experiments are difficult or overly time consuming. The intent of this paper is to enhance the visibility and encourage the application of these uses of XPS.

As should be expected, the information that can be obtained and what might be useful will vary with the analysis needs and type of sample. An incomplete list of accessible information includes sample polarizability and dielectric constants,^{17–19} controlled surface charging,²⁰ chemically resolved electrical measurements (CREMs),² local electric field and potential measurements,²² band offsets and bending,^{23–25} the nature of electrical double layers (EDLs),²⁶ local charge dynamics in electrochemical systems,²⁷ the extent of sp² and sp³ carbon bonding, and changes in microbial cell walls in response to external stimuli.²⁶ Furthermore, most of the common XPS analyses of surface composition implicitly, and often incorrectly, assume that the analyzed surface layer is uniform and ignore the impact sample structure has on XPS signals.²⁸ There is information contained within XPS spectra, including background signals, that can provide information about elemental distribution in the surface region,^{28,29} as well as information about coating thickness and uniformity,^{29–32} and even size of nanoparticles.^{33,34}

Most of the data collection and analysis approaches described are readily accomplished using standard laboratory instruments without any special capabilities or instrument alteration. However, they may require specific planning to ensure that needed data are collected. Also described, at somewhat greater length, are two powerful approaches that require either special capabilities or nonstandard sample configuration (electrical biasing and cryocooling).

The topics to be addressed in this paper are listed in Table I g along with an indication of some of the information they can provide. These topics include (1) considerations beyond the "traditional" uniform surface layer composition calculation, (2) using the Auger parameter to determine a sample property, (3) use of the D parameter to identify sp²and sp³ carbon information, (4) information from the XPS valence band, (5) using rapid cryocooling to expand range of samples that can be analyzed and minimize damage, and (6) using electrical potential effects on XPS signals to extract band alignment and electrical property information.

The discussion in Secs. II–VII is relevant to traditional laboratory XPS instrumentation. Although not focused on them, some of the examples involve or can relate to newer versions of instrumentation such as hard x-ray photoemission spectroscopy (HAXPES)³⁵ and near-ambient pressure XPS (NAP-XPS),^{36,37} which offer interesting and potential extensions for extracting insightful and important information from the approaches described in this paper. This paper also does not attempt to address other existing areas of surface analysis such as real time measurements, the multiple types of *in situ* possibilities, or new approaches toward the analysis of buried interfaces.³⁸

The examples presented in this paper provide only an introduction or, in some cases, a simple pointer to the more detailed work existing in the literature. No attempt is made to provide a complete discussion of the approaches and readers are referred to



TABLE I. Overview of topics discussed in specific sections this paper and information that can be obtained.

Underused aspects of XPS	Information available
II. Considerations beyond the uniform surface layer calculation A. Calculating impact of an adventitious carbon overlayer	Carbon overlayer thickness, corrected underlayer intensities for improved composition calculations.
B. Information on nanostructure by visual inspection of the survey spectrum	Rough indication of the nanostructure from XPS survey.
C. Software to model overlayers and nanostructures	Multiquant, SESSA, QUASES software available to calculate intensities and backgrounds.
D. Nanoscale structure of surfaces using QUASES	Nanostructure of surface, island formation, depths and thickness of buried layers, nanoparticle size, and analysis of depths below where peaks clearly observed.
E. Structure from simplified background analysis suitable for automation	Depth distributions and film thicknesses.
F. Using photoelectron or Auger signals from same element with different energies	Estimate of layer or coating thickness and nanoparticle size.
III. Using the Auger parameter to determine a sample property	Surface polarizability, sensitive to index of refraction, local valence charge, and Madelung potential.
IV. Use of the D parameter to identify sp ² and sp ³ carbon information	Help identify the nature of carbon present.
V. Information from the XPS valence band	Distinguish phases with same chemical composition (e.g., α -Al ₂ O ₃ and γ -Al ₂ O ₃), assist oxidation state information when core level binding energy shifts are small. Ability to use calculations to predict spectral features; identification of the Fermi edge.
VI. Cryogenic XPS: probing intact interfaces in nature and life	Facilitates measurements of wet materials, provides access to solid/ liquid interface (electrical double layer, electrolyte concentration at surfaces, protonation constants), minimize damage for analysis of biological samples (nanomedicines, cell walls, and microorganism surfaces).
VII. Chemically resolved electrical measurements (CREMs)	
A. XPS measures of interfacial potentials	Band bending, band offsets, heterojunction band discontinuities, and Schottky barrier heights.
B. Top-contact-free CREM modes	Measuring sample electrical properties, directly from the XPS data including I–V curves within heterostructures, localized photovoltaic measurements, and nanoscale electron transport and capacitance.
C. DC and AC biasing	Local charge dynamics, nature of double layer formation, and local electrical properties of ionic liquid/metal interfaces.

the noted references and the important and foundational references they contain for the detailed information.

II. CONSIDERATIONS BEYOND THE "CONVENTIONAL" UNIFORM SURFACE LAYER COMPOSITION CALCULATION

Tougaard, among others, has noted that the traditional calculation of surface composition implicitly assumes a uniform composition in the surface layer analyzed using XPS. For most cases, this approximation is not correct.

The problem is illustrated in Fig. 1. Quantitative composition analysis by XPS is traditionally reported as atomic concentrations of the elements. The underlying calculation relies on peak intensities (or peak areas) and assumes that the sample is homogeneous in the outermost \sim 5 nm of the surface in which case the concentration of atoms X_A is constant in that region. Then,

$X_A = F \cdot I_A$,

where I_A is the peak area and F is a factor that depends on the inelastic mean free path λ , the photoionization cross section, characteristics of the spectrometer, and renormalization corresponding to the intensity from other elements in the sample.

However, most samples we analyze with XPS are strongly inhomogeneous in the surface region²⁸ and this simplistic calculation is not valid. It is easy to correct for this and make a valid

Concentration X_A of atoms from XPS intensity I_A



FIG. 1. Standard formalism used for XPS analysis implicitly assumes a uniform layer, which in most circumstances is not correct. Reproduced with permission from Tougaard, Surf. Interface Anal. 50(6), 657 (2018). Copyright 2018, John Wiley & Sons, Ltd.

quantification from peak areas if you know in advance exactly which type of structure you have²⁸ but this is rarely the case.

Although these concentrations are faulty, they can be useful. For example, when comparing a set of spectra, the evolution in these concentrations gives an idea of which elements have increased/decreased abundances in the set. However, depending on the experimental situation, such variations may also just reflect that there is a reorganization of the depth distribution of the various atoms. The reported concentrations from this conventional calculation should, therefore, be interpreted with great care.

In addition to these problems, samples are frequently covered by a layer of adventitious carbon and possibly other types of contamination. In Sec. II A, we address this problem, and in Secs. II B–II D, we deal with the problems addressed in Fig. 1.

A. Consideration of the impact of an adventitious carbon overlayer

As noted above, adventitious carbon layers are frequently present. Such a layer impacts quantitative analysis in two ways. First, if carbon is not an actual component of the sample and, therefore, not of interest, the presence of surface carbon can distort quantitative analysis. If carbon is included in the calculation, but only surface contamination, the presence of a significant carbon concentration will give misleading results that do not reflect the actual carbon concentration in the sample. Some analysts simply ignore the carbon in the calculation, which distorts the analysis because the surface layer alters the relative peak intensities from the underlaying layer depending on their kinetic energy (KE). One approach used to minimize the impact of an adventitious carbon layer is to correct for the impact of such a layer by estimating how much it attenuated the signals of the other elements (which are still assumed to be in a uniform layer under the carbon). Methods to determine if the carbon is an adventitious layer and a correction method are discussed by Castle³⁹ using an approach developed by Smith.⁴⁰

B. Information on nanostructure by visual inspection of the survey spectrum

As mentioned above, the surface concentrations, which are usually reported are based on the (often faulty) assumption that the sample is homogeneous in the surface region, and since this is usually not the case, such concentrations must be interpreted with great care.

The origin and implications of this phenomenon are illustrated in Fig. 2. On their way out of the solid, the XPS electrons will, on average, undergo inelastic scattering and lose energy (typically, 10–30 eV) for each path length λ traveled.^{41,42} Consequently, the peak intensity drops exponentially with the depth of origin z. The lost electrons are found at lower kinetic energies as a background intensity. This background will vary characteristically depending on the concentration depth distribution. Consequently, there is an interplay between XPS peak intensity, the inelastic background, and the atom depth distribution.

This relationship is illustrated in Fig. 3, which shows model spectra (calculated with QUASES software⁴³) for different nanostructures. Figure 3 shows that different nanostructures give rise to characteristic peak shapes in the 50–100 eV energy range below the peak. This implies that the peak intensity combined with the shape of the spectrum can be used to get information on the atom distribution from a visual inspection of the XPS survey spectrum. This method was suggested in Refs. 28 and 29, and we will illustrate here $\frac{1}{29}$



FIG. 2. Interplay between peak intensity, inelastic background, and depth of origin. Reproduced with permission from Tougaard, J. Vac. Sci. Technol. A 39(1), 011201 (2021). Copyright 2021, American Vacuum Society.



FIG. 3. Model Au 4d XPS for different distributions of Au atoms. The host material has λ = 1.5 nm. Adapted with permission from Tougaard, Surf. Interface Anal. 50(6), 657 (2018). Copyright 2018, John Wiley & Sons, Ltd.





FIG. 4. Upper part: XPS by conventional analysis based on peak areas. The upper right part illustrates that it is not possible from peak areas alone to distinguish between widely different structures. The lower part shows how a simple visual comparison to the model structures in Fig. 3 can give a rough indication of the actual structure of the sample. Adapted with permission from Tougaard, J. Vac. Sci. Technol. A **39**(1), 011201 (2021). Copyright 2021, American Vacuum Society.

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its practical application by analysis of the spectrum in Fig. 4, which shows XPS of a sample containing Ni and Au. The conventional analysis based on Ni 2p3/2 and Au 4d5/2 peak intensities (using CASAXPS software⁴⁴) is shown in the inset. This implies that we have 84% Au and 16% Ni concentration in the surface region. However, the same ratio of Ni 2p3/2 to Au 4d5/2 peak intensities can arise from other structures shown in the upper right part of Fig. 4. Consequently, the structure is undefined, and the Au concentration at the surface can be anywhere between 0% and 100%.

Now, if the shape of Ni 2p and Au 4d is similar and both close to the spectrum in Fig. 3(d), then Ni and Au are roughly homogeneously distributed in the surface region, and the Au_{0.84}Ni_{0.16} result is correct. This is obviously not the case here. The spectrum around Ni 2p is similar to Fig. 3(c) with $z \sim 1\lambda$, and the spectrum around Au 4d resembles the spectrum in Fig. 3(a) with $z \sim 2\lambda$. The smaller overlayer thickness estimate for Ni is real and due to the distribution of Au as low and very tall islands; see Fig. 5. So, the conclusion from this simple visual inspection of the XPS survey is that Au forms a $\sim 2\lambda$ ($\sim 3 \text{ nm}$ with $\lambda \sim 1.4 \text{ nm}$ for1150 eV electrons in Au^{45,46}) thick overlayer on top of a Ni substrate. This is very useful information to supplement the Au_{0.84}Ni_{0.16} information from conventional XPS analysis. Although this is only rough qualitative information, such structure information is often crucial for the practical understanding of the physical and chemical properties of a given surface. Several other examples where this qualitative method was used to get a rough idea of the structure from the XPS survey can be found in Refs. 28 and 29. It should be noted that if a peak that originates from a different atom is present in the range $<\sim$ 30–50 eV below the peak energy, this peak will interfere with the peak shape, and the method should not be used (or used with caution) in such cases.²

Some avoid taking the XPS survey because it takes time. However, energy resolution is not important for this analysis and for the QUASES analysis discussed below. Therefore, it is advised to use the highest possible pass energy of the analyzer and record the spectrum with 1 eV energy step that will reduce the typical time for a survey XPS, with a good signal-to-noise ratio, to a couple of minutes.

It must be noted that the advantage of this simple analysis is that it is extremely fast. It is good practice to always accompany the conventional atomic concentrations with the result from a simple visual inspection of the XPS survey (using Fig. 3 as a template or using the extended templates in Ref. 28) to help understand the meaning of these concentrations. However, it can only give a rough indication of the sample structure and cannot differentiate between finer details in the structure. This can be done with the QUASES software discussed in Sec. II D.

C. Modeling of overlayers and nanostructures

Software is available to calculate changes in peak intensities and backgrounds. Both simulation of electron spectra for surface analysis (SESSA)⁴⁷ and Multiquant⁴⁸ programs can be used to predict peak intensities, while SESSA can also predict a full spectrum shape including peak backgrounds based upon known or assumed surface composition and geometries, allowing the impact of layers or factors such as surface curvature and particle size to be assessed.⁴⁹ The quantitative analysis of surfaces by electron spectroscopy (QUASES)⁴³ software is dedicated to the practical extraction of nanostructures by analyzing the peak and its associated background. In QUASES, the photoexcited core electrons move along straight lines from their point of excitation, while with SESSA, it is possible to include elastic electron scattering.

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SESSA is mainly applied to calculate accurate peak intensities and is rarely used for analysis of the background. However, a systematic comparison of the ability of QUASES and SESSA to determine depth distributions from analysis of the background was performed by Zborowski *et al.*⁵⁰ In the Conclusion section of the paper, they summarize their results as: "QUASES-Tougaard is a quick and accurate solution to determine the structure of the sample. SESSA is very accurate as well but needs the depth distribution determined by QUASES-Tougaard as input for complex samples. Then it allows to confirm the depth distribution obtained from the analysis in QUASES-Tougaard or even refine it or add additional information like the elemental state."

The QUASES software can be used to both extract nanostructure from spectra and predict the impact of various surface nanostructures on the background signals, such as the structures shown in Fig. 3. The extraction of nanostructures with QUASES is, in many cases, simple and straight forward. It has been applied for XPS quantification of surface nanostructures for 30 years, and multiple papers describe the method and practical examples including those in Refs. 28–31, 34, 41, and 42. Particularly interesting is the ability to determine the depth of a buried layer even for layers so deep that a clear photoelectron peak cannot be observed.⁵¹ Because of the value and uniqueness of obtained quantitative information from background signals, a few examples using QUASES follow in Sec. II D.

D. Nanoscale structure of surfaces using QUASES

As discussed above, valuable qualitative information on the structure of samples can often be found by a simple visual inspection of $\vec{\sigma}$ the XPS survey spectrum. However, much more thorough quantitative information can be obtained from a detailed analysis of the background in XPS spectra using QUASES software.43 With this, one can analyze the shape of the peak and its associated background assuming different classes of depth profiles such as layered structures, island structures on surfaces, and exponential profiles. The parameters defining the structure can be varied and are determined as the structure that gives the best match to the measured spectrum in a wide energy range below the peak. The adjustment of the parameters that define the structure can be done manually and there is also a facility that automatically determines the parameters that give the best fit without operator interaction. The analysis gives a unique solution, so both the class of depth profile and the parameters defining the details of the structure are uniquely (within the experimental and theoretical uncertainty) determined. The analysis is often quite simple and fast. Videos in Ref. 52 show examples of the steps in QUASES analysis from raw spectra to final analysis. The method requires only two input parameters, which are the inelastic mean free path $\lambda^{45,46}$ and the cross section for inelastic electron scattering. 41,42 The choice for these parameters is normally straightforward 29,30,41,42 and values supplied with the software are usually sufficient. The analysis is simple only when a peak and its background can be isolated without any interfering peak (that originate from atoms with a different depth distribution) in the



FIG. 5. QUASES analysis of the Au 4d spectrum in Fig. 4. Assuming a uniformly thick layer on the Ni surface as shown in (a) does not fit the full spectrum as well as a uniform layer with tall islands as shown in (b). Videos 2 and 3 in https://zenodo.org/records/5499741 show the detailed steps from raw spectra to final analysis.

< 30–50 eV range below the peak. When interference is present the analysis with QUASES is still possible but can become more involved.^{29,30}

Four examples of practical use of QUASES are as follows (Figs. 5–8):

1. Example 1: Layer with islands

Figure 5 shows the analysis of the Au–Ni spectrum in Fig. 4. Analyzing the Au 4d spectrum shows that a good account for the background is obtained with Au as a 3.5 nm overlayer on a Ni substrate [Fig. 5(a)]. With $\lambda \sim 1.4$ nm, this is close to the estimate from the visual analysis in Fig. 4. Looking closer, it is evident that the match is not perfect in the far-left energy region. Upon changing the structure to consist of two types of islands with different heights and coverages on the surface, perfect agreement is obtained in the full energy range [Fig. 5(b)]. So, the conclusion is that Au has grown on Ni to form islands where some are very tall, and others are a few monolayers thick.

Video 2 in Ref. 52 shows the detailed steps from raw spectra to final analysis. The video also shows the corresponding Ni 2p analysis, and Ni is found to be consistent with the Au structure. The absolute island heights (14.5 and 1.5 nm) and their relative surface coverage (0.3-0.7) are uniquely determined. This means that no other



FIG. 6. QUASES analysis of a coated nanoparticle. The analysis shows that the coating of the PTFE core is incomplete. Data from Müller *et al.*, J. Phys. Chem. C 123, 29765 (2019). For detailed step by step analysis, see Video 13 in https://

combination of island heights will give the same quality of the fit, and the relative coverage is 0.3 to 0.7, i.e., an analysis with, e.g., surface coverages 0.15 and 0.35 (but unchanged heights) for the two islands will give the exact same quality of the fit. To determine the absolute coverage, it is necessary to calibrate the intensity scale of the spectrometer, which is easily done by analysis of a reference spectrum. The background corrected reference spectrum on an absolute intensity scale is conveniently determined from analysis of a spectrum from a pure homogeneous material containing the atom under investigation (in this case, a pure Au foil). Analysis of this spectrum, using that the concentration is known to be constant and equal to 100% at all depths, determines an absolute reference background corrected spectrum, which is then used by a simple procedure in the software to scale the intensities and, thus, to find the absolute distribution of coverages. Video 3 in Ref. 52 shows how this is done, and the result is that the coverages are 0.3 and 0.7 so the complete

zenodo.org/records/5499741.

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FIG. 7. QUASES analysis of a Ta layer in a stack. Reproduced with permission from Zborowski *et al.*, J. Appl. Phys. **124**, 085115 (2018). Copyright 2018, AIP Publishing LLC.

surface is covered [as illustrated in Fig. 5(b)]. This distribution of Au explains why the rough overlayer estimate for Ni in Fig. 4 was $\sim 1\lambda$ rather than $\sim 2\lambda$ found for Au because the region covered by 14.5 nm Au completely annihilates the Ni signal and only the effect of the 1.5 nm Au layer is seen in the Ni inelastic background spectrum.

Note that the depth distribution is already determined without using a reference, which is only needed to obtain the absolute concentrations. In general, the reference spectrum does not need to be from a homogeneous sample. For example, if one is studying a set of samples with varying concentration depth distributions, one may choose one of these as a reference. Thus, if one of the samples in a series is expected to have a certain concentration depth distribution, this spectrum is first analyzed using this assumption. The resulting background corrected reference spectrum is then used to find the absolute concentrations in the other samples.

2. Example 2: Nanoparticle application

Figure 6 shows another example from a paper by Müller *et al.*³¹ where coated nanoparticles were studied. The nanoparticles, consisting of a PTFE core coated with polystyrene, were deposited as a submonolayer on a Si wafer. The analysis is done on the F 1s peak, which originates from the PTFE core. The upper panel shows the best possible fit using a model with uniform coating thickness. The fit is quite poor but indicates that the coating thickness is roughly 3 nm. A much-improved analysis (Fig. 6, lower panel) is obtained when it is assumed that the coating is incomplete, and the core is sticking out through the coating. Because the particles are randomly oriented on the surface, some will have the PTFE core pointing downward and some pointing upward, and these situations correspond to the fractions 0.6 and 0.4 found in the analysis (nanoparticles with other orientations will also occur and their contribution



FIG. 8. Ir 3D region measured with an x-ray photon energy of 9 keV for various overlayer thicknesses. Yellow lines show inelastic background modeling using the QUASES software package. Reproduced from Spencer *et al.*, Appl. Surf. Sci. **541**, 148635 (2021). Copyright 2021, Author(s), licensed under a Creative Commons Attribution license.

will average out in the background spectra). In the paper,³¹ PTFE nanoparticles coated with PDMA were also studied, and, in contrast, it was found by a similar analysis that in this case, the PTFE core is fully coated but the core is off center. Details of the steps involved in the analysis in Fig. 6 are shown in Video 13.⁵²

The probing depth with this method is $\sim 10\lambda^{41}$ and can be even larger if the background can be detected over an energy range of several hundreds of electron volts.³⁰ This is considerably larger compared to XPS analysis based on peak intensities where it is usually quoted as 3λ . The reason is that the electrons detected in the background have lost energy and, therefore, will originate from deeper layers compared to the electrons that survive at the peak energy. With HAXPES, the photon energy is considerably larger (~3 to 10 keV) compared to conventional XPS (~1.5 keV), and the kinetic energy of the XPS peaks and thereby λ can be considerably larger.⁴⁶ Probing depths of >100 nm have been achieved with HAXPES using both synchrotrons and the new lab based HAXPES instruments, and examples can be found in Refs. 30, 51, 53, and 54.

3. Example 3: HAXPES multilayer application

Figure 7 shows an example from a paper by Zborowski et al.,⁵⁴ where HAXPES was used to determine the depth and thickness of a Ta layer in a stack. It is seen that the calculated background matches the measured spectrum extremely well for a Ta layer extending from 16.5 ± 0.5 to 45 ± 5 nm depth. The sample was also analyzed with TEM and the above result deviated by only 4.2% from the TEM result. Note that the HAXPES analysis is much simpler and faster compared to TEM. TEM is also destructive, whereas XPS background analysis is nondestructive and as a result, it is possible to study variations in sample composition, for example, as a function of annealing time temperature. This was used in the paper⁵⁴ where the gradual diffusion of Ta atoms (both toward the surface and into the bulk) could be followed quantitatively as a function of annealing time and temperature.

4. Example 4: Deeply buried layer with no visible peak

As a final example, Fig. 8 shows a QUASES-HAXPES study by Spencer *et al.*,⁵¹ of a thin layer of an Ir–organic complex buried up to 140 nm beneath an organic material. The modeled backgrounds match the spectra very well and the determined thicknesses are within 5% in agreement with thicknesses determined by ellipsometry. It is interesting that the background analysis is still possible, and accurate, even in cases (seen for layers of 75 nm and above) where the Ir 3d peak is not visible.

E. Structure from simplified background analysis suitable for automation

Two early methods for quantitative XPS that are still being used primarily because of their robustness and suitability for automated analysis are briefly mentioned here. Tougaard started the development of quantitative application of the inelastic background around 1985. The first model was based on the observation that, as seen in Fig. 3, the peak area (Ap) and the increase (B) in background intensity 30 eV below the peak energy vary in opposite directions with the depth distribution. As a result, the ratio Ap/B is very sensitive to the depth distribution of atoms. For a homogeneous atomic distribution, it was found that Ap/B is roughly constant (\sim 23 eV) independent of the material and peak energy. Deviations from this value can then be used to evaluate the depth distribution of atoms and to estimate thin film thicknesses.

This approach is similar to the visual inspection method (Sec. II B), but it takes into account in a quantitative way that it is the full peak intensity, i.e., the peak area and not the peak height that counts. It also gives a quantitative number that enables objective comparison of the depth location of atoms in two samples. When applied to a series of spectra, the Ap/B ratio clearly indicates the relative film thicknesses across the series. Since it relies on the ratio of intensities at two energies that differ very little in energy,

the method is highly robust against variations in the details of the experimental setup and completely independent of, e.g., the photon flux. When applied to a specific system on the production line, one is not concerned with the type of growth since this is constant and has already been established for the specific system produced, and one only needs a criterion (specified by a certain Ap/B value) to decide when to stop deposition of layers. The method is highly effective for automated control of layer growth on the production line and is used in, e.g., the semiconductor industry. For further details on this Ap/B method and examples of its practical application, the reader is referred to the review in Sec. V B of Ref. 29 (free download at https://doi.org/10.1116/6.0000661).

Around 1988, an increasingly better understanding of the probability for inelastic scattering in different materials and more comprehensive mathematical modeling resulted in increasingly more detailed and more accurate algorithms for depth analysis. One of these, known as $(AOS)_{3\lambda}$, was first suggested in 1990 and later improved. This approach determines just two numbers: $(AOS)_{3\lambda}$, which is the number of atoms (or the amount of substance) within the outermost 3λ depth, and the decay length L characterizing the depth distribution. Despite its simplicity, the method achieves a typical accuracy of 10%-20%. It is a simplified version of the more comprehensive QUASES approach. Whereas QUASES is designed to extract the maximum amount of information regarding the detailed atomic depth distribution, the $(AOS)_{3\lambda}$ approach deliberately retrieves less information than is inherently available in the spectrum. This results in a very robust algorithm, which is well suited for automated analysis. It has been successfully applied to XPS imaging where automation is essential. For further details on the $(AOS)_{3\lambda}$ method and examples of its practical application, the reader is referred to the review in Sec. V C of Ref. 29 8 (free download at https://doi.org/10.1116/6.0000661) and the g example in Ref. 55. Given the robustness of the approach and demonstration on a variety of systems, users have found it surprising of that the approach has not been widely incorporated into commercial software systems for routine analysis.²

F. Information using photoelectron signals with different energies

As noted above, photoelectron peaks with higher kinetic energy ($E_{\rm KE}$), lower binding energy ($E_{\rm B}$)—can arise from deeper in a material than those with lower $E_{\rm KE}$ but higher $E_{\rm B}$.^{45,46} These differences can be quite useful in understanding the nature of the material being examined. Specifically, when a layer thickness is less than a few times the size of the electron path lengths for the photoelectron or Auger peaks involved, differences in relative signal intensities for two peaks from the same element with different path lengths (different kinetic energies) can be used to provide a measure of elemental distribution in the surface region. Castle used differences in the analysis depths of pairs of photoelectron signals from metals in a corrosion film (e.g., Fe 2p and Fe 3p) to get indications of elemental enrichment or depletion in corrosion layers along with an indication of passive film thickness.³⁹

As another example, Davis⁵⁶ proposed that the mean particle size of a supported metal can be estimated using the ratio of the intensities of two photoemission lines (or Auger lines) of metal with significantly differing kinetic energies. The limitations of this approach



FIG. 9. Calculation of average particle diameter d based on the ratio, R, of the Cu 2p to Cu 3d photoelectron peaks following information in Yang *et al.*, Appl. Surf. Sci. **173**, 134 (2001).

using conventional x-ray sources along with opportunities using higher energy sources have been discussed by Smirnov *et al.*⁵⁷ and Artyushkova *et al.*³⁵ Yang *et al.*³³ applied this method to get an average measure of the size of Cu nanoparticles. They measured the intensity of Cu 2p3/2 and Cu 3d photoelectron peaks and were able to use that information to determine a measure of the average size of Cu nanoparticles which nicely compared to those obtained by TEM and AFM. The relevant equation, derived in their paper, shows how the different analysis depths enable the measurement.

The link between measured peak ratios, escape depths, and particle diameter is shown in Eq. (1),

$$R = I_1^o \left[1 - \exp\left(-\frac{d}{1}\right) \right] / I_2^o \left[1 - \exp\left(-\frac{d}{2}\right) \right], \tag{1}$$

where R is the intensity ratio of measured values for different photoelectron peaks I_1 and I_2 from the same element in the nanoparticle; I_1^o and I_2^o are the intensities associated with the intensities of the two peaks that would be obtained from very thick (bulk from the view of XPS) material (the ratio of these bulk intensities would be equal to the ratio of appropriately determined sensitivity factors); d is the average cluster diameter and the two λs are the appropriate IMFPs for the kinetic energies of the two measured transitions. For the copper study of Yang et al.,33 the parameters used in the equation were based on the Cu 2p3/2 peak ($E_B = 932.5 \text{ eV}$, $\lambda = 1.3 \text{ nm}$) and Cu 3d peak $(E_{\rm B} = 4 \text{ eV}, \lambda = 5.0 \text{ nm})$. Assuming that $I_1^o/I_2^o \cong 12$ the relationship between R and d would be as shown in Fig. 9. There would be a reasonable sensitivity for an average particle size below about 10 nm in diameter. This approach is limited by the availability of photoelectron peaks with adequate energy separation and the effects of coating or contamination on the signal intensities.57

III. USING THE AUGER PARAMETER TO DETERMINE A SAMPLE PROPERTY

All users that regularly examine XPS survey spectra will be familiar with the presence of Auger peaks that result from the de-excitation of the core hole that gives rise to the photoelectron

peak. Some of these peaks are known to contain chemical information, and it was this feature that led to Siegbahn coining the (now deprecated) terms of electron spectroscopy for chemical analysis for the new method in the mid-1960s. Seeking a more precise title, many researchers adopted the term x-ray photoelectron spectroscopy (XPS) as early as the 1970s, and this has become the preferred term today. In spite of the gradual change in nomenclature, the x-ray-induced Auger transitions are still there and provide an important source of information. Such peaks are often identified by the acronym X-AES to avoid confusion with the traditional form of Auger analysis using a finely focused electron beam, AES. Unlike XPS, X-AES does not provide chemical information for all elements, and the reason for this lies in the source of outermost two electrons of the three electron Auger transition. If the two outermost electrons are core (rather than valence) electrons, they will carry the same chemical information as the comparable XPS transition, and the energy of the Auger peak will reflect the energies of these well-defined core, or indeed corelike, electrons. In a conventional XPS spectrum, the F KLL, Na KLL, and Cu LMM are three examples of Auger transitions with chemical information and are known as core-core (CCC) transitions. If the outermost two electrons of the Auger transition are from the valence band, the term core-valence-valence (CVV) is used. Valence bands are invariably broad, and the degeneracy is superimposed on the Auger peak itself and the peak becomes a broad feature, and it becomes difficult to define a unique energy, thus chemical information is limited. Although it should be noted that some CVV Auger peaks exhibit changes in shape that can be interpreted in terms of chemistry. The C KLL is a good example of this as described in Sec. IV. As a sweeping generalization X-AES can be considered to provide useful chemical information for about half the elements in the periodic table.

The kinetic energy of a $KL_{2,3}L_{2,3}$ Auger electron is approximately equal to the difference between the energy of the core hole is and the energy levels of the two outer electrons, $E_{L2,3}$ (the term $L_{2,3}$ is used in this case because, for light elements, such as oxygen or carbon, L_2 and L_3 cannot be resolved),

$$E_{KL_{2,3}L_{2,3}} \approx E_K - E_{L_{2,3}} - E_{L_{2,3}}$$

This equation does not take into account the interaction energies between the core holes ($L_{2,3}$ and $L_{2,3}$) in the final atomic state nor the inter- and extrarelaxation energies, which come about as a result of the additional core screening needed but will suffice for the current purposes to indicate the interrelationship of Auger energy with that of the binding energy of the constituent electrons.

Very early on in the development of XPS, it was noted that the combination of the primary XPS line with X-AES line (if sharp) could be a useful approach. This led to the definition of the Auger parameter (α) by Wagner.⁵⁸ In its original form, where the kinetic energies of both X-AES and XPS peaks were considered, this was given by

$$\alpha = E_{jkl}^K - E_i^K,$$



which, using the XPS peak binding energy, is equivalent to

$$\alpha = E_{ikl}^{K} + E_{i}^{B} - hv.$$

This, of course, means that the value of the Auger parameter was a function of x-ray source used for analysis (generally, Al K α or Mg K α). This was recognized by Garenstroom and Winograd,⁵⁹ who defined a modified Auger parameter (α *), by the simple expedient of the addition of the photon energy,

$$\alpha^* = \alpha + h\nu = E_{ikl}^K + E_i^B$$

This provided a more convenient form, which simply required the addition of binding and kinetic energies of the relevant XPS and X-AES lines, values that are likely to be readily handed to the analyst. To avoid referring to the modified Auger parameter, Castle¹⁷ used the designation AP to refer to this parameter, and we followed that convention. Wagner further extended his analysis of this concept by the definition of chemical state plots (often referred to as Wagner plots)^{58,60} in which the binding and kinetic energies are plotted on orthogonal axes, the AP being represented by a



FIG. 10. Chemical state plot for arsenic compounds. Reproduced with permission from Watts and Wolstenholme, *Introduction to Surface Analysis by XPS and AES*, 2nd edition. Copyright 2019, John Wiley & Sons, Ltd.

diagonal grid of slope 1. A typical example of such a plot is illustrated in Fig. 10.

One of the major advantages of this type of approach, along with the potential for additional chemical state information, is that it is independent of electrostatic charging of the type often observed in the XPS analysis of insulators. This was recognized very early after the adoption of the method, and it is often described as a "portable" measurement independent of charge compensation measurements that may differ slightly between laboratories. So long as the linearity of the energy scale has been established the measurement is secure. This might be accomplished in several ways, each vendor will have a method they use, and for traditional laboratory x-ray sources, ISO 15472 and ASTM2108 provide standard procedures for energy scale calibration. As noted below, higher energy x-ray sources are useful to AP measurements as they expand the range of AP information available. However, the x-ray sources used for HAXPES require newer approaches to energy scale calibration and energy scale linearity checks.⁶¹ A comprehensive approach to energy scale linearity for HAXPES has been described by Leadley.⁶² This method involves the use of ion etched silver and recording high resolution spectra of Ag 3d5/2 and Ag $M_4N_{4,5}N_{4,5}$ peaks, the former on the usual binding energy scale and the latter converted to kinetic energy. As these peaks represent relatively low binding and kinetic energy peaks (368 and 358 eV, respectively), they cover the majority of a HAXPES energy scale. If the energy values are adjusted to the standard values, as described by Leadley, this provides the additional advantage that the energy scale is correctly calibrated. To establish the scale linearity, the sep-2 aration of the two peaks should be checked prior to HAXPES Auger parameter measurement. Such a rigorous procedure has two potentially minor disadvantages; if monochromator settings have been adjusted, to optimize performance, for example, this may bottom potentially bring about a slight change in photon energy (compromising the binding energy to kinetic energy conversion for the $\vec{\sigma}$ Auger peak); additionally, the process is somewhat time consuming. The solution for this is to record high and low binding energy peaks at the high and low energy ends of the binding energy scale. The choice of material will naturally depend on the x-ray energy employed, but for Ag La radiation, gold serves the purpose very well. In addition to the usual Au 4f7/2, the Au 3d5/2 peak at 2206 eV is recorded and the separation is routinely monitored to ensure consistency of the energy scale. For higher energy sources, alternative metals will be required, for example, for Ga Ka (hv = 9252 eV), clean iron would provide a Fe 2p3/2 peak at 706 eV on a binding energy scale and Fe 1s at 7111 eV, once again separation will reveal any changes in energy scale linearity.

The AP is often referred to as the final-state Auger parameter as it is dominated by extra-atomic relaxation and associated effects. A complementary Auger parameter has been defined which reflects initial-state effects and is often given the symbol ξ . The ξ parameter contains not only the binding energy of the initial core hole XPS peak but also that of the outer two electrons in the following form:

$$\xi = KE_{(ijj)} + BE_{(i)} + 2BE_{(j)}.$$

Because of the involvement of three binding energies and one Auger kinetic energy, the value of this Auger parameter is very



sensitive to charge referencing protocols, and for this reason, is nowhere as popular as the α^* Auger parameter.

Thus, the Auger parameter, usually as AP (α^*) is widely used in the chemical speciation of many elements as exemplified by the data of Fig. 10. The need to use CCC Auger transitions limits those elements amenable to this form of analysis in conventional (Al K α excited) XPS to about a third of the periodic table. To extend this range further, one needs to extend the kinetic range of an XPS spectrum by the use of higher energy photon sources. Currently, there are three commercial systems based around higher energy sources, but a variety has been successfully employed over the years as recently described by Watts and Castle.⁶³ In their review, a number of sources are described ranging from Si K α with a photon energy of hv = 1739.5 eV (to access Al 1s) through to Cu K α , hv = 8048.0 eV (to access Fe 1s).

In addition to chemical information, it must be noted that the Auger parameter can be used to access other properties of materials not readily accessible by conventional methods. As described by Castle¹⁷ "the value of the AP is its sensitivity to the polarization of electrons in the orbitals of neighboring ions towards the photo-ionized atom, and is thus related to other optoelectronic properties of the material." There is the additional advantage that XPS, as a surface sensitive technique, can be used in a very straightforward manner for the analysis of other properties of thin films where bulk techniques would not be of use. The one potential difficulty in the use of the AP is the lack of a unified scale. Each element will have a scale relating directly to the binding and kinetic energies of the electrons involved. This conundrum was addressed by Castle, who proposed a unified scale for the AP by normalizing against the refractive index of a material, using the Lorentz–Lorenz relationship described below.¹⁷

This approach stems from much earlier work from West and Castle,¹⁸ where a linear correlation was shown by consideration of the AP with refractive index (both a measure of polarizability of the material) for a series of aluminosilicate minerals. The AP was measured for Si 1s-Si *KLL* and Al 1s-Al *KLL* pairs using Zr L α radiation (hv = 2042.4 eV) and then manipulated to provide a measure of polarizability. The refractive index is related to this quantity by the Lorentz–Lorenz relationship ($4\pi N\alpha = (n^2 - 1)/(n^2 + 2)$, where *n* is the refractive index and α is the polarizability). The excellent agreement between these two methods is clearly shown in Fig. 11.

This link to polarizability was first noted by Wagner in 1975,⁵⁸ he stated that differences in the Auger parameter "are attributable solely to changes in the polarizability of the solid compounds." More than 30 year later, Moretti⁶⁰ observed that the chemical and physical insights provided the Auger parameter had not been fully investigated. In a 2013 paper, he showed the use of the Wagner plot of the AP to get information on the local valence charge and Madelung (molecular) potential (initial-state effects) and on the extra-atomic relaxation energy gained from the environment (final-state effects) for a core-ionized atom.

The possibility of deducing structural data from the AP was first suggested by West and Castle¹⁸ on the basis of their work on aluminosilicates, cited above. By calculating the oxygen polarizability of aluminum and silicon bonds from the respective APs, and plotting the data on orthogonal axes, they were able to show a clear correlation between tetrahedral and octahedral coordination of oxygen around the major cations as shown in Fig. 12.



FIG. 11. Correlation between bulk polarizability based on refractive index and AP measure of polarizability. Reproduced with permission from West and Castle, Surf. Interface Anal. 4, 68 (1982). Copyright 1982, John Wiley & Sons, Ltd.



FIG. 12. Oxygen polarizabilities around Al and Si ions as calculated from AP measurements. The distinction between tetrahedral and octahedral polarization is clearly seen. Reproduced with permission from West and Castle, Surf. Interface Anal. 4, 68 (1982). Copyright 1982, John Wiley & Sons, Ltd.



As pointed out above, the AP provides a measure of the screening efficiency of a material following the generation of a core hole as experienced during photoemission. This has been shown to be the case for many inorganic compounds but in the case of metals, the situation is rather different. Following the Drude–Lorenz theory of metallic bonding, metals exhibit perfect screening and, thus, an alternative explanation must be sought for changes in the AP. The apparent reduction in screening (a lower AP) means that the metal atom is in a less metallic environment, conversely, an increase in AP indicates and an increase in metallic character. Such observations can be particularly important in understanding changes in metals that occur in the formation of an alloy, being related to charge redistribution or even charge transfer. The theory relating to the estimation of charge transfer on alloying based on changes in the AP can be traced back to Thomas and Weightman's seminal work of some 40 years ago.⁶⁴

IV. USE OF THE D-PARAMETER TO IDENTIFY sp² AND sp³ CARBON INFORMATION

The D-parameter, as described below, obtained from x-ray excited C KVV Auger spectra, can be a useful tool assisting in understanding the chemistry of carbon at sample surfaces. Knowledge of carbon surface chemistry is important in a diverse range of fields, including catalysis, composite materials, energy storage, and sensors.⁶⁵ A recent examination of six months of XPS data from three multidisciplinary journals revealed that carbon was the most frequently analyzed element using XPS. However, this study also revealed significant errors in the interpretation of much of the XPS data.⁸ Results from the study lead some of the authors to publish a useful practical guide to the interpretation of the C 1s spectrum for systems containing graphitic carbon.⁶⁶

The influence of ligands and functional groups on XPS derived binding energies cannot be ignored, and, therefore, complementary information from photoelectron peaks other than the C 1s, such as the O 1s or N 1s signals, should be accounted for and will aid in an improved analysis of the C 1s spectrum.⁶⁶ From data presented in the literature, it is not clear if this is always the case; however, it is evident that in many cases, asymmetric peak shapes appropriate for graphitic carbon are not used. To fit, with any degree of confidence, the C 1s envelope for such carbons not only requires the aforementioned analysis but also an appreciation for the degree of sp² hybridization, which may be derived from the C KVV Auger peak in the form of the D-parameter.^{67,68} We note here that we focus our discussion on the use of the D-parameter for graphitic-type carbons, and while some utility has been found in the analysis of polymer systems,⁶⁹ we do not discuss its application to polymers herein.

As defined by Lascovich and co-workers,⁶⁸ the D-parameter is the separation (in eV) between the maximum and minimum



FIG. 13. (a) Relationship between the XPS derived D parameter and the relative amounts of sp² and sp³ carbon present on the surface of a specimen as reported by Lascovich *et al.* (Ref. 68). (b) Examples of derivative spectra of C KVV peaks and the measured D parameters. Figure adapted from Morgan, C 7, 51 (2021). Copyright 2021, Author(s), licensed under a Creative Commons Attribution (CC BY) license.



peaks from the first derivative spectra of the C KVV Auger peaks, as shown for the two pure sp² (HOPG) and sp³ (diamond) reference materials in Fig. 13, together with a plot of the data taken from Lascovich *et al.*⁶⁸ This method has been used with success by a number of researchers to qualify the amount of sp² carbon in the near-surface region.^{67,68} Thus, the D-parameter can provide information about the general nature of carbon on a surface without peak fitting, see, for example, Grey *et al.*⁷⁰ and also serve to guide, as noted below, relevant aspects of appropriate peak fitting for the C 1s photoelectron peaks. D-parameter analysis has also found utility in the mapping of carbon chemistry over heterogeneously prepared carbon surfaces, for example, Barlow *et al.*⁷¹ have successfully used what they term multivariate Auger feature imaging to map the reduction of graphene oxide by laser irradiation.

Derivatives of AES spectra are frequently used to highlight spectral features, are often used for quantitative analysis of AES spectra, and serve to highlight changes in peak shapes. As demonstrated in Ref. 68, the X-AES C KVV derivative spectra have more distinct features than the N(E) spectra, and the changes in the shapes of the spectra are associated with loss peaks and binding energies of the valence band states involved in the C KVV Auger process.⁶⁸ The C KVV peak is generally recorded at a higher pass energy, such as 100 eV and a step size of 0.5–1 eV, to ensure good signal-to-noise levels to allow extraction of reliable information, however methods of extracting such information from noisier data have been presented by Fairley *et al.*⁷² Many manufacturers' data-systems and third-party analysis software now have routines to derive the D-parameter. Morgan has explored the effect of the parameters used to derive the D-parameter, finding that the accuracy/reproducibility of using different methods to determine the D-parameter is estimated to be ±0.5 eV, corresponding to an accuracy better than ca. 5%.⁶⁷

It is notable that the electron kinetic energy for the C KVV and C 1s peaks are separated by ca. 900 eV, so a difference in the information depth is expected. Given the low kinetic energy of the Auger peak (ca. 270 eV), the measurement is very surface sensitive, with an electron mean free path of 1.2 nm, while for the C 1s peak (ca. 1200 eV), this value is 3.3 nm, yielding information depths of 3.6 and 9.9 nm. Since it is only a measure of the degree of sp^2/sp^3 carbon present in the near-surface region of a sample, the D-parameter does not provide exact information about the nature



FIG. 14. Flow chart to guide and assess C 1s spectra peak fitting for graphitic materials based on the derived D-parameter for sp³ carbon content and the O 1s concentration. Figure adapted from Morgan, C 7, 51 (2021). Copyright 2021, Author(s), licensed under a Creative Commons Attribution (CC BY) license.



carbon on a sample. However, it offers a simple and useful guide to the nature of the carbon present and what needs to be considered if attempting a peak fit, while also serving as an indication of when the carbon on a surface differs without the need for detailed peak fitting. Where peak fitting is required, the D-parameter, together with, for example, the oxygen concentration and speciation, can help inform fitting of the C 1s envelope. Figure 14 shows a flow diagram (adapted from Ref. 67) to illustrate the checks, such as the percentage of sp³ carbon derived from the D-parameter, degree of peak asymmetry, and likely functionalities from the O 1s spectrum, to guide the fitting of the C 1s spectrum.

V. INFORMATION FROM THE XPS VALENCE BAND

XPS survey spectra routines usually collect data starting with a binding energy of nearly 0 eV. However, the low binding energy region (<30 eV) is generally ignored.⁷³ This region corresponds to valence band (VB), thus it is identified as VBXPS, and although often neglected, it contains information that may not be readily available from XPS core level photoelectron peaks. It is generally known that this region directly measures the occupied density of states and is often used to identify band edges as described in Sec. VII. However, it has important additional uses as described below.

This region is generally of much lower intensity than the core regions and detailed studies of this region may require longer collection times that other regions of an XPS survey spectra for good statistics. However, modern instruments can readily obtain high quality valence band information relatively quickly.

In a review of the surface applications of XPS, Krishna and Philip⁷⁴ note the strengths and uses of core level XPS, but also highlight the availability of missing information that VBXPS can provide, "Despite the ability of XPS for determining the surface chemistry by conventional core level analysis, it cannot provide the phase information of the surface chemical species. In principle, by analyzing the valence band of XPS, information of the crystal structure or phase of a sample surface can be obtained." They further note that determination of surface phase composition in the outer 10 nm of a sample is both difficult and highly important. Surface and near-surface chemical structural information is hard to collect by other methods and such information is required for many modern material applications such as photo catalysis, microelectronics, electrochemical energy storage, and multifunctional coatings.

In addition to the ability to distinguish⁷⁵ and map⁷⁶ phases with the same compositions, but different structures, VBXPS can sometimes enable oxidation state identification⁷⁷ or assist determination of the relative amounts of when multiple oxidation states present,⁷⁸ especially when the binding energies of core lines have shifts too small or peak structures too complex to be readily analyzed.

There are several reasons why the valence band region using photons in the x-ray region can provide valuable information not available from core level peaks or, in many cases, other analysis methods.

• The region differs from the core region because the spectral features do not depend upon the chemical shift of a core level but rather the interactions between the atomic orbitals of the individual atoms to give rise to molecular orbitals, which in a solid correspond to the ground state density of states. The observed

spectrum is, thus, a "pattern" made up of the ground state density of states adjusted by the photoelectric cross sections and convoluted with a photon function. The information provided is often more sensitive to subtle chemical changes than the chemical shifts in the core region.

- Core and valence band XPS can be interpreted by comparison with previously recorded samples with known spectra, however, while there is a large database of core XPS spectra, collecting spectra of samples of known composition as standards depends upon the surface of the standard having the same composition as the known bulk composition. Core binding energies can be calculated for the standard, but this is of limited help in establishing the composition of the sample of interest as many compounds of different composition have the same or similar core binding energies. In contrast, the "pattern" in valence band XPS can be calculated to give what is usually a "pattern" that is unique to a particular composition because of the high sensitivity of valence band XPS to subtle chemical differences.
- The calibration issue of core photoelectron peaks is not a fully resolved issue despite extensive studies over the past 60 yearsuncertainties remain in exact chemical shift determination. In the valence band, one is looking for the characteristic "pattern" of a specific surface species rather than a specific binding energy.
- When x-ray photons are used, the kinetic energy of the valence band photoelectrons is greater than those of the core region making the valence band XPS relatively less surface sensitive. This can be helpful if less than completely clean surfaces are studied such as found for many practical systems. When photons in the UV region are used the spectra are more complex to interpret as they depend on the joint density of states (initial and final states) 2025 and are highly surface sensitive.

In cases where the bands are relatively flat, it is possible to $\ddot{\Xi}$ model the valence band spectrum with a calculation of a cluster rep- $\vec{\sigma}$ resentative of the solid. In other cases, such as metals, which have considerable dispersion (the bands are not flat), the spectra can only be understood if a calculated spectrum based upon the density of states from a band structure calculation is generated. The orthophosphate ion (PO_4^{3-}) provides a simple example of a cluster calculation where the bands are nearly flat. Figure 15 shows the calculated spectrum (details can be found elsewhere⁷⁹) for orthophosphates such as sodium orthophosphate showing the predicted "pattern" and the representation of atomic orbitals in the spectral features. This spectrum cannot be curve fitted to specific atomic orbitals as in core XPS because the features cannot be associated with a particular atomic orbital. More details of the approach to calculating valence band spectra are given elseware⁸⁰ with specific examples in Refs. 81–84. Calculations may be based on a cluster representative of the solid or a band structure calculation where an infinite model is appropriate using calculations that use models of various sophistication including those that use the density functional theory.

There are many examples of cases where valence band XPS can reveal differences between solids of similar composition, which cannot be distinguished by core XPS, for example, Fig. 16 shows other phosphorus species, all of which have the same P 2p binding energy but a significantly different valence band spectrum, which agrees with the calculated spectrum from band structure





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calculations.⁸⁵ Other examples where binding energies are similar but the valence band distinguishes among species present are given below:

- Diamond and graphite and other forms of carbon.⁸⁶
- Polymers.⁸
- Carbonates and bicarbonates.⁹¹
- Sulfate and bisulfate.⁹²
- Oxidized⁸² aluminum species.⁹³
- Titania phases.^{75,76}
- SnO and SnO_2 .⁷⁷

Changes can be seen in the outer valence band region, which give additional insights. For example,

- Angle resolved photoemission from single crystal samples can provide symmetry information, for example, the relative intensities of the e_g and t_{2g} regions in solids with octahedral arrangements (e.g., MnF₂) can vary with take-off angle leading to spectral changes.⁹⁴
- Information about the valence band edge (valence band maximum—VBM) along with core level measurements can be

used to help understand built-in potentials at interfaces and band bending, see also Sec. VII A.^{24,95,96}

There are some issues that one needs to be aware of that need to be considered when using valence band data, VBXPS, in particular,

- The outer valence band region (the region with binding energies below 18 eV), typically, appears very different when the spectrum is obtained with achromatic and with monochromatic X-radiation. This is because many valence band spectra have intense features in the inner valence band region (the region between 30 and 18 eV) and the weak x-ray satellites from Mg and Al X-radiation from the inner region fall in the outer region (e.g., as in Fig. 16). Even though these satellites have a total intensity that is only about 15% of the main K $\alpha_{1,2}$ x-rays, their origin from the inner valence band region. The photon function used in generating a calculated spectrum can be modified to include the satellites, so that the spectral features from spectra using achromatic radiation can be predicted. In practice, *it is better to use monochromatic X-radiation for valence band XPS*.
- The analysis of mixtures requires matching the observed spectrum with a synthetic spectrum made up of adding together the





FIG. 16. Experimental (using monochromatic X-radiation) and calculated (from band structure calculations) outer valence band spectra of P/O compounds. All the P/O compounds have features in the region of the lines 1, 2, 3, and 4 and are different from aluminum oxide. Reproduced with permission from Sherwood, Surf. Sci. Spectra 9, 62 (2002). Copyright 2002, American Vacuum Society.

spectra of the expected components of the mixture. In such a case, the analysis is less clear cut than an analysis of single components.

The importance of valence band XPS has long been appreciated as a means of better understanding the solid state, but its powerful abilities have been largely ignored by the surface analyst.

VI. CRYOGENIC XPS: PROBING INTACT INTERFACES IN NATURE AND LIFE

Conventional XPS has limited applications for wet (usually aqueous) samples due to their high vapor pressure and alterations when in ultrahigh vacuum (UHV) conditions. Cooling to low temperatures can facilitate analysis of unstable and volatile samples.⁹⁷ Rapidly cooling, fast-freezing, of samples can further stabilize structures and enable examination of environmental and biological structures and samples not normally considered amenable for XPS study by minimizing water loss and related alteration. The major challenge is developing reliable and reproducible sample preparation techniques that maintain the composition and structure of the solidsolution/solution-gas (vacuum) interface, ensure a solution layer at the solid–liquid (SL) interface thinner than XPS depth of analysis, and produce UHV-stable samples. Effective sample preparation approaches and example results are provided in Secs. VI A–VI D. Different XPS approaches to study hydrated/wet samples can be found in the literature and several are discussed in Refs. 26 and 98.

A. Instrumental requirements

REVIEW

Measurements under liquid nitrogen (LN₂) cooling are common practice with modern electron spectrometers to study volatile and unstable bulk materials;⁹⁷ however, a critical step in cryo-XPS is the fast-freezing of the sample in an air-lock chamber. Fast-freezing refers to a cooling rate higher than 15–20 °C/s.⁹⁹ This can be achieved by incorporating a "cold finger" in the sampleloading chamber and utilizing sample holders with good thermal conductivity to provide a sufficient cryogenic cooling rate up to -170 °C. For liquid samples, a small drop is pipetted directly onto a precooled sample holder. However, for aqueous suspensions and dense gels, centrifugation is often necessary to separate excess supernatant/solution. At Umeå University, a common approach to creating and mounting centrifuged paste is to centrifuge suspensions in 15 or 50 ml tubes to get a wet paste for sampling. For easy collection, it is ideal to have 50 mg of wet paste at the bottom after centrifugation. It g means 1 mg/ml (50 ml tube)-3 mg/ml (15 ml tube).



FIG. 17. Image of fast-frozen $6\,\mu l$ drop of aqueous solution with viruses in the analysis chamber. Vacuum ${\sim}4.4\times10^{-9}$ Torr.

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To improve the fast-freezing rate and secure the sample attachment to the holder, a stainless steel or copper mesh built-in to the holder is a great help. Additionally, for air-sensitive wet samples, a glove box attached to the spectrometer air-lock or an inert sample transfer device should be utilized to ensure sample integrity. Sample temperature control during the measurements is crucial, with a maximum temperature of -140 °C, to avoid ice sublimation in the UHV environment.

These measurements are made in a conventional laboratory XPS system that includes the sample cryocooling capability. The wet frozen samples are dielectric and require application of external surface charge compensation.

B. Sample requirements

Cryogenic XPS assumes the presence of ice in the UHV environment of the electron spectrometer. Implying the sample to investigate is in equilibrium with its wet environment, a key requirement is to use the minimum amount of sample necessary. For an aqueous solution, a $6-7 \mu$ l drop provides a sufficient area for the analysis. In the case of centrifuged wet pastes/gels, the sample should be "smeared" to cover an area slightly larger than the x-rays irradiation spot. To measure signal from the sample, the solid content for aqueous suspensions should be not less than 20-50 mg. By only using a small amount of fast-frozen sample, it becomes possible to leave the sample after cryo-XPS measurements in the spectrometer analysis chamber and allow a slow increase in sample temperature up to room temperature, thus sublimating the ice and pumping out volatile species from the SL interface. Conventional XPS measurements of the dry sample (in the same analytical position) on the following day provide important additional information on changes in the surface/interface chemical composition caused by water loss. In addition, it allows estimation of the thickness of the solution layer in the fast-frozen sample. Routinely, samples must be prepared/equilibrated immediately before the cryo-XPS measurements. Sample storage and transportation are possible only if the SL interface does not change.

For biological samples, the aqueous solution should not otherwise contain any organic molecules containing nitrogen to ensure biochemical analysis of the cell wall in terms of lipids, sugars, and proteins. Low concentrations of cells/microorganisms/organic nanoparticles in solutions are not usually problematic as they tend to aggregate close to the liquid-gas (LG) interface and are clearly seen in cryo-XPS spectra of the fast-frozen drop. The desired electrolyte concentration for all types of samples should be between 20 and 50 mM to minimize solution input to the SL interface's composition. For a more effective separation of concentrated aqueous solution, tubes with in-built microfilters for centrifugation might be of great help and will be explored in future work.

A rapidly frozen 6μ l drop of aqueous solution with viruses in the spectrometer surface analysis chamber (SAC) at 4.4×10^{-9} Torr is shown in Fig. 17.

C. Example applications

Cryo-XPS has been found highly useful for extracting important information from multiple types of samples. Examples below focus on those related to geochemical relevant examples and those of biological interest including microorganism surfaces and nanomedicine. The types of analyses conducted provide information



FIG. 18. Surface concentration profiles of hematite suspensions in contact with 50 mM NaCl (■), KCl (♦), RbCl (▲), and CsCl (●) electrolytes as a function of pH. Concentrations are presented as atomic ratio of elements with respect to iron. Open and closed symbols represent the chloride ions and alkaline metal ions, respectively. The curves show the increase in interfacial concentration of cations with respect to pH of the bulk solution, whereas chloride ions show the opposite trend. General trends are illustrated by dotted (NaCI), short-dotted (KCI), and long-dotted (RbCI) and solid (CsCI) lines. The order of interfacial concentrations of cation below pH 9 is in order of Na⁺ > K⁺ > Rb⁺ \approx Cs⁺. Reproduced with permission from Shimizu et al., Surf. Sci. 606, 1005 (2012). Copyright 2012, Elsevier.

such as (1) ionic loadings on particle surfaces, (2) electrolyte atom $\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$ ratios relating to mineral surface charge, (3) electric double layer by potentials influence on measured binding energies, (4) protonation $\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$ constants, (5) cell and microorganism surface chemistry, and (6) $\frac{2}{3}$ surface chemistry of organic/soft-matter nanomaterials.

1. Important properties at mineral/solution/biological interfaces

A fundamental phenomenon occurring at most solid-aqueous solution interfaces is the formation of an EDL. The chemical composition, structure, surface charge, and potential profile of the EDL, and specific chemical interactions within the EDL at this dielectric interface are of crucial interest in many situations. Charging of a solid surface in aqueous solution results in a redistribution of electrolyte ions and reorientation of water dipoles at the SL interface. Cryo-XPS data have demonstrated that the development of surface charge at the solid part of an SL interface can be readily followed by a corresponding change in the atomic ratio of the measured electrolyte ions 98,100,101 and, thus, calculating this ratio for fastfrozen samples allows determination of the mineral surface point of zero charge (pzc). In the case of gibbsite [Al(OH)₃] and goethite (FeOOH), the pH dependence and the changes of this ratio due to water loss indicate a ligand-exchange reaction between a surface hydroxyl group and Cl⁻ counter ion ("back hydrolysis") in the acidic region and the formation of sodium aluminate at $pH > pH_{pzc}$ for gibbsite.9



FIG. 19. Binding energy differences in the 530.0 eV oxide peak of the O 1s region when normalized to carbon at 285.0 eV. NaCl (\blacksquare), KCl (\blacklozenge), RbCl (\blacktriangle), and CsCl (\bigcirc) electrolyte ions. The dotted line suggests the general direction in which the energy difference shifts with *p*H. Reproduced with permission from Shimizu *et al.*, Surf. Sci. **606**, 1005 (2012). Copyright 2012, Elsevier.

The effect of solution conditions (pH, ionic strength, and solute identity) on ion loadings on a hematite (Fe₂O₃) surface can be readily studied.¹⁰²⁻¹⁰⁴ For example, the surface loadings of cations and chloride vary systematically with pH as shown in Fig. 18 and follow classic electrolyte ion distributions within an EDL at a charged solid surface.¹⁰⁵ Cation and chloride data cross at a "point of zero charge" at pH 9.1 \pm 0.4. However, in other cases, the measured results show behaviors not expected from traditional macroscopic models. For example, it has been shown¹⁰² that halide anions binding on nanosized hematite spheroids of ~35 nm in diameter partially deviate from an expected Hofmeister-like series with loading decreasing in the order $F^- > I^- \approx CI^- > Br^-$, while sodium loadings in the corresponding 1:1 NaX (X = anion) electrolyte followed the order of Na(F) > Na(I) > Na(Br) > Na(Cl). In a separate study, cryo-XPS data showed that micrometer-sized tabular microcrystals reacted with aqueous solutions of NaCl acquired 13-86 times more sodium and chloride (per detected Fe) than when contacted with nanosized particles.^{103,106} The atomic ratios Na/Cl/H₂O of ~1:1:2 were, moreover, strongly suggestive of the formation of hydrohalite (NaCl · 2H2O), a thermodynamically stable cryogenic phase that precipitates out of aqueous solutions of NaCl below -0.2 °C. Because hydrohalite was not formed in nanosized particles, and only on hematite particles with a strongly expressed basal (001) face, it was suggested that its stabilization could be related to the predominance of this face. Formation of a hydrohalite interface phase at the surface of hematite platelets with a well-developed basal face was also confirmed for the NaBr, NaI, and NaF electrolytes,¹⁰⁷ with the NaF cryosalt being more hydrated and coexisting with hydrated HF.

An EDL at a dielectric interface is chemically built-in without an external electrical field applied, therefore, the influence of EDL potential on photoemission can be studied as a drop in KE of photoelectrons passing throughout the entire frozen interface or by measuring the BE shift after EDL collapse due to warming of fastfrozen sample in the SAC.^{98,100,108} The pH dependence of the O 1s oxide peak of hematite in fast-frozen pastes, when referenced to 285.0 eV of the C 1s component of surface contamination, clearly illustrates this effect as seen in Fig. 19.105 Moreover, binding energies of photoelectrons emitted from electrolyte ions, NaCl, KCl, RbCl, and CsCl, increased with pH (from 2 to 11) at roughly 0.04 eV per pH unit. As these shifts are inferior to slopes in corresponding zeta potential values (0.08-0.09 V/pH), they suggest that electrolyte ions of the fast-frozen paste are concentrated between the hematite surface and share plane of the EDL/interface. The influence of the EDL potential on the binding energy of photoelectrons makes the referencing of the binding energy scale challenging. For the fast-frozen samples, carbon species are located at the surface of the sample, namely, on top of the ice, thus not experiencing the surface electric potential. Referencing the BE scale to the 530.0 eV oxide component of the hematite O 1s spectrum as an "internal" standard is proposed for cryogenic XPS studies involving this iron oxide¹⁰⁵ and has to be used for other oxide minerals.

Finally, cryo-XPS measurements of inorganic dielectric interfaces allow determination of protonation constants of acid-base active moieties adsorbed at the interface. As an example, the pK_a value (pH 5) of amine group protonation in N-(phosphonomethyl) glycine (PMG) molecule adsorbed on the surface of goethite (a-FeOOH) was found to be significantly lower than in the solution (pH 9) as measured with fast-frozen droplets of the PMG solution and pH 10 determined by potentiometric titration.¹⁰⁹ A similar effect was observed in the case of ammonium species stabilized by 2 hematite surface (hydr)oxo groups¹⁰⁴ emphasizing important differences in ammonia speciation in water and in hematite wet pastes. Moreover, N 1s spectra of fast-frozen wet hematite paste treated in 50 mM NH₄Cl at pH 6.2 after drying in the analysis $\frac{56}{20}$ chamber strongly support the formation of dehydrogenated $\frac{56}{20}$ ammonia species (NH2) and the formation of direct Fe-N interac- or tions,¹⁰⁴ which may be one of the first steps in prebiotic synthesis.

It is worth noting some practical applications of cryo-XPS in mineral processing, including flotation,^{110,111} leaching, and bioleaching^{112,113} of sulfide minerals. Probably more important is the possibility of using cryo-XPS to study chemical processes occurring in the environment. A few examples are the seasonal layers of varved lake sediments,¹¹⁴ the formation of surface polysulfides during interaction between ferric (hydr)oxides and aqueous sulfide¹¹⁵ and atmospheric ice nucleation.¹¹⁶ Monitoring the interfacial chemistry of bone graft substitute materials conditioned in α -minimum essential medium (α -MEM)¹¹⁷ and α -MEM with addition of proteins (10% fetal bovine serum)¹¹⁸ made it possible to reveal two major phenomena: the biomaterial particle's surface charge and formation of the protein interfacial layer, important for subsequent cell recognition and the initiation of biomineralization.¹¹⁹

2. Microorganism surfaces and cell walls

Any unaltered biointerface is *a priori* more complex than an abiotic one due to the inherent heterogeneity in composition, topography, morphology, and reactivity of biological surfaces. As our planet is colonized by a huge quantity of microorganisms



FIG. 20. Carbon 1s spectra for the lipid particles, analyzed by both cryo-XPS in a hydrated state and room-temperature XPS dried onto the sample holder. The observed differences between cryo-XPS and standard XPS measurements indicate the potential of cryo-XPS for providing quantitative measurements of such nanoparticle systems in hydrated conditions. Reproduced with permission from Cant *et al.*, J. Phys. Chem. A **127**, 8220 (2023). Copyright 2023, American Chemical Society.

inhabiting all ecosystems including human beings, surface chemical composition of their cell wall or cell envelope is a key factor mediating interaction of microorganisms with the surroundings. In this context, cryo-XPS is unique in enabling the study of intact fastfrozen hydrated biological samples without the need for pretreatment procedures, e.g., freeze-drying, that may cause the cell structure to collapse or change due to the loss of water. Identification and quantification of proton-active surface sites in the bacterial cell wall allowed observation of differences in acid-base properties of both freeze-dried and intact (fast-frozen) gram-positive Bacillus subtilis cells.^{120,121} In contrast to freeze-dried B. subtilis cells, cryo-XPS data made it possible to observe two interfacial phenomena that seem to be related to bacterial metabolic activity (pH dependent secreting of nitrogen-containing cell metabolites) and cell ionic channels activity (ion exchange reaction, $H^+ \leftrightarrow Na^+$), to buffer the microenvironment of bacteria with pH change.²⁶

Based on the multivariate spectral analysis of C 1s cryo-XPS spectra obtained with a set of gram-negative *Escherichia coli* strains, the biochemical analytical tool (Umeå method) was developed to obtain the content of protein/peptidoglycan, lipid, and sugar in the surface layer of intact bacterial cells.¹²² This approach allowed observation and monitoring of variations in the chemical composition of bacterial cell walls that result from mutations or external stimuli.^{122,123} Recent applications of this method include the study of the surface chemical composition of algae,¹²⁴ fungi, and viruses.¹²⁵ Detailed sample preparation and experimental protocols for cryo-XPS¹²⁶ and the first bacterial (strain *Pseudomonas fluorescens* DSM50090) reference set of cryo-XPS spectra¹²⁷ are available.

3. Nanomedicine applications

Recently, the application of cryo-XPS to organic/soft-matter nanomaterials has also been investigated, particularly those used in nanomedicines.¹²⁸ Organic nanoparticles are commonly used today in the pharmaceutical field in the development of nanomedicines, complex therapeutics, and vaccines.¹²⁹⁻¹³¹ Typically, this involves the use of a nanoparticle to encapsulate an active pharmaceutical ingredient that acts as a delivery platform. For example, several recently developed mRNA-based vaccines for COVID used encapsulation of the mRNA in lipid nanoparticles (LNPs) to prevent its degradation and allow uptake into cells.¹³² Polymeric systems are also common delivery platforms, e.g., for encapsulation of chemotherapy drugs¹³³ Commonly, the outer coating of these "nanocarriers," for both LNPs and polymeric NPs, utilizes polyethylene glycol (PEG) for its ability to prolong the lifetime of the nanoparticle in the circulatory system. In the future, more advanced systems are expected to use specific coatings to enable targeted delivery of a given therapeutic. Quantifying these coatings is, therefore, highly desirable for rapid development of effective nanomedicines and yet requires analysis under hydrated conditions. However, nanoparticles designed to be used in aqueous environments, particularly those formed of organic materials, may yield incongruous results when measured in the dry environment of high vacuum. This mismatch may range from causing apparent inconsistencies of shell thickness when measured dry as compared to the hydrated state,¹ to rearrangement or disruption of the nanoparticle structure.

In order to perform surface chemistry measurements of these nanomedicines, cryo-XPS is, therefore, of significant potential value due to the capability to measure samples in their hydrated state; cryo-TEM and other cryogenic analysis techniques are already commonly used for these systems and are observed to retain the nanoparticle structure.^{135,136} Recent analysis of both polymeric NPs and LNPs in aqueous solution using cryo-XPS has demonstrated the retention of PEG at the surface of the particle when compared to B "dry" analysis¹²⁸ (Fig. 20) and provided an estimate for the PEG surface coverage of the LNPs. Given the existing capabilities for b nanoparticle analysis with standard XPS, it may be possible to adapt of methods used for dry nanoparticle analysis toward cryogenically prepared samples to obtain even greater information about the surface chemistry of these systems. Near-ambient pressure-XPS (NAP-XPS) would also allow for measurement of nanoparticles in a partially hydrated state, however appropriate complementary structural measurements such as environmental SEM or similar would be necessary to confirm retention of the nanoparticle structure. Additionally, much of the existing metrology for XPS may be applied to cryo-XPS, whereas NAP-XPS requires additional developments in terms of, e.g., transmission calibrations. Intercomparison of these two techniques is required with regard to their application to soft-matter nanomaterials, and whether their outputs are comparable.

D. Limitations, challenges, and opportunities

Cryo-XPS can enable analysis of several important surfaces and interfaces that are not easily available in conventional XPS. As a reminder, there are challenges and limitations in the application. Reliable and reproducible sample preparation is critical and requires consistent care, checking, and validation. Also noted earlier, the inherent charge in solution formed electrical double layers shifts binding energy positions. Therefore, care is required for appropriate referencing and interpretation. It is also noted that generally surface carbon is not a good energy reference for mineral (inorganic) samples, although it is necessary and appropriate for organic materials. Also, aqueous solutions contain O and, thus, the O 1s photoelectron peak is not consistent or reliable for solid phase analysis.

Cryo-XPS analysis of microorganisms requires careful consideration of possible safety hazards associated with analyzing biological materials: personal health, servicing the instrument, sample transportation, storage and utilization, etc.

The biochemical analytical tool (Umeå method)¹²² might require further development and improvement including simultaneous PCA analysis of C 1s and N 1s spectra and extension of XPS reference database for biomolecules "building blocks"—sugars, nucleobases, amino acids, etc.

Finally, it is worth noting that cryo-XPS nicely mimics cosmochemistry/astrochemistry conditions inside the spectrometer, allowing for the study of solids with adsorbed organic molecules and ice under UHV, cryogenic temperatures, x-rays, low energy electrons, and, if simultaneously excited by tunable wavelength laser, creates the possibility to study prebiotic synthesis/the origin of life.

VII. CHEMICALLY RESOLVED ELECTRICAL MEASUREMENTS

A promising aspect of XPS is offered by the electric information available in photoelectron spectroscopy. Electrons, in general, and photoelectrons too, have an inherent sensitivity to electric fields. This property is used routinely as a means of signal collection and filtering, e.g., the "electron lens assembly" and the electron analyzer. On the other hand, electric fields that emerge *within* the sample are frequently treated as artifacts and their removal has become the subject of a large number of studies.^{137,138} The latter may be expressed via the condition for energy conservation under the event of photoemission. The measured electron kinetic energy (*Ek*) at the detector is then determined by

$$Ek = hv - E_B - W_D + eV + \cdots, \qquad (2)$$

where hv is the photon energy, E_B is the binding energy of the level the electron was emitted from, W_D is an instrumental constant accounting for the work function of the detector, e refers to the electron charge, and V is the electrostatic potential at the site of emission such that eV expresses the corresponding local electrostatic energy. Additional terms may be added when higher order effects are to be considered.

Differentiating between E_B and eV is not necessarily trivial, yet very helpful in data interpretation. E_B carries important chemical information on the identity and oxidation state of atoms, whereas the eVterm expresses the nonatomic, larger-scale, electrostatic energy. In many works,^{137,138} E_B is the term of interest, while the eV term is either ignored (note its absence from the expression of energy conservation in most textbooks) or treated in a simplistic manner as a charging artifact that should be eliminated in order to get the "pure" chemical information. However, as exemplified below, exciting information is frequently hidden in this electrostatic term and once treated properly, one can expand the XPS technique capabilities into valuable new areas. A dedicated technique that focuses on the electrostatic term in Eq. (2) was demonstrated a couple of decades ago, termed chemically resolved electrical measurements (CREM).^{20,21} It showed that the XPS spectrometer can be used as a unique voltmeter, with two important advantages: (1) it works in a noncontact mode and (2) it can read potentials from various spectral lines and thus become a kind of a multichannel voltmeter because the different XPS lines propose markers at which local potentials are measured. Thus, the surface potential unfolds into a set of potentials at corresponding (chemical) addresses.^{139–141}

More fundamentally, CREM offered a conceptual (and *semantic*) generalization by claiming that the phenomena traditionally associated with "charging" should be treated as "electrical" phenomena; electrical in its most general context, including capacitive, ohmic, pyroelectric, spontaneously built-in potentials, and any other appearance of electric phenomena.^{142–145} This generalization underlines the central message of the present chapter: We show that XPS-based electrical measurements open a whole new dimension of sample properties potentially available for future researchers, *in situ* and by the XPS spectrometer.

A variety of electrical properties and measurement modes have already been demonstrated, starting from spatial arrangements of atoms across the surface, electrically derived, ^{20,139,146} and ending in the direct derivation of sample properties, electrical and optoelectronic, in particular.^{21,147–150} Upon the development of biasmodulated measurements, alternating current (AC) modes have been enabled, proposing richer examination of samples' dielectric properties down to the sub-millisecond time scales.¹⁵¹

Electric potential profiles within materials can be established in multiple ways including,

- Potential gradients and abrupt potential steps may appear naturally at interfaces within a sample, in which case they are sometimes called "built-in" potentials. The physical origin of such built-in potentials frequently stems from impurities or the spontaneous formation of space charge near interfaces of dissimilar materials. Such cases usually involve band bending, which directly affects the band-offsets, i.e., those abrupt steps across interfaces in valence and conduction band energies.^{16,152} Such naturally occurring potentials are of central importance to the understanding of phenomena in electrochemistry, electrical engineering, and materials science.^{149,153} The use of XPS measurements in probing these effects is discussed in Sec. VII A.
- 2. To be distinguished from the former, potential variations within and across a sample can be stimulated intentionally by the researcher, such as to extract electrical characteristics, including I–V plots *per se*, as well as other types of information. Two different approaches to these measurements are briefly described in Secs. VII B and VII C. A variety of modes of CREM operation have already been demonstrated and no attempt is made to cover all of them here. It is believed that additional new and creative ways of access to the wide variety of electronic properties at near-surface regions await future researchers.
- 3. Charge accumulation on poorly conducting surfaces, not intentionally formed by the researcher, is frequently unavoidable, because the x-ray irradiation is accompanied by massive emission of electrons to the vacuum as mentioned above.^{137,138} This



"artifact" can be used in some cases to get complementary information on samples. However, being dealt with extensively in previous reviews, this type of experiment is not discussed in the present review.

In Secs. VII A–VII C, examples of three approaches to measuring and extracting information from internal potentials are described.

- A. First, experiments are discussed that examine the effects of built-in potentials at heterojunctions including band-offsets and band-bending. These experiments are of significant interest because they yield valuable information on built-in potentials that are not directly available from any other technique. While some insight into these quantities can be inferred by modeling electrical transport data, properly interpreted photoemission spectra yield detailed, quantitatively accurate band-edge profiles that facilitate enhanced understanding of transport data.
- B. Second, a versatile contactless method designed explicitly to controllably vary and examine the internal potentials is described.^{20,21} The examples provided exploit the electron flood gun (eFG) as a means of power supply and light illumination is employed at selected wavelength regimes in order to also study photovoltaic effects.¹⁴⁵

C. Section VII C also describes externally stimulated electrical measurements; however using top electrodes to get better control over the externally applied voltages and, thus enable both DC and AC measurements along sample surface regimes.

A. Built-in potentials, band offsets, and band bending

The electronic structure of a material near its surface and within the photoemission probe depth has a direct influence on core and valence electron binding energies and line shapes. Because of this sensitivity, it is possible to simultaneously extract information about, for example, built-in potentials and band discontinuities that result from heterojunction formation.^{16,152} As noted by Chambers,⁹⁶ since the 1980s, synchrotron and laboratory instruments have been used to study such built-in interfacial potential effects including band bending at semiconductor surfaces, Schottky barrier formation, and potential steps at epitaxial semiconductor heterointerfaces.

These measurements are often made with standard laboratory XPS instruments. However, the use of higher energy x-ray sources, in laboratory instruments or at synchrotron beam lines allows such interfaces to be examined at greater depths.¹⁵² It is important that the materials being examined be sufficiently conductive to prevent unwanted charge accumulation at the surface during the XPS measurement. A challenging example of charging corrected, CREM-based band-bending derivations, applied to a five-layer



FIG. 21. Sr 3d photoelectron spectra for La0.88Sr0.12FeO₃/Nb:STO heterojunctions at different film thicknesses [defined in terms of the number of unit cells (u.c.)]. The fits shown were chosen solely to reproduce the experimental spectra and identify single features (marked by arrows or stars) for band offset determination. The fitting parameters (except for amplitude) were kept constant for all thicknesses. Arrows mark peaks from the substrate. The stars mark peaks that originate in the films. Adapted with permission from Wang *et al.*, Appl. Phys. Lett. **112**(26), 261601 (2018). Copyright 2018, AIP Publishing LLC.



FIG. 22. Schematic diagram to illustrate the effect of a built-in potential on a core-level line shape. Provided the FWHM is smaller than approximately twice the built-in potential, the measured core-level spectrum (which is effectively a sum of spectra over layers within the probe depth) will be asymmetrically broadened due to the monotonic change in binding energy relative to that measured for a pure reference material without band bending. Reprinted with permission from Chambers, Surf. Sci. Rep. **79**, 100638 (2024). Copyright 2024, Elsevier.



FIG. 23. Valence band XPS for pure Nb:STO(001) and La_{0.88}Sr_{0.12}FeO₃:STO (001) heterojunctions with films of thickness equal to 3, 5, 9, and 35 u.c.. The solid lines indicate the linear part of the leading edge that can be extrapolated to the binding energy axis to determine the valence band maxima (E_v). The 35 u.c. film is the proxy for bulk LSFO because its thickness (~14 nm) exceeds the XPS probe depth such that no XPS signals from the underlying STO are detected. The monotonic increase in VBM with film thickness reveals the presence of a built-in potential. Adapted with permission from Wang *et al.*, Appl. Phys. Lett. **112**(26), 261601(2018). Copyright 2018, AIP Publishing LLC.

solar-cell structure with limited conductivity altogether, can be found in Itzhaik *et al.*¹⁴⁹

The impact of built-in potentials on photoelectron signals is not difficult to understand. It is well known that the application of an external bias to conducting samples shifts the measured energies by the amount of the applied voltage. Similar energy shifts are seen in semiconducting samples when built-in potentials, due to band bending at interfaces, are present. Internal electric fields produce depth-dependent binding energies. Consequently, as discussed in more detail below, measured core-level and VB spectra consist of sums of spatially unresolvable photoelectron peaks from multiple layers at differing potentials and the sums will have binding energies and line shapes that differ from those from the same material with no potential gradient. Examples of the useful information that can be extracted from these spectra are shown below.

Data from samples consisting of thin epitaxial films of $La_{0.88}Sr_{0.12}FeO_3$ (LSFO) on an n-SrTi_{0.99}N_{0.01}O₃(001) (Nb:STO) substrate provide examples of the impact of band bending, band offsets, and the total electrostatic potential in the vicinity of a p-n semiconductor junction. Data are shown for both XPS core line positions and valence band edges. These data are from Wang *et al.*¹⁵⁴ Because Sr is present in both LSFO and Nb:STO, Sr 3d peaks are observed from both the substrate and the overlayers. Thus, the impact of the differing total electrostatic potentials in the two materials is readily observed. Figure 21 shows the Sr 3d spectra



FIG. 24. Energy diagram showing band alignments and built-in potentials for 3, 5, and 9 u.c. p-LSFO/n-STO(001) heterojunctions based on decomposition of the La 4d spectra into layer-resolved contributions. ΔE_c is the conduction band offset, and ΔE_V is the valence band offset. Reprinted with permission from Wang *et al.*, Appl. Phys. Lett. **112**(26), 261601 (2018). Copyright 2018, AIP Publishing LLC.

for different film thicknesses of LSFO, in terms of the number of unit cells (u.c.). The substrate peaks (marked with green arrows, green online) are always observed, and a second Sr doublet 8 (marked with stars, orange online) becomes more prominent as the film gets thicker. As discussed by Chambers et al.96 and Wang 8 et al.¹ ⁴ "The Sr 3d spectra were fit with two pairs of spin-orbit $\vec{\sigma}$ doublet peaks. The most intense signals were assigned to Sr⁺² in the substrate and the smaller peaks to $\mathrm{Sr}^{\mathrm{+2}}$ in the LSFO. The binding energy differences are attributed to the band discontinuity at the interface and a built-in potential in the film." Again, the effect of the built-in potential at the interface is to shift observed core level binding energies of the overlayer relative to the substrate and is readily apparent because Sr⁺² is present in both the substrate and the film. Moreover, other photoelectron peaks in the deposited film are shifted by the potential they experience in a similar way.¹¹ Note also that the Sr doublet from the LSFO broadens and shifts as the film thickens. This occurs because of the built-in potential created by band bending across the thin film.

The influence of a built-in potential on a core-level binding energy profile in the region of a simple homojunction is shown schematically in Fig. 22. Generally, potential steps at interfaces are accompanied by band bending. Depending on the carrier density and dielectric constant of the material, built-in electric fields can act over distances ranging from a few to several hundred nm in the direction normal to the surface.¹⁶ Thus, built-in potential steps do not form abrupt jumps in potential but rather produce a potential gradient across the interface. Photoelectrons produced from atoms at different depths across the interface will exhibit shifted energies relative to one another [see Eq. (2)] when detected by the electron



FIG. 25. Schematic of a top-contact-free CREM setup. The standard eFG is used as a detached current source and the standard spectrometer as a voltmeter to read local surface potentials from a sample. The sample back-contact is used for (1) recording the sample current and (2) sample biasing, if needed. The light source allows photovoltaic processes to be examined. The two indicated spectra reveal a binding energy shift due to a change in the electrostatic term, eV. Very small shifts can be detected, far below the spectral line widths, as enabled statistically by the large number of datapoints in each spectrum.

spectrometer. As detected together, the sum over the layers will produce a broadened and shifted peak.¹⁶

Built-in electrical potential effects are observed not only by core-level broadening and shifting but can also be seen in changes to the x-ray excited valence band spectra. The dependence of the valence band maximum (VBM or Ev) on film thickness is shown in Fig. 23 for the LSFO on Nb:STO. Note that the figure contains data for films of 3, 5, and 9 u.c. thickness as well as Nb:STO with no LSFO and for a 35 u.c. layer of LSFO that is effectively bulk LSFO.

The types of data for the LSFO and Nb:STO system shown above have been used by Wang *et al.*¹⁵⁴ to map the potential profile as shown in Fig. 24. The analysis method leading to this figure has also been described by Chambers¹⁶ and Chambers *et al.*,⁹⁶ and it provides a way to measure both built-in potentials and band bending. The method is more accurate than the traditional Kraut method,¹⁶ which does not consider band bending effects. Although such band-edge profiles can be measured in some systems using conventional XPS, the higher energy x-rays now available in laboratory systems as well as at synchrotrons (HAXPES), create opportunities to extract potential profiles from more deeply buried interfaces.¹⁵²

B. Top-contact-free CREM modes

As already mentioned, CREM exploits the spectrometer as a voltmeter. Added to that, and of particular interest, are those CREM modes that produce current-voltage (I–V) characteristics by using the standard neutralizer of the system (the eFG) as a *noncontact power supply.* The eFG is designed to controllably send a flux of slow electrons to the surface of the sample. Complementarily, the current on the sample back-contact can be recorded. Thus, I–V curves are produced *in situ*, along with the XPS-based chemical information. Figure 25 presents schematically the instrumental configuration, including the electron analyzer, the eFG, the back contact functions (bias voltage and pico-ammeter) and, also, light sources to be described below. Having the combined electrical and chemical information within the same apparatus suggests an important extension of the XPS spectrometer capabilities.

Moreover, in addition to the powerful combination of electrical + chemical probing capabilities, the use of an eFG as a power supply introduces unusual features, valuable with respect to any of the standard electrical tools. These features emerge from the fact that the current supplied to the sample is a current of *hot*-electrons, namely, electrons at energies significantly above the Fermi level.

Two examples are described hereafter. The first one presents an experiment demonstrating part of the unique information that can be harvested by this CREM mode.¹⁵⁵ The second example, with potential links to photocatalysis, exploits another CREM mode of interest: Light illumination during the XPS scans, frequently used to controllably excite pairs of hot-electrons and holes.¹⁵⁶ Here, it demonstrates atomic-scale electron transfer between two neighboring atoms. Common to both examples, the sample surface remains fully open. Namely, both the "signal-in" means and the readout of surface potentials are all obtained in a noncontact manner. The only contact to the sample is at its back side, where bias supply and sample current measurements are applied.

1. Example 1: Elemental I-V curves in SiO_2 and SiON layers

A straightforward demonstration of CREM benefits is given of by layered heterostructures, in which differences in the chemical composition enable measurements of local, layer specific, potentials. The example shown in Fig. 26 describes a study of thin Si-oxide layers, prepared at material quality and thicknesses commonly used in microelectronics.¹⁵⁵ In an attempt to shrink device dimensions and yet improve the dielectric quality of such layers, processes for adding nitrogen to the SiO₂ films have become popular. Commonly, the SiON layers give rise to improved gateoxide integrity with, importantly, only minor influence on the I-V characteristics of the layer. The capability of CREM to reproduce these characteristics was, therefore, an interesting test case for the technique. Moreover, noting that all standard electrical tools are basically limited to probe the integral volume between electrodes, here the added value of CREM capabilities in resolving layerspecific characteristics could be tested.

Demonstration of the latter capability is given by Fig. 26(a). It presents elemental I-V curves for a 3.6 nm SiON layer on a Si substrate,¹⁵⁵ as derived from a set of measurements taken with controlled eFG settings, upon step-wise variations of the eFG bias voltage. Local potentials were then extracted by simply evaluating the four-elemental line shifts (Si^W, O, Si^{ox}, N), each referring to its initial peak position as recorded under eFG-off and low x-ray source power. The electric current, *I*, is detected in these measurements on



FIG. 26. Elemental I–V CREM curves, comparing thin SiON and SiO₂ layers on Si wafers: (a) a 3.6 nm SiON layer, where Si^W is the substrate curve and Si^{ox}, O and N are the oxide curves as derived from corresponding core-level XPS lines. (b) The same as in (a) but for a 3.7 nm SiO₂ layer. (c) Net curves, O minus Si^W, for the samples in (a) and (b), manifesting pronounced differences between the samples. (d) CREM Ir-curves recorded from the same SiON and SiO₂ layers, however, after depositing an Ir top contact, 20 nm thick, on each. The inset shows schematically a sample with its top pad. Note the effective disappearance of differences between the two samples when CREM is measured on the top pad. Adapted with permission from Rosenblat *et al.*, Appl. Phys Lett. **94**, 213501 (2009). Copyright 2009, AIP Publishing LLC.

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the sample's back contact and, therefore, is the same for all signals recorded under each specific eFG setting (in practice, slight variations may be observed due to the effects of the Kratos magnetic lens). Technically, if significant positive charging is encountered initially, more elaborate procedures may be needed to determine the zero-voltage point. Yet, *relative* changes by themselves are usually informative and very useful. Line-shape changes were not treated here: detailed evaluation of such effects can be found in the bandbending Sec. VII A and in the earlier literature.^{20,147}

As seen in Fig. 26, the inspected elemental peaks exhibit considerable local potential differences, reflecting the development of eFG-stimulated electric fields across the studied structure. The related line shifts reveal details of the *vertical potential profile*, thus allowing, even for this very simple system, an access to valuable information. To begin with, the wafer I-V curve (Si^W) governs all back contact impedance plus any wafer band bending contributions. All oxide potentials necessarily float on that of the substrate, because the top surface is open while the back contact is grounded. Hence, by subtracting the Si^W shifts (and recalling the absence of any top electrode), "contact free" characteristics of the oxide layer can be extracted. Next, one notes that both O and Si^{ox} curves are practically the same in Fig. 26(a). On the other hand, the N-curve Another interesting observation in Fig. 26 regards the comparison between CREM of Si-oxide layers with and without the nitrogen content. Figures 26(a) and 26(b) show I-V curves under identical eFG conditions, recorded, respectively, from SiON and SiO₂ layers of nearly identical thicknesses. Net O-curves (after subtraction of corresponding wafer potentials from each O-data point) are shown in Fig. 26(c), demonstrating a marked difference between the two samples: The SiON layer develops much higher potentials than the SiO₂ layer (note that the actual difference would become even more pronounced if the N-curve of SiON is used instead of the O-curve). As a reference, standard contact measurements were performed (not shown here), as well as CREM on the same layers but with a 20 nm thick Ir layer on top of each

probes considerably larger potentials, which indicates that the N-distribution within this layer is spatially very different from that of O and oxidized Si. In fact, Fig. 26(a) reflects a major enrichment of nitrogen at the top of the layer (additional experiments showed a secondary N-enrichment at the inner interface, between the oxide and the wafer). This analytical feature upon which structural information is extracted, mostly used for depth compositional profiles, has been already demonstrated with a variety of systems and specimen geometries.^{20,139,147,157,158}





FIG. 27. Photovoltaic CREM of Mo₁₃₂-POMs with 10 equivalents of Mn ions: (a) schematics of the POM structure. (b) The "radial" structure of the POM skeleton, indicating the electron transfer revealed under white light illumination. (c) Raw Mn 2p spectra recorded at dark (bottom) and under white-LED illumination (top). (d) The same as in panel (c) but for the Mo 3d doublet. (e) A summary of the light-induced line-shape changes, expressed as intensity ratios between the two relevant oxidation states in Mo and in Mn. The experiment was performed under fixed low x-ray power, 15 W, with illumination conditions as follows: dark, white LED, dark, white LED, dark, red LED, dark. As indicated by the time scale, early steps were faster, in order to better account for beam-induced artifacts. Adapted from Haviv *et al.*, J. Am. Chem. Soc. **124**, 14504 (2020). Copyright 2020, Author(s), licensed under a Creative Commons Attribution (CC BY) license.



insulating layer [see Fig. 26(d)]. Figure 26(d) exhibits only negligible differences between the samples, in full agreement with reference contact measurements.

Where does this CREM sensitivity, Fig. 26(c), come from? Can CREM sense dielectric quality differences that are hidden from (or hardly measurable by) any of the standard electrical tools? Briefly, the answer is positive. This unique sensitivity has already been demonstrated for a number of systems and is associated with the physical means of charge injection.^{155,159} The eFG electrons are hot electrons. They arrive at the surface at energies above the vacuum level and, therefore, are accessible to all trap states in the broad bandgap of the oxide. This situation is fundamentally different from any "Fermi-energy injection" of charges by contact electrodes. The reader may also note the pronounced hysteresis in Fig. 26(c), which is practically eliminated by the top pads, Fig. 26(d). The hysteresis, by itself, proposes a valuable piece of information, to be discussed elsewhere (Hagai Cohen, in preparation). Thus, this example demonstrates: (1) enhanced sensitivity to hidden dielectric quality issues, a feature with clear applicative consequences, still under continued study and (2) unique CREM capabilities in resolving details of the potential profile, a capability gaining increased importance when multilayer stacks are to be inspected.

2. Example 2: Atomic-scale photo-induced charge transfer

A challenge encountered in a system of nanocages is exemplified in Fig. 27. The related research project exploits polyoxometalate (POM) nanocapsules [see Fig. 27(a)]^{160,161} as a host for transition-metal guests in organic media. Here, the inorganic framework is a complex Mo-oxide icosahedral structure, with 132 Mo atoms, stabilized by outer counter cations and inner oxalate ligands, see Figs. 27(a) and 27(b).¹⁵⁶ Mn(II) ions were chosen as guests due to their potential roles in catalytic reactions. Solution of Mn(II) salt was slowly injected into a preprepared solution of the POM, where spontaneous encapsulation of the Mn-guests was expected through pores in the POM framework, followed by binding to phosphate inner ligands.

Standard XPS data confirm that 72 Mo atoms in these cages are in a 6+ oxidation state and 60 are in the 5+ state. However, the success of guest encapsulation was not a trivial question, because it was unknown whether the Mn cations, initially Mn²⁺, would undergo a change in their oxidation state upon encapsulation within the POM. Second, it was not clear if and to what extent the POM framework itself would take part in binding the Mn cations. An answer to these questions was achieved by using a specific CREM mode, in which optical excitation is employed, other than pure electron injection as realized with the eFG in the previous example. Advantages of this mode have already demonstrated in various studies.^{141,145,149} Here, we mostly used our triple-LED source such as to match, or intentionally exclude, the ~450 nm absorption peak of the POM (with a tail down to 630 nm).¹⁵⁶

The presence of Mn ions, at both Mn^{2+} and Mn^{3+} states, was confirmed by standard XPS measurements, however, with no direct evidence for successful encapsulation into the POM cages [see expected Mn-ion position in Fig. 27(b)]. On the other hand, as demonstrated in Fig. 27(c), under the white-LED illumination, slight changes in the Mn line shape were observed.¹⁵⁶ These changes were reversed upon switching the light source off and could be regained by repeated illumination cycles, see Fig. 27(e). Complementarily, line-shape changes in the Mo 3d doublet, Fig. 27(d), were also seen, anticorrelated to the Mn ones. Clearly, a much better signal-to-noise ratio was available with the Mo data. However, in this case, an additional, irreversible, process was encountered, on top of which the reversible modulation was superimposed. The Mo curve in Fig. 27(e) shows both (1) an *irreversible* increase in the Mo⁵⁺ component and (2) smaller yet reversible modulations that retain anticorrelation with the Mn-modulations (see original report¹⁵⁶ for the explanation of slow, irreversible Mo-reduction). Finally, vanishing amplitudes of the anticorrelated Mn–Mo modulations were measured when red light (630 nm, same configuration, and same power) was used [two final steps in Fig. 27(e)].

As a technical note, the reader is referred to the considerable challenge of quantitatively evaluating small changes in the noisy Mn 2p spectra. First, low x-ray source power was used to improve the light-induced versus x-ray-induced e-h (electron-hole) excitations. Also, the scanning dwell time could not be pushed too high because of irreversible effects that limited the total length of each experiment. Therefore, signal-to-noise improvements were unfortunately limited. Second, a full curve-fitting procedure would require many parameters due to the inherent asymmetry in the Mn 2p line shape, for which the shake-up features (in the capsule environment) were practically unpredictable. Therefore, a detailed curvefitting was first performed for one of the initial scans and, then, it was used as a zero-order solution for each of the following spectra, allowing mainly (but not strictly) intensity changes in the main peaks of Mn^{2+} and Mn^{3+} [see arrows in Fig. 27(c)]. Figure 27(e) \aleph depicts the estimated experimental error in this entire procedure.

The above photo-induced results capture an in-capsule process $\overset{\circ}{\otimes}$ of electron transfer (ET) from Mn²⁺ to Mo⁶⁺ (and vice versa, from of Mo^{5+} to Mn^{3+} , upon switching the light off). Remarkably, it is a fine and selective atomic-scale process, revealed by a macroscopic probe, thanks to the use of atomic addresses. As a reference, the process is not activated under red light, suggesting that POM bandgap excitation is essential. Needless to say, the occurrence of such ET processes proves (in full agreement with independent NMR and EPR-based measurements¹⁵⁶) the success of Mn-ion encapsulation into POM cavities. Moreover, no line-shape changes were detected at the P signals, nor at the O signals, which indicates that the two metal atoms, Mn and Mo, drive this atomic-scale electron transfer via tunneling across the entire intermediate phosphate group, see Fig. 27(b). Consequently, besides answering a challenging analytical question, CREM reveals here an interesting photocatalytic potential and further suggests that CREM can serve as a probe of such catalysis.

A couple of experimental complications should be noted in this respect. First, the Si substrate, on which those POMs were spincoated, is optically active by itself. As a p-type semiconductor, under bandgap light illumination it tends to enrich the surface with electrons. The slow irreversible reduction of Mo, see Fig. 27(e), is found to originate from this substrate photoactivity. Second, the XPS x-ray irradiation by itself excites electrons and, therefore, prevents from "perfect dark" conditions. Using low x-ray source power is a partial answer to the problem, which in turn, imposes







FIG. 28. Two-electrode cell configurations. (a) A few layers graphene resistive sheet between electrodes. (b) An electrochemical cell having an ionic liquid as the electrolyte. (c) XP spectra and the chemical structure of the IL used in this work.

limitations on signal-to-noise ratios. Moreover, these experiments deal with fine spectral details. As such, the sensitivity to beam-induced irreversible effects, including damage per se, becomes of increased role. Therefore, dedicated case-specific experimental protocols should frequently be designed in similar experiments.

Overall, this example presents a successful application of the CREM approach as a probe of photovoltages under light illumination. Specifically, the system allowed the remarkable derivation of *atomic-scale* information, a consequence of the fact that individual atoms are the ones serving as addresses from which the local potential is read. Similar experiments with self-assembled molecular layers have also revealed valuable atomic-scale characteristics, taking advantage of the superior control over inner structure enabled when presynthesized molecules are used as the building blocks of a larger structure.^{140,150}

3. Noncontact-CREM summary

A diverse variety of added values has already been demonstrated by the top-contact-free CREM; tested for various modes and applied to a broad range of systems. First, CREM can frequently assist the "pure" XPS chemical analysis, e.g., by providing complementary information on the location of atoms, their oxidation state, and, obviously, by allowing improved elimination of charging artifacts. Second, within the same instrument and under the very same experimental configuration, CREM opens capabilities for harvesting electric information from a sample, in addition to compositional and chemical state information. Third, there are cases where CREM reveals features that are hidden from standard electric probes, sometimes at a resolution that is particularly challenging for any electrode-based probe, as demonstrated above for inner layer characteristics and atomic-scale photo-activity.

C. Recording XPS under DC and/or AC biasing–A simple to implement, yet a very powerful variant of XPS measurements

XPS measurements under voltage bias have been practiced since the early days of the introduction of the technique, and the majority of its usage has concentrated on mitigating the charging effects and/or the useful differentiation of inhomogeneous surface structures.^{20,139,151,162–171} Another very useful, but under-utilized, form of XPS biasing experiments involves electrical contacts and applied voltages (AC or DC) to control the electrical potentials across test systems.

To realize this application, it is necessary to employ an electrical potential difference between two sides of an otherwise all grounded sample, which in effect turns the sample into an electrical/electrochemical cell-like structure, where the biased electrode acts as the (current) source and the other grounded one as the drain. The simplest device in macro dimensions (1-10 mm) consists of two conductive electrodes having a resistive medium (ca. 2 mm) in between, as schematically shown in Fig. 28(a), which is fixed on top of an insulating substrate (typically, a~1 mm thick glass microscope slide) and copper wires are attached for electrical connections. In this example, the medium between the two gold electrodes is a few-layer graphene sheet, having more or less a uniform (and/or nonuniform as shown later) chemical and electrical composition across. A DC power supply with an adequate current capability (>100 mA) is sufficient to impose and maintain a stable electrical potential difference across the resistive medium during XPS measurements. We used a Keithley Model 2400 source meter as our power supply for DC measurements.

The second geometry, illustrated in Fig. 28(b), is a **coplanar capacitor**, fabricated by depositing two equivalent Au electrodes onto a porous polyethylene membrane (PEM), separated by a distance of ~6 mm, and having an ionic liquid (IL) film of ~100 micrometer thickness in between and over the metal electrodes.



FIG. 29. XP spectra on the two-electrode (source–drain) device. (a) Schematics of the device. (b) Au 4f spin–orbit doublet of the gold source electrode, recorded without and under +6 V DC bias. (c) Au 4f and C 1s line spectra recorded under +6 V bias along the center of the device. Each frame depicts 60 individual spectra at different positions, which are separated by $50 \mu m$ steps and with an x-ray beam spot, having a diameter of $50 \mu m$. (d) Areal map of the extracted C 1s binding energies of a 1.8 × 3.0 mm rectangular area, spanned with the $50 \mu m$ steps and with a $50 \mu m$ x-ray beam spot size. Adapted with permission from Kocabas and Suzer, Anal. Chem. **85**, 4172 (2013). Copyright 2013, American Chemical Society.

ILs are composed entirely of large anions and cations, having strong attractive electrostatic and van der Waals interactions. As a result, they cannot crystallize at room temperature, which is also called room-temperature-molten-salt. Due to the strong attraction between the ions, they have very low vapor pressures, in addition to having reasonable electrical conductivities. These properties render them to be very suitable for XPS investigations.

This device also acts as an electrochemical cell, where the electrolyte is the IL (DEME-TFSI) film, as depicted in Fig. 28(b). In Fig. 28(c), we show the XP spectra recorded when both electrodes are grounded. The chemical formula of the IL is given as an inset. The ionic liquid, diethylmethyl(2-methoxyethyl)ammonium bis(tri-fluoromethylsulfonyl)imide was purchased from Io-Ii-Tec (Ionic Liquids Technologies) and used after degassing overnight in the vacuum chamber of the spectrometer.

Five examples are shown demonstrating DC and then AC biasing of a purely resistive sample and others, where the presence of the IL electrolyte enables capturing double layer formation at the interface.





FIG. 30. C 1s XP spectra on the two-electrode (source-drain) device, recorded under +6 V DC bias, before (a) and (b), and after the exposure to a mild oxygen RF plasma etching (c) and (d). The (a) and (c) frames depict 60 individual C 1s line spectra recorded along the center of the device, at different positions, which are separated by 50 μ m steps and with an x-ray beam spot size of 50 μ m. However, areal maps shown in (b) and (d) are the extracted binding energy positions of the spectra of a 1.8 × 3.0 mm rectangular area, spanned with the 100 μ m steps and 100 μ m spot sizes. All together 18 × 30 = 540 spectra were gathered and analyzed. Adapted with permission from Aydogan *et al.*, J. Vac. Sci. Technol. A **34**, 041516 (2016). Copyright 2016, American Vacuum Society (AVS).

1. DC biasing examples

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a. Example 1: Few layers graphene—Pristine and damaged. XPS analysis is based on measuring the kinetic energy of the emitted photoelectrons with respect to the Fermi energy of the spectrometer, hence any local electrical potential, created intentionally or otherwise, influences the extracted binding energy of all related core-level peaks. Accordingly, on the grounded electrode, the measured binding energy of the Au $4f_{7/2}$ spin–orbit component is 84.0 eV everywhere on the electrode, ¹⁷² even under +6 V bias. However, the corresponding peak has 90.0 eV binding energy on the source electrode, as depicted in Fig. 29(b), indicating a faithful and trivial 1 eV:1 V bias shift.¹⁷²

If the medium is physically and chemically uniform (i.e., crack and defect-free), the bias results in a continuous potential drop (IR drop) between the two electrodes, which can be probed noninvasively via the position-dependent binding energy shifts of the representative atomic core levels (i.e., C 1s). Using the line scan mode, the C 1s region is recorded at every step, along the line in the middle of the device, starting from the source electrode toward the drain, with an x-ray beam size of $50 \,\mu$ m and with $50 \,\mu$ m steps as shown in Fig. 29(c). The C 1s peak has 285.0 eV BE at the drain electrode, and it is gradually and linearly shifted to 291.0 eV at the source side, revealing the uniformity of the graphene sheet. The corresponding 2D shifts, extracted from a 1.8×3.2 mm rectangular areal scan of the C 1s peak with again 50 μ m step and spot sizes, are shown as a twodimensional graph in Fig. 29(d), where the z-axis corresponds to the measured C 1s BE shifts, x and y are the physical dimensions of the rectangular area. The uniformity of the graphene, in terms of the electrical potential variations, within our experimental uncertainty in measuring the binding energies (±0.05 eV), over a relatively large area, is quite remarkable.

If the uniformity is disrupted during the production of the graphene sheet and/or in the cell fabrication steps, the sample can also be tested using the same analysis strategy. For creating defects on the graphene sheet on purpose, we exposed the two-electrode device to a mild oxygen plasma etching process (5 W RF Power) for 2 s. The overall resistance of the sample was ~300 Ω before and increased to ~4000 Ω after the oxidation process.¹⁷³ This process introduced various physical and chemical defects, which had manifested and captured locally by XPS analyses, both in line and areal scans as shown in Figs. 30(c) and 30(d), respectively, since the voltage bias amplifies the presence of physical and chemical non-uniformities. This mild oxidation process also introduces chemical

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FIG. 31. Line scan F 1s XP spectra of the device, having an IL film in between the metal electrodes, recorded under +3, 0, and -3 V DC bias are shown in (a), (b), and (c), respectively. Each frame depicts 100 individual F 1s spectra, recorded along the line in the center of the device, at different positions, which are separated by 100 μ m steps and with an x-ray beam spot of 100 μ m. The two DC bias correspond to the long time-limits (t = infinite), where the applied voltages on the metal electrodes are effectively screened by the oppositely charged mobile ions through the formation of two equivalent EDLs, hence only half of the applied potential is measured on F 1s peak positions, as represented by the schematic sketched in (d). Adapted with permission from Camci *et al.*, Phys. Chem. Chem. Phys. **18**(41), 28434 (2016). Copyright 2016, Royal Society of Chemistry.

deformations, such as sp^3 carbons, the presence of which were additionally supported by Raman spectroscopy, through the appearance of *D* and *D'* bands, and the decrease in the 2D/G peaks intensity ratio.^{174,175}

b. Example 2: Ionic liquid electrolyte. This DC example and the following three AC examples involve the use of ionic liquids. As noted below they are stable in vacuum and facilitate study, in a conventional XPS system, of phenomena that occur in liquids such as substrate dissolution/nanoparticle formation, static and dynamic properties of electrical double layers, interface behaviors relevant to batteries, fuel cells, supercapacitors, and some types of catalysis. They also create opportunities to examine fundamental electrochemical interface processes at the level not generally possible.

The DC conductivities of the ionic liquids are usually comparatively lower than graphene layers since the current is transported by the relatively slower ionic conduction across the device. Nevertheless, similar XPS analyses can also be carried out on the second device, without the need for any charge compensation procedure, like using a flood gun. The only difference is that the amplitude of the bias must be limited (typically, below 3.5 V), to prevent decomposition of the IL through oxidative and/or reductive processes. The core-level F 1s spectrum, which is the most intense XPS peak is given in Figs. 31(a)-31(c), recorded as the line-scans and under +3, 0, and -3 V DC bias, respectively. The results, however, are very different, and more or less uniform voltage drops are measured across the entire 6 mm IL medium in between the Au metal electrodes, as well as on top of them.

The measured constant BE shift of the F 1s peak throughout the device is approximately +1.5 and -1.5 under +3 and -3 V, respectively, i.e., only half of the applied bias. This is interpreted as stemming from the two equal, but oppositely charged EDL





FIG. 32. Responses of the graphene (resistive) and ionic liquid (capacitive) media under 3 V SQW modulation at 10 mHz frequency. (a) Schematics of recording XP spectra under positive and negative 2.5 V DC bias, as well as under 2.5 SQW AC bias having a very low frequency of 10 mHz. Time-resolved C 1s and F 1s XP spectra under 2.5 V SQW-10 mHz pulses, recorded at three designated positions of the graphene only device and with the IL are shown in (b) and (c), respectively.



FIG. 33. XP spectra recorded under +3, 0, and -3 V DC bias of the region at the end of the electrocorroded Au electrode and extending into the membrane soaked with the ionic liquid. On the left-hand side, Au 4f peaks are displayed under +3, 0, and -3 V bias, respectively. The right-hand side displays the corresponding F 1s spectra. The bias causes the F 1s peaks to shift only about 1.5 eV (half of the bias) up and down. However, it causes the Au 4f peaks to split and shift to full bias of 3.0 eV on the metal electrode, but only 1.5 eV for the tailing secondary gold moieties, tightly correlated with those of the F 1s peaks of the ionic liquid. The strong featureless signal appearing in some of the F 1s spectra stems from the underneath metal electrode and ends at the membrane interface. Adapted from Camci *et al.*, ACS Omega **2**(2), 478 (2017). Copyright 2017, American Chemical Society.

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formations at the two metal electrode–IL interfaces, causing a total of $(2 \times 0.75=) \sim 1.5$ eV potential drops. A schematic diagram for the time-dependent voltage profiles across the device, including the electrodes is depicted in Fig. 31(d). Hence, although the EDLs, themselves, cannot be probed directly, since they are too small (a few nanometers) compared to our probe size $(100 \,\mu\text{m})$, their presence is captured, unequivocally, throughout macrodimensions (6 mm).

2. AC-square-wave-biasing examples

a. Example 1: Square wave biasing (SQW) comparison of graphene (purely resistive) and graphene with an ionic liquid (double layer formation). Time-dependent measurements can also be accomplished using AC-modulated biasing for the very same devices. The use of square waves rather than sine waves are preferable since they impose minimal deformation on the XPS peak shapes, as was recently discussed in detail.¹⁷⁶ To implement the SQW wave biasing a signal generator is needed, which was the SRS Model DS340 in our case. However, no new information can be garnered when simple resistive devices are analyzed, as exemplified in Fig. 32(a) for the graphene based 2-electrode geometry

illustrated in Fig. 28(a). Under SQW AC modulation, every peak is twinned, and the measured binding energy difference in the peak positions of the twinned peaks is extracted. Such a procedure does not produce any new information for the resistive graphene sheet as shown by the C1 s spectra in Figs. 32(a) and 32(b), except for resurfacing the variations of the local electrical potentials in the form of IR drops, which is static with no observable timedependent features.

A widely contrasting behavior is captured in the case of the ionic liquid based electrochemical cell, with very strong time- and position-dependency as shown in the XP spectra of the F1 s in Fig. 32(c) at three different locations.¹⁷⁷ At the point near the source electrode, when +5 V cycle of the 10 mHz SQW pulse starts, the F 1s peak is instantly shifted from its 688.5 eV grounded position to ~693.5 eV, and slowly returns to its equilibrium position of 691.0 eV (i.e., 2.5 eV above its grounded position) under positive polarization, due to screening of the electrode potential by the anions, which are slow. After 50 s, -5 V cycle sets in, which also instantly shifts the F1 s peak to ~683.5 eV, and slowly decays to 686.0 eV, which is the equilibrium position under negative



FIG. 34. Time-resolved XP spectra recorded under 3 V and 10 mHz SQW pulses. Au 4f spectra recorded at a point (point 1) on the electrified electrode shows up and down 3 eV shifts for both positive and negative going pulses, with no apparent time dependency. No corresponding Au 4f shifts are observable on the grounded electrode (point 4). The situation is very different for the same Au 4f peaks at points away from the electrodes (points 2 and 3), which are tightly correlated with the F 1s peaks of the ionic liquid, which display varying time-dependent behaviors at all four points. Adapted from Camci *et al.*, ACS Omega **2**(2), 478 (2017). Copyright 2017, American Chemical Society.



polarization. Moving away from the source toward the middle of the device, the time dependency dies away as is seen in the corresponding F 1s spectra in the middle. Near the ground electrode, the time dependency materializes again as seen in the spectra displayed at the bottom, where the time-dependence is reversed. Accordingly, the F 1s peak starts from the negative equilibrium position of 686.0 eV and shifts toward, 691.0 eV under +5 V cycle in 50 s, and starts from the positive equilibrium position of 691.0 and shifts toward 686.0 eV under the -5 V cycle. Note that when the source electrode is positively polarized, the drain electrode becomes negatively polarized and vice versa.

This time- and position-dependent data reveals the formation of two similar, but oppositely polarized, EDLs at both electrodes, as was mentioned above, and the voltage drops at the metal electrode–IL medium interfaces, are a direct experimental demonstration of the theoretical predictions of von Herman Helmholtz, dating back to 1873.¹⁷⁸ Furthermore, the laterally resolved information, retrieved from the chemically addressed XPS F 1s signals, also brings a new and equally important finding, where it is shown that the device is partitioned into a cathodically and anodically polarized regions and they meet at a neutral point in the middle. This finding is related to the fact that the effects of the electrode potential screening by the mobile ionic components are translated to an unexpectedly long lateral range of millimeters, reminiscent of soliton waves.^{27,179}

b. Example 2: Using square wave biasing to identify the nature of Au nanoparticles formed due to biasing. Another application of the methodology is related to the identification of the medium of the Au-NPs formed due to the dissolution of electrodes via an electrochemical process. Herein, we tried to answer an important question; "Are the NPs within the ionic liquid electrolyte or adsorbed on the electrode surfaces?." This problem was encountered during the prolonged application of +3 V bias, which led to the formation of Au-NPs in the vicinity of the polarized electrodes.¹⁸⁰ To elucidate the chemical nature of the new Au species formed, we zoomed near the interface and recorded line scan Au 4f spectra with $50 \,\mu$ m step sizes for a distance of ~1 mm while imposing +3, 0, and -3 V DC bias, as depicted in Fig. 33.

The secondary Au species appeared as a tail of the electrodes, and their measured binding energies were not different from those of the metallic Au 4f ones, when the device was grounded. However, they get completely separated under both positive and negative biases, which can also be correlated with the peak positions to the F 1s peak



FIG. 35. F 1s XP spectra recorded as line-scans at two different frequencies. Schematics of the data gathering under 2.5 V SQW at 10 kHz and 0.1 Hz are given in (a) and (b), respectively, and (c) shows the device. We display 120 F 1s line-scan spectra, recorded under (d) 10 kHz and (e) 0.1 Hz. Note that the XPS data-gathering time window is only 5 μ s under 10 kHz, and the corresponding data are averaged over 40 000 cycles, i.e., 4 s in every step. Under 0.1 Hz, the time window is 5 s and only 16 cycles are averaged. Reproduced with permission from Başaran *et al.*, Faraday Discuss. **236**, 86–102 (2022). Copyright 2022, Royal Society of Chemistry.

of the IL, which are also shown in the same figure. Therefore, using the correlated shifts of the F 1s and Au 4f peaks under simple DC and AC biasing, it was determined, beyond any doubt, that the secondary gold nanoparticles are within the IL medium, i.e., in electrical contact with the liquid and not with the metal electrode. This is also depicted as a schematic in the same figures.

Recording the very same Au 4f and F 1s peaks at different locations of the device under AC biasing as shown in Fig. 34, reinforces our conclusion.¹⁸⁰ At the electrodes, points 1 and 4, the Au 4f signals do not shift potential as a function of time, while the F 1s signal from the IL does change as observed in earlier work. However, near but away from the electrodes, the Au 4f signal changes in a manner consistent with the F 1s confirming that the Au nanoparticles are in the solution.

c. Example 3: Variation of local potentials as a function of square wave frequency. The last example of AC biasing utilizes capturing the local potential variations within the time window of the XPS measurements, akin to oscilloscope measurements.¹⁸¹ This is described in Fig. 35, under a very fast (10 kHz) and a very slow (0.1 Hz) SQW modulations. When 10 kHz modulation is imposed, the sample is exposed to the positive and negative 2.5 V bias for only a duration of $50 \mu s$, which is very short for ions to move, therefore, they are practically frozen. As a result, we only observe the F 1s peak twinned with a separation of $(2 \times 2.5=)$ 5 eV, all throughout the electrified electrode, and no twinning is observable on the entire drain electrode. In the middle due to the IR drop, the twinned peaks get less and less separated and a V-shaped appearance develops. Since 5 s are allowed for the bias in the positive and negative cycles under 0.1 Hz, the ions move in opposite directions, and screen the applied potential by forming the two electrical double layers. This manifests as a decrease in the measured binding energy difference of the twinned peaks on the electrified side, resulting in (5.0-0.8=) 4.2 eV at the very top, and an increase from the 0 eV difference of the twinned peaks on the grounded electrode (anodic and cathodic polarization).

The majority of electrochemical measurements are carried out by measuring the system's current (amperometric) under various stimuli. Our methodology, however, allows measuring another important and additional parameter of the system, the local electrical potential variations, hence provides complementing information of paramount interest. Moreover, the methodology is very simple to implement, and should be vital in developments of the next generation energy harvesting and storage technologies, like batteries, fuel cells, and supercapacitor.

3. Opportunities regarding DC and AC biasing

We conclude by reiterating our introduction sentence that, there is still plenty of room for utilizing the old XPS technique, with relatively simple new tricks. A further example is that even a simple addition of an external circuit element, like a resistor to the two-electrode device having the IL as the electrolyte, it was possible to induce much unexpected ion-movement reversals within the ionic liquid medium on top of the electrodes, as demonstrated in our most recent publications.^{182,176}

VIII. SUMMARY AND OPPORTUNITIES

In a 1984 paper, Duke¹⁸³ described the impact of the then new techniques of Auger electron spectroscopy, XPS, and other surface sensitive analysis methods as enabling a modern scientific revolution. "The ... explosive development of surface characterization spectroscopies [...] led to a fundamental alteration in our perception of a surface or interface. Whereas in the mid-1960s an interface was regarded merely as the boundary between two bulk media, today it is seen as an independent entity: a state of matter determined by its history and exhibiting its own unique composition, structure, and electronic properties." Forty years after Duke's statement, the characterization and understanding of the properties of surfaces and interfaces are highly important in an increasing number of areas including the development of advanced electronic and energy materials, improving chemical processes through advanced catalysts, understanding of environmental and biological processes, and increasingly in medical and health related areas.¹¹ Consequently, the use of surface sensitive tools is of high importance, and literature citations of XPS have been growing at an exponential rate.¹

In this paper, we have highlighted aspects of underused structure and property information available about surfaces and interfaces using XPS, information that may be otherwise unavailable. As noted earlier in the quote from Martin Seah, XPS is a very data rich method,⁷ and it is doubtful that the limits of information available enabled by instrument advances and/or data analysis have been reached. It remains an opportunity rich method. As demonstrated from summaries of applications and types of data shown in this paper, XPS can provide a much wider variety of information about the near-surface region of a sample than the standard composition analysis conducted most frequently. This region is critically important for many technological applications and one for which detailed information of many types can be otherwise very difficult or impossible to obtain. Consequently, there are many opportunities to expand the uses of XPS to extract information critical to several types of research and technology development.

The information available, as highlighted in this paper, includes optical, electronic, and electrical properties, as well as additional information about nanostructure, layering, expanded chemical and phase information, and enhanced ability to explore solid/liquid interfaces and biological systems. Most of the underused aspects of XPS presented are relatively easy to apply, and many require little or no equipment alteration or expansion. They may require a degree of experimental or analysis planning beyond that practiced by some analysts, but the references provide the information needed to implement the methods.

In addition to XPS, many of the surface tools that contribute to the modern scientific revolution described by Duke are being continually developed and creatively applied to extract properties of the surfaces and interfaces beyond composition. Increasingly vendors are adding complementary measurements as components to XPS systems. In 2024, a Physical Electronics webinar titled *Beyond Chemical Composition: How Surface Science Can Measure Electronic Properties* discussed XPS in combination with other methods including reflection electron energy loss spectroscopy and low energy inverse photoemission spectroscopy.¹⁸⁵ Secondary ion



mass spectrometry has been adapted and applied in a variety of areas including real time measurements of electrochemical double layers and solid-electrolyte-layers in batteries.¹⁸ ³⁶ An increasing number of variants of scanning probe microscopy have been developed to extract a wide variety of physical, chemical, and biological properties of surfaces. It is our hope that this paper encourages and inspires analysts to explore ways that XPS and other surface analysis methods can contribute to the important need to understand not only the composition but also the physical, chemical, electronic, and other properties relevant to fundamental research, development of advanced technologies, and understanding of environmental and biological processes.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Donald R. Baer: Conceptualization (equal); Writing - original draft (equal); Writing - review & editing (equal). Merve Taner Camci: Investigation (equal); Visualization (equal); Writing - original draft (equal). David J. H. Cant: Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal). Scott A. Chambers: Investigation (equal); Writing - original draft (equal); Writing review & editing (equal). Hagai Cohen: Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal). Pinar Aydogan Gokturk: Investigation (equal); Visualization (equal); Writing - original draft (equal). David J. Morgan: Investigation (equal); Writing - original draft (equal); Writing review & editing (equal). Andrey Shchukarev: Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal). Peter M. A. Sherwood: Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal). Sefik Suzer: Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal). Sven Tougaard: Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal). John F. Watts:

Investigation (equal); Writing - original draft (equal); Writing review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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