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Published in:
Applied Surface Science

DOI:
10.1016/j.apsusc.2020.148635

Publication date:
2021

Document version
Final published version

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Citation for published version (APA):
Spencer, B. F., Maniyarasu, S., Reed, B. P., Cant, D. J. H., Ahumada-Lazo, R., Thomas, A. G., Muryn, C. A., Maschek, M., Eriksson, S. K., Wiell, T., Lee, T. L., Tougaard, S., Shard, A. G., & Flavell, W. R. (2021). Inelastic background modelling applied to hard X-ray photoelectron spectroscopy of deeply buried layers: A comparison of synchrotron and lab-based (9.25 keV) measurements. Applied Surface Science, 541, [148635]. https://doi.org/10.1016/j.apsusc.2020.148635

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Download date: 13. May. 2021
Inelastic background modelling applied to hard X-ray photoelectron spectroscopy of deeply buried layers: A comparison of synchrotron and lab-based (9.25 keV) measurements

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ABSTRACT

Hard X-ray Photoelectron Spectroscopy (HAXPES) provides minimally destructive depth profiling into the bulk, extending the photoelectron sampling depth. Detection of deeply buried layers beyond the elastic limit is enabled through inelastic background analysis. To test the robustness of this technique, we present results on a thin (18 nm) layer of metal–organic complex buried up to 200 nm beneath organic material. Overlayers with thicknesses 25–140 nm were measured using photon energies ranging 6–10 keV at the I09 end station at Diamond Light Source, and a new fixed energy Ga K\(_\alpha\) (9.25 keV) laboratory-based HAXPES spectrometer was also used to measure samples with overlayers up to 200 nm thick. The sampling depth was varied: at Diamond Light Source by changing the photon energy, and in the lab system by performing angle-resolved measurements. For all the different overlayers and sampling depths, inelastic background modelling consistently provided thicknesses which agreed, within reasonable error, with the ellipsometric thickness. Relative sensitivity factors were calculated, and these factors consistently provided reasonable agreement with the expected nominal stoichiometry, suggesting the calculation method can be extended to any element. These results demonstrate the potential for the characterisation of deeply buried layers using synchrotron and laboratory-based HAXPES.

1. Introduction

There is a need to obtain elemental and chemical state information non-destructively on length scales of 50–150 nm into the material surface, across a wide range of materials science, physics and chemistry. This is true both in the research environment and increasingly important in industry as structures on this depth scale become prevalent in electronic, photonic, magnetic and even medical devices. The extension of X-ray Photoelectron Spectroscopy (XPS) to examine chemical states deeper into the bulk of a material is made possible by Hard X-ray Photoelectron Spectroscopy (HAXPES) [1,2]. The initial peak intensity, \(I_0\), of a photoelectron signal is attenuated with depth \(z\) as,

\[
I = I_0 \exp\left(-\frac{z}{\lambda}\right)
\]

(1)

where \(L\) is the electron effective attenuation length. This is related to the inelastic mean free path (IMFP, \(\lambda\)) of photoelectrons, and for the organic materials used here, where elastic scattering has a negligible influence (the single scattering albedo, \(\omega\), is approximately 0), \(L \approx \lambda\) [3,4]. The sampling depth for photoelectron spectroscopy may be estimated as,
\[ d_I = \frac{3 \lambda \cos \theta}{\alpha} \]  

(2)

where the intensity is diminished to 5% for electrons originating from this depth according to Eq. (1) with \( \theta = 0 \) (normal emission). \( \theta \) is the emission angle of photoelectrons leaving the sample with respect to the surface normal; increasing this angle decreases the sampling depth. For traditional XPS (X-rays with energies \( h \nu \sim 200–1500 \) eV), \( d_I \) is in the range 1–10 nm. With higher energy X-rays \((h \nu > 5000 \) eV\), \( d_I \) may be extended up to \( \approx 50 \) nm since the IMFP of an electron increases with the kinetic-energy [5–7]; the latter are often well accounted for using the TPP-2 M formula [5–7].

The sampling depth as defined in Eq. (2) applies to the use of photoelectron peaks, i.e., those electrons which have escaped the surface to detection without inelastic scattering. These ‘elastic’ peaks are used for chemical state determination (as chemical state changes lead to chemical shifts in core level electron binding energies), and for the measurement of the distribution of elements near the surface. Probing beyond the elastic limit can be achieved by modelling the inelastic (secondary electron) background associated with each core level excitation at kinetic energies (KEs) lower than the peak [8–12]. The shape of this background is dependent on the depth distribution below the surface [13], and this background signal remains significant even after the signals from the core level peaks have been attenuated by overlayers. This may be used to yield information from depths much larger than 3\( \lambda \) [8]. The mean energy loss is approximately linear with the distance the electron has travelled, meaning that extracting a depth distribution requires measurement of the inelastic background over several hundred eV [13]. This technique can be applied to surface-sensitive XPS with photon energies \( \sim 1.5 \) keV. However, in conventional XPS, the inelastic background from a single core level is often obscured by other core level peaks and Auger lines present in the spectrum, meaning the energy range over which the inelastic background is measured may be limited. The information depth has been found to be \( \sim 8\lambda \) when the background is measured over a range of \( \sim 100 \) eV to low kinetic energy of the primary peak, as might be typical in XPS [14]. In HAXPES there is a significant advantage because, in general and depending on the elements of interest, rather few Auger lines (up to \( \sim 2–3 \) keV kinetic energy) are present in the regions of interest (e.g., core levels up to \( \sim 6 \) keV binding energy), meaning that often the inelastic background can be measured over very wide kinetic energy ranges. This is especially true for heavier atoms when deep core levels are measured, such as the Ir 3d core level at \( \sim 2000 \) eV binding energy measured in this work. The information depth is reported to be as high as \( 20\lambda \) when the background can be measured over a range of \( \sim 1000 \) eV [8].

The maximum depth probed depends on the X-ray photon energy, given the relationship between electron kinetic energy and inelastic mean free path is approximately linear for photon energies above \( \sim 1000 \) eV [15]. This can be varied at a synchrotron radiation source, or using lab instruments with multiple X-ray sources [16–18], or by varying the angle of photoelectron emission using angle-resolved measurements [19], as the sampling depth is reduced with increasing electron emission angle, \( \theta \). In the latter case, at larger angles, surface roughness is often a problem due to shadowing effects and measurements at \( \theta > 30^\circ \) should be avoided unless the sample surface is known to be very flat [20]. In the present work we are able to test the performance of the background analysis method as a function of angle of emission because the samples are known to be adequately flat. Angle-resolved measurements can be performed mechanically by tilting the sample [21], or by using an electron energy analyser with a wide acceptance angle in an angle-resolved mode, as demonstrated here. In addition, HAXPES of heavier atoms \((Z > 12)\) yields multiple core level signals with large differences in binding energy, and thus kinetic energy, allowing information from several sampling depths to be extracted from one spectrum.

Here we demonstrate overlay thickness determination for a buried layer of an iridium-containing metal-organic complex beneath an organic overlayer of 25–200 nm thickness (equivalent to thicknesses in the range 2–15 \( \lambda \) for the Ir 3d electrons measured here), by modelling the inelastic background of the Ir 3d core level. In order to demonstrate the robustness of this modelling, the sampling depth through the layers was varied using X-ray photon energies between 6 and 10 keV at the I09 endstation of Diamond Light Source [22], and the samples were also measured using the first high-throughput laboratory-based HAXPES system (HAXPES-lab, Scienta Omicron GmbH) using a micro-focussed 9.25 keV Ga Kx metal X-ray source (Excillum) and an EW-4000 analyser [18]. Measurements of the iridium-containing organic complex at multiple photon energies have also been used to calculate and test theoretical relative sensitivity factors (RSFs) for Ir, C, O and N, in order to measure the known stoichiometry. These measurements enable benchmarking of the laboratory based HAXPES system against synchrotron HAXPES, and highlight the potential of the Ga Kx system for routine non-destructive analysis on the length scales of 10 s to 100 s nm required for characterising a wide range of advanced functional materials.

2. Materials and methods

Layers of Irganox1010 \((\text{C}_{37} \text{H}_{100} \text{O}_{12})\) (BASF) and an iridium-containing organic complex \((\text{Ir}([\text{ppy}]_2 \text{acac})_2 \text{C}_{27} \text{H}_{23} \text{IrN}_2 \text{O}_2)\) (Sigma-Aldrich) were created on silicon wafer substrates using vacuum coating (QBox, Mantis Deposition Ltd, U.K.) as described previously [23,24]. This resulted in high quality, uniform layers (as monitored using a quartz crystal microbalance which had previously been calibrated to thickness as measured by spectroscopic ellipsometry (M2000DL, Woolam, New England, U.S.A.)) with a measured maximum variation in total layer thickness across a sample of less than 2% [23,24], with a surface roughness typically less than 1 nm.

First, a thick Irganox1010 underlayer (200 nm or 1000 nm) was deposited on the silicon substrate and then a thin layer of the Ir-complex layer (18 nm thick), followed by a variety of Irganox1010 overlayers varying from 25 nm to 200 nm thick. The underlayer directly on top of the silicon wafer was necessary to minimize the influence of the substrate on the measurements. Thick (\( > 200 \) nm) layers of Irganox1010 alone and the Ir-complex alone were also made as reference samples.

Synchrotron measurements were performed at the I09 beamline at Diamond Light Source [22], using photon energies in the range 6–10 keV (monochromated by a Si(1 1 1) double-crystal monochromator) to change the effective sampling depth of the emitted photoelectrons. Samples were measured at grazing incidence to the surface, close to normal emission (\( \theta = 5^\circ \)), in order to maximise photoelectron counts, with a total energy resolution of ca. 730 meV at 6 keV [22]. Detuning the X-rays through the monochromator was performed at each beam energy to reduce the X-ray flux by more than three orders of magnitude (as monitored by a current reading on the last mirror) in order to minimise sample damage under the beam. Beam current was measured using the drain current on the last X-ray mirror, which is coated with rhenium, and which has been shown to exhibit an approximately flat absorption spectrum over 5–10 keV X-ray photon energies. Detuning was performed by reducing this drain current to approximately 50\( \mu \)A at each photon energy used. Measurements were performed with pass energy 500 eV in Angular45 lens mode, where the intensity was integrated over all angles.

Lab-based HAXPES was performed at the Henry Royce Institute [25], using a high-throughput HAXPES-lab system (ScientaOmicron GmbH) [18]; the system includes a gallium metal jet X-ray source (Excillum) [26,27], bespoke monochromator and EW-4000 electron energy analyser (the same analyser as used at the I09 beamline). The X-rays are monochromated using Bragg reflection at a silicon crystal, where the angle between incident and outgoing X-rays is 45.2° and the analyser axis is at 90° to the monochromator-sample plane. The X-ray beam is micro-focussed to 50 \( \mu \)m in order to yield an X-ray flux approximately three orders of magnitude greater than traditional twin-anode Al/Mg K\alpha lab-based X-ray sources, thus mitigating the large decrease in photon-electron cross sections at higher photon energies [18]. The system has a
minimum measured total energy resolution of ~500 meV as required for chemical state determination [18]. Transmission-mode measurements were carried out at grazing incidence to the surface, with pass energy 500 eV for wide scans and 100 eV for narrow core level scans, and angle-resolved measurements were performed with the sample normal held both at 20° and at 60° with respect to the analyser normal (which is at 90° to the incident X-rays). The Angular56 lens mode of the EW-4000 analyser was used for angle-resolved measurements, again using a pass energy of 500 eV, allowing the extraction of angular information over a range of approximately ±20° to either side of the normal to the analyser entrance slit, i.e. yielding 40° of angular information. Fig. 1 illustrates how when the sample normal is rotated to 20° from the analyser (configuration A), the angular mode can be used to measure photoelectron emission angles between θ = 0° (normal emission) and 40°; when the sample normal is rotated to 60° with respect to the analyser, the analyser can be used to track photoemission angles between 40° and 80° from the surface normal (configuration B). In order to set up the angular mode, a clean gold calibration sample was used. The X-ray focus was carefully moved with respect to the analyser entrance slits, using the mechanical table on which the gallium metal jet X-ray source and monochromator are mounted. As the focus of the X-ray beam was adjusted, the sample position was optimised, and the angular spectra of the gold photoelectron peaks (3d and 4f) were measured, until a roughly uniform angular profile was obtained across the working angular range measured at both kinetic energies (Au 3d at ~ 7040 and Au 4f at ~ 9160 eV). This ensures correct alignment of the photoelectron beam entering the analyser, where the optimal X-ray focal point position at the sample is located at the working distance of the analyser entrance slits, as well as being centred both laterally and in height. This optimization is also required for maximising the angular resolution, and thus depth resolution, of the measurements. Setting this mode of operation at a synchrotron is therefore more challenging than in the laboratory environment due to time constraints.

Buried Ir-complex layers with very thick Irganox1010 underlayers of 1000 nm could not be measured at the synchrotron because of sample charging; however, these samples were measurable using the lab-based system, because the lab-based X-ray flux is much lower and the instrument is also equipped with a FS40A (PREVAC) electron flood source charge neutraliser (which was required despite the lower X-ray flux). 200 nm-thick underlayers were therefore used at I09, and for comparison, measurements of these samples were also made using the lab-based source for benchmarking and comparison. At I09 the sample was moved between each measurement (as the photon energy was changed) to minimise sample damage. This was confirmed afterwards using ellipsometry and X-ray beam damage was quantified at less than 1% of total thickness (see Supplementary Material (SM), §A, Fig. S1). Moving the sample was not performed using the lab-based source since the flux (approximately 7 × 10⁸ photons/s [18]) is ~ 4 orders of magnitude lower than synchrotron sources, and no detectable damage was therefore expected.

3. Theory and calculations

3.1. Relative sensitivity factors

Use of HAXPES for characterisation of a wide range of materials requires development of accurate relative sensitivity factors (RSFs) for each element and core level in order to quantify elemental concentrations (using core level photoelectron peaks, giving information over the sampling depth defined by Eq. (2)). Atomic concentrations are calculated according to [17,28]:

$$X_A = 100\% \times \frac{A_A/I_A}{\sum A_i/I_i}$$  (3)

where $X_A$ is the atomic percentage of element $A$ in sample $X$, $A_A$ is the measured XPS peak intensity for element $A$, $I_A$ is the RSF of that core level, and $A_i$ and $I_i$ are intensities and associated RSFs for every detectable element in the sample.

This quantification has been well established using lab-based Al Kα X-rays [17,28,29], and now requires extension to the hard X-ray regime beyond 5 keV photon energy. Theoretical RSFs may be calculated from the variables upon which photoelectron intensities are dependent.

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**Fig. 1.** (Color) Two configurations for measuring photoelectrons from different photoemission angles ($\theta$) using an angle-resolved mode of the EW4000 ( ScientaOmicron GmbH) electron energy analyser, where collection occurs in a 40° range (20° either side of the normal to the analyser entrance slit, green dotted lines). Configuration A has the surface normal (orange dashed line) held at 20° with respect to the analyser normal, allowing for measurement of photoelectrons emerging at normal emission (\(\theta = 0^\circ\)) through to 40°. Configuration B shows the sample rotated with the surface normal at 60° with respect to the analyser normal allowing for measurement at photoemission angles from 40° to 80° from the surface normal. The Ga Kα X-ray beam (blue line) is at 90° with respect to the normal to the analyser entrance slit.
\[ I \alpha j_{w} T d \frac{\sigma}{4 \pi} (1 + \beta) \]  

(4)

where \( I \) is the calculated photoelectron intensity for a given peak, \( \sigma \) is the photoionization cross section for the relevant subshell and \( \beta \) is the dipole asymmetry parameter. Non-dipole terms are excluded due to the geometry of the experimental setup, elastic scattering is excluded because of the material properties, and the monochromator X-rays are assumed to be linearly polarized. Detector linearity and negligible internal electron scattering in the analyser are also assumed, and the effect of the solid angle of collection of the analyser is not taken into account (see SM \( \beta \)B for further details). \( \sigma \) and \( \beta \) are extracted or interpolated from the important recent works of Trzhaskovskaya and Yarzhemsky [30,31], noting that the cross-sections closely follow a power law dependence with photon energy, whereas polynomial interpolation is more appropriate for the asymmetry parameters [17]. \( j_{w} \) is the X-ray flux, which is measured using the drain current at the final mirror in synchrotron measurements (see SM \( \beta \)B for details), and is constant in lab-based measurements. The transmission function of the analyser is represented by \( T_d \). At a given pass energy, analyser operating mode and fixed illumination area of the sample, this is assumed to be a function only of the electron kinetic energy, \( E \). The transmission function may vary at different pass energies and using different lens modes. Eq. (4) can therefore be simplified to obtain an RSF for element \( A \) using

\[ I_{A} = \lambda_{A} \sigma_{A} (1 + \beta_{A}) \]  

(5)

which can be further simplified to IMFP multiplied by cross section \( \lambda_{A} = \lambda_{A} \sigma_{A} \) when using s-orbital photoelectron peaks given the variation of \( \beta \) is small (approximately 1–2%) for these core levels [30,31].

In the laboratory HAXPES instrument, Bragg reflection at the monochromator crystal leads to partial polarization of the X-rays which impacts upon the photoionization cross sections [32]. Given the incident and outgoing X-rays at the monochromator and the electron analyser lie in the same (horizontal) plane, Herrera-Gomez defines the differential cross section for monochromated (subscript ‘m’) X-rays as [32]:

\[ \frac{d \sigma}{d \Omega_{m}} = \frac{\sigma}{4 \pi} \left[ 1 + \frac{\beta}{2} \left( 3 \sin^{2} \alpha - \frac{1}{1 + \cos^{2} 2 \chi} - 1 \right) \right] \]  

(6)

where \( \alpha \) is the angle between the monochromated (reflected) X-ray and the analyser axis (the direction of the measured photoelectron), and \( 2 \chi \) is the angle between incoming and outgoing X-ray at the monochromator, which here is 45.2°. For transmission mode measurements at grazing incidence, \( \alpha \) is 90°, i.e., the same geometry as used at the synchrotron. Non-dipole terms are again ignored here due to this geometry. The instrument geometry means \( \cos^{2} 2 \chi = 0.5 \) and \( \sin^{2} \alpha = 1 \), meaning there is no influence from the asymmetry parameter \( \beta \) upon the photoionization cross section, as the term in curved brackets reduces to 0. RSFs may therefore be obtained using a simplified version of Eq. (5) assuming constant X-ray flux during measurements and minimal change in transmission function across the kinetic energy range measured. Use of angle-resolved modes changes \( \alpha \) and therefore the influence of the asymmetry parameter cannot be neglected: for photoelectrons measured at 20° from the analyser axis (\( \alpha = 70° \), 100°) Eq. (6) results in \( \sigma /4 \pi [1 - 0.06] \). The influence here is similar compared to traditional Al K\( \alpha \) lab sources (typically \( \alpha = 54.7° \) and \( 2 \chi = 23.5° \) [32]) where Eq. (6) results in \( \sigma /4 \pi [1 - 0.05] \). Such a small influence of the asymmetry parameter is often ignored.

### 3.2. Inelastic background modelling

Use of the inelastic background associated with each core photoelectron peak (at lower kinetic energy) for extraction of depth information in XPS was developed as early as the 1980s [14,33,34]. More recently, this analysis method has been used more widely as HAXPES has been applied to a greater variety of materials systems. With the advent of relatively high flux HAXPES in the laboratory environment, further accelerated and widespread application is expected. The analysis was recently refined to allow the use of a hybrid inelastic mean free path for photoelectrons travelling through contrasting media (such as metallic layers with large differences in density and/or plasmon energy) [10], as well as a correction factor for more deeply buried layers (greater than \( \sim 3 \lambda \) below the surface) [6,8] where elastic scattering of electrons can also influence the spectra [35,36]. In the present work, these complications have been minimized by choice of an Ir-organic-complex as the buried layer, where the inelastic mean free path is expected to be very similar to the organic Irganos layers above and below it (as the Ir-organic complex contains only \( \sim 3 \) atomic % Ir, which in terms of area density is equivalent to a single monolayer of Ir for the 18-nm-layer of organic complex used here), and by use of organic materials that minimize the effects of elastic scattering at larger depth scales; thus this material system is an ideal case for demonstrating the technique.

In the QUASES-Tougaard software [37], which has been used here, quantification by analysis of the inelastic background can be performed either by using algorithms that remove the background (the ‘QUASES-Analyze’ part of the software) or by using algorithms that create model spectra where the peak intensity and the inelastic background signal is analyzable and a correction factor for more deeply buried layers (greater than \( \sim 3 \lambda \) below the surface) [6,8] where elastic scattering of electrons can also influence the spectra [35,36]. In the present work, these complications have been minimized by choice of an Ir-organic-complex as the buried layer, where the inelastic mean free path is expected to be very similar to the organic Irganos layers above and below it (as the Ir-organic complex contains only \( \sim 3 \) atomic % Ir, which in terms of area density is equivalent to a single monolayer of Ir for the 18-nm-layer of organic complex used here), and by use of organic materials that minimize the effects of elastic scattering at larger depth scales; thus this material system is an ideal case for demonstrating the technique.

The theory behind the software, which has been described in detail before, is rather complex [38,39]; here we give a brief summary. The spectrum \( J(E, \Omega) \), which includes intensity from inelastic scattering, is modelled directly and compared to the measured spectrum. This is described by [38]:

\[ J(E, \Omega) = \int \Omega_{f} F(E, \Omega) \int_{0}^{\infty} f(z) G(E, \Omega_{s} \cos \theta) d z \]  

(7)

\[ G(E, \Omega_{s} \cos \theta) = \frac{1}{2 \pi} \int_{-\infty}^{\infty} \Omega_{f} e^{-i \Omega_{s} \cos \theta} d \Omega_{s} \]  

(8)

\[ \Sigma(s) = \frac{1}{2} \int_{0}^{\infty} K(T) e^{-sT} d T \]  

(9)

\( F(E, \Omega) \) is the primary excited spectrum, also called the atomic excitation function, \( J(E, \Omega) \) is the measured spectrum, \( T = (E - E_{f}) \) the energy loss, \( K(T) \) the cross section for energy loss \( T, z / \cos \theta \) is the travelled distance, \( f(z) \) is the concentration distribution as a function of the depth \( z \), \( t = \sqrt{T} \), and \( s \) is a mathematical integration variable without physical meaning. This analysis uses the straight-path upon inelastic scattering approximation.

A rigorous solution to the integral equation Eq. (7) for the primary excited spectrum \( F(E, \Omega) \) was found according to [38]:

\[ F(E, \Omega) = \frac{1}{P_{1}} J(E, \Omega) - \frac{1}{2 \pi} \int d E' J(E', \Omega) \int_{0}^{\infty} e^{i (E-E')} \left( 1 - \frac{P_{1}}{P_{2}} \right) d s \]  

(10)

\[ P_{1}(s) = \int \int_{0}^{\infty} f(z) e^{i \Omega_{s} \cos \theta} d z \]  

(11)

\[ F(E, \Omega) \] is required as an input in Eq.(7) and can be determined by analysis (with Eqs. (9–11)) of a spectrum from a sample with known depth distribution, e.g., a reference spectrum from a pure homogeneous sample. It was found, however, that it is both a practical and computational advantage to reformulate Eq. (7) such that the reference spectrum enters directly into the formalism [38,39]. This is what is done in the QUASES-Generator software (except for the “Several Buried Layers” optional profile) which therefore requires the input of a reference spectrum from a homogeneous sample (such as a thick pure piece of the...
buried layer material).

The rather complex numerical evaluation of Eqs. (7–11) has been implemented in the QUASES-Tougaard software [30]. To summarize, the QUASES-Analyze software, which removes the inelastic background, is based on Eqs. (9–11) and two input parameters are required which are the inelastic mean free path, $\lambda$, and the inelastic scattering cross section, $K(E, T)$; both parameters are well known in this case, and accounted for using the TPP-2 M formula (for IMFP) [6,40], and the standard polymer cross section for inelastic scattering which may be selected as an option in the software [41]. The universal cross sections in [40] are expected to be valid at very high energies because they are modelled as a single wide peak largely ignoring the surface loss structure which will play an even smaller role at higher electron energies. The QUASES-Generate software calculates the spectrum of emitted electrons based on Eqs. (7–9). This requires in addition to the same two input parameters ($\lambda$ and $K(E, T)$), the spectrum from a pure reference sample (for the materials here, this was a reference sample without any organic overlayer on top of the Ir-organic-complex layer).

It should be noted that for thicker overlayers (here meaning in excess of ~50 nm), where the core photoelectron peaks of the buried layer are completely attenuated, the use of QUASES-Generate and a spectrum from a pure reference sample (where photoelectron peaks are present) is required in order to maintain accuracy in the overlayer thicknesses calculated [9]. Finally, inelastic background modelling may also be used to calculate the atomic concentration of buried elements, again using reference spectra, although this was not necessary in this work.

Photoelectrons which have lost energy have travelled a longer distance than those that give rise to the core peak signal, and therefore the information depth is considerably larger than the information depth for the elastic peak (Eq. (2)). If the spectrum can be measured over a large range of energy loss, as in HAXPES, the information depth may be substantially increased up to $\sim 20 \lambda$ [8]. As such it is useful to define an inelastic sampling depth, $d_{S,i}$, analogous to Eq. (2), given by

$$d_{S,i} = 20\lambda\cos\theta$$  \hspace{1cm} (12)  

in order to differentiate the depth from which information can be gathered using inelastic background analysis and the information depth using core level peaks.

4. Results

4.1. Atomic concentration calculations

To test the validity of calculating RSFs using Eq. (5) for photon energies exceeding 5 keV, a 200-nm-thick Ir complex layer was measured at 6–10 keV photon energy at Diamond Light Source (an example survey and higher-resolution spectra using 10 keV X-rays are available in Fig. S2 in the SM, [B]). Calculated RSFs were used to obtain the atomic concentration of C, N, Ir and O in the material according to Eq. (3) for comparison with the nominal atomic concentration excluding hydrogen (3.125% Ir, 6.25% O, 6.25% N, 84.375% C). All the accessible core levels of iridium were measured except 4f, 5 s and 5p levels, which are weak and overlap each other, as well as C 1 s, N 1 s and O 1 s. Peak intensities were extracted using CasaXPS [42] using a Tougaard background. While the X-ray flux $\mu_n$ was adjusted to be approximately the same for each photon energy by detuning, small variations in X-ray flux as measured using the drain current on the last Ru-coated mirror were recorded and used to normalise these measured intensities, as well as any changes in dwell time used for data collection. Peak intensities were divided by RSFs calculated using Eq. (5) and compared to the nominal stoichiometry at each photon energy. Fig. 2 shows good agreement between calculated and nominal percentages for O, N, and C for all photon energies used, and for all ten of the Ir core levels used (Ir 3s, 3p, …, 4d, 5s). A closer examination of these results is provided in the SM [B]; tables of the measured and expected peak intensities for every core level are given in tables S1 and S2, and the ratios of the measured to theoretical intensities for each Ir core level measured at each photon energy is shown in Fig. S3. The measurements indicate a slight excess of oxygen. An important conclusion is that the transmission function of the analyser must be relatively constant (to within ~10%) and therefore not an important factor in calculating stoichiometries using electron kinetic energies in the range 3–10 keV. The largest source of error (making the largest contribution to the standard deviations shown in Fig. 2) is the extraction of the peak intensities from the data. 2 standard deviations on the extracted atomic concentrations is approximately ±0.8%.

A thick Irganox(1010) sample was also measured and the carbon percentage was calculated, using the peak intensities and RSFs for O 1 s and C 1 s, to be 85.4% with a standard deviation of 0.4% compared to the expected value of 85.9% (Table S3, SM [B]).

RSFs were applied to these two control samples using lab-based HAXPES at 9.25 keV photon energy, measured in transmission mode at grazing incidence. The Irganox(1010) sample was measured to contain 85.3% carbon, compared to the expected 85.9%, and for the 200-nm-thick Ir complex layer, using the C 1 s, N 1 s, O 1 s, and Ir 4d photoelectron peaks, yielded equivalent homogeneous atomic concentrations of 80.0% C, 6.0% N, 11.6% O, and 2.4% Ir. The result demonstrates significant oxidation at the surface, as expected because of the time delay of several months between the synchrotron beam time and delivery of the HAXPES-lab instrument.

4.2. Inelastic background modelling – Synchrotron HAXPES

Buried Ir-complex layers with overlayer thicknesses of 25, 50, 75, 100, and 140 nm were measured at the I09 HAXPES beamline at Diamond Light Source, using photon energies varying from 6 to 10 keV in order to change the sampling depth. Sampling depths for the organic material used in these samples (Irganox1010) at these energies and for the lab-based source at 9.25 keV are listed in Table 1. Here two sampling depths are listed as defined by Eqs. (2) and (12) for the elastic and inelastic cases respectively [8]. The IMFP $\lambda$ has been calculated using the
Fig. 3 shows a stack of spectra taken at 9 keV photon energy over the Ir 3s, 3p and 3d photoelectron region for the silicon substrate with 200 nm organic underlayer, with an added 18 nm Ir-containing layer (the reference spectrum), and with additional organic overlayers of between 25 and 140 nm thickness. Core level peaks are observed for the 25 nm and 50 nm overlayers, and, while the core level signals are lost for the 75, 100 and 140 nm layers, the inelastic background is still clear. Distinct features in the inelastic background are seen to lower kinetic energy (higher binding energy) of each core level peak for the 25 nm overlayer sample. These features change as the overlayer thickness is increased, and it can be seen that the onset of the inelastic background from the Ir core levels shifts to lower kinetic energy as the Ir photoelectrons travel through more overlayer material, and therefore lose more energy to inelastic scattering, before escaping the surface to detection.

Table 1

| ψ (keV) | Inelastic Mean Free Path (nm) | Elastic sampling depth (nm) | Inelastic sampling depth (nm) |
|---------|-------------------------------|-----------------------------|-------------------------------|
| 6.00    | 9.0                           | 27.0                        | 180.0                         |
| 7.00    | 10.9                          | 32.7                        | 218.0                         |
| 8.00    | 12.7                          | 38.1                        | 254.0                         |
| 9.00    | 14.5                          | 43.5                        | 290.0                         |
| 9.25*   | 15.0                          | 45.0                        | 300.0                         |
| 10.00   | 16.3                          | 48.9                        | 326.0                         |

TPP-2 M formula [5,6,40].

Fig. 3 shows a stack of spectra taken at 9 keV photon energy over the Ir 3s, 3p and 3d photoelectron region for the silicon substrate with 200 nm organic underlayer, with an added 18 nm Ir-containing layer (the reference spectrum), and with additional organic overlayers of between 25 and 140 nm thickness. Core level peaks are observed for the 25 nm and 50 nm overlayers, and, while the core level signals are lost for the 75, 100 and 140 nm layers, the inelastic background is still clear. Distinct features in the inelastic background are seen to lower kinetic energy (higher binding energy) of each core level peak for the 25 nm overlayer sample. These features change as the overlayer thickness is increased, and it can be seen that the onset of the inelastic background from the Ir core levels shifts to lower kinetic energy as the Ir photoelectrons travel through more overlayer material, and therefore lose more energy to inelastic scattering, before escaping the surface to detection.

A key observation is that, in the case of the Si wafer with 200 nm organic underlayer (bottom spectrum), the spectrum is not flat because of the inelastic background originating from the substrate: the Si 1 s core level has a binding energy of ~ 1840 eV, and the inelastic background originating from the buried substrate slowly increases to a maximum at ~ 2500 eV binding energy. This shows that information from layers deeper than 200 nm under organic films is extractable, consistent with the inelastic sampling depth at this photon energy (Table 1). We note that samples with 200 nm organic underlayers between the substrate and the Ir-complex layer did not charge under the X-ray beam, but those with 1000 nm underlayers did (§2). This is linked with the inelastic sampling depth; the fact that inelastic signal originating from the substrate is observable under a 200 nm overlayer means that electrons removed from the sample can be compensated by secondary electrons from the conductive substrate.

Fig. 4 shows the Ir 3d region for a 25 nm overlayer measured using different X-ray photon energies at the I09 beamline. By decreasing the photon energy, the sampling depth is reduced according to Table 1, and so there is less influence from the underlying silicon substrate (which contributes to the background above ~ 2000 eV BE, as shown in Fig. 3) and the shape of the background changes dramatically. The inelastic background was modelled as described in §3, using Tougaard analysis

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**Table 1**

| Inelastic mean free paths and sampling depths for Irganox(1010) associated with the elastic case using core level photoelectron peaks (Eq. (2)) and the inelastic case (Eq. (12)) for normal emission (θ = 0) of Ir 3d photoelectrons (~ 2050 eV binding energy), with IMFPs calculated using the TPP-2 M formula [5,6,40], at various photon energies. *Ga Kα lab-based hard X-ray source.

| hν (keV) | Inelastic Mean Free Path (nm) | Elastic sampling depth (nm) | Inelastic sampling depth (nm) |
|----------|-------------------------------|-----------------------------|-------------------------------|
| 6.00     | 9.0                           | 27.0                        | 180.0                         |
| 7.00     | 10.9                          | 32.7                        | 218.0                         |
| 8.00     | 12.7                          | 38.1                        | 254.0                         |
| 9.00     | 14.5                          | 43.5                        | 290.0                         |
| 9.25*    | 15.0                          | 45.0                        | 300.0                         |
| 10.00    | 16.3                          | 48.9                        | 326.0                         |
with the QUASES-Analyze software package. A buried layer profile was modelled by varying the start depth of the layer (with the end depth of the layer defined as (start depth + 18 nm)) until the best match of the background to the measured spectrum was achieved. This consistently gave an overlayer thickness within 5% of the ellipsometric overlayer thickness (25 nm) at each photon energy, as tabulated in Table S4 in the SM |C, in each case generating a satisfactory fit to the data. Fig. S4 in the SM |C shows a similar analysis of a sample with a 50 nm overlayer: here the overlayer thickness obtained was 50 nm, again within a 5% error for each different photon energy. This demonstrates the robustness of this modelling technique.

For thicknesses > 75 nm, where the Ir 3d peak is completely attenuated, it was found that it was still possible to account for the background with the QUASES-Analyze method, but the uncertainty on the determined thicknesses was quite large (> 20%). In these cases, it was found that a much more accurate analysis was obtained by using the QUASES-Generate analysis (see |3.2) using the reference Ir 3d spectrum from a sample terminating in the Ir-complex layer, without an overlayer. Figs. S5, S6 and S7 in SM |C shows this analysis of the spectra for 75 nm, 100 nm and 140 nm overlayers. Again the agreement between the models and the measured spectra is excellent over the full energy range and the determined overlayer thicknesses are within 5% of the nominal thickness for each photon energy. Deeply buried layers can therefore be pinpointed if there are reference spectra available for the layer material.

Fig. 5 shows data taken using 9 keV photon energy for various overlayer thicknesses, i.e., these measurements all have the same sampling depth (Table 1). The spectra for 25 nm and 50 nm overlayers were modelled using QUASES-Analyze. For the samples with 75 nm, 100 nm and 140 nm overlayers, where the Ir 3d peak cannot be detected, the Ir 3d reference spectrum at 9 keV was used with QUASES-Generate to model the inelastic background. Again the determined overlayer thickness obtained using background analysis is found to be equal to the nominal value to within 5% for each overlayer thickness. It should be noted that the reference spectrum used was that for the stack (Si + 200 nm underlayer + 18 nm Ir-complex layer) so that the influence of the Si 1s inelastic background on the Ir 3d background signal was taken into account; for thicker overlayers this influence is diminished. The onset of the inelastic background signal from Ir 3d for the 140 nm overlayer is clearly shifted to higher binding energy, i.e., lower kinetic energy, compared to the 100 nm and 75 nm overlayers, because the iridium photoelectrons have travelled through more material and lost more energy through inelastic scattering.

4.3. Inelastic background modelling – Ga Ka laboratory HAXPES

The laboratory Ga Ka HAXPES instrument enables measurements of insulating samples because a charge neutraliser (a low energy electron gun pointing at the sample) is installed on the analysis vacuum chamber (see §2). This enabled measurement of buried Ir-complex layers on much thicker organic underlayers, 1000 nm compared to the 200-nm-thick underlayer samples measured at Diamond Light Source, where a much greater X-ray flux also enhances charging effects. The much thicker underlayer ensures that Ir 3d spectra measured from these samples are not influenced by the inelastic background from Si 1s, because the depth of the underlayer is now much greater than the inelastic sampling depth (Table 1). Fig. 6 shows Ir 3s/3p/3d spectral regions and inelastic background modelling using Ir 3d for the reference sample (18 nm Ir-complex layer without an overlayer) and for samples with additional overlayers of 50, 100, and 200 nm. Fig. 6a (Reference spectrum) shows that there is no additional background from Si 1s influencing the spectra over the 1800–3400 binding energy range, because the background returns to an approximately flat function to the high binding energy side of each Ir core level (compare with Fig. 3). The thicker organic underlayer in these samples therefore makes visual inspection and interpretation of the measured spectra more straightforward. As observed in Fig. 3, core level peaks are measured for a 50 nm organic overlayer, but for the thicker 100 nm and 200 nm overlayers, only the inelastic background can be observed. For the 200 nm overlayer, the progressive shift of the inelastic background onset to higher binding energy/ lower kinetic energy (as iridium photoelectrons undergo more and more inelastic scattering as they travel through more material) becomes such that features associated with Ir 3s and Ir 3p1/2 photoelectrons become indistinguishable and part of the background is shifted beyond 3400 eV binding energy. For the overlayer samples, the inelastic background was modelled using QUASES-Generate using the reference spectrum, again obtaining the ellipsometric overlayer thickness within an error of ± 5% for the 50 and 100 nm overlayers, and ± 10% for the thicker 200 nm overlayer sample. For Ir 3d photoelectrons generated with Ga Ka X-rays, a 200 nm overlayer thickness equates to approximately 15 times the IMFP, and photoelectrons from this depth are measurable because this depth is still less than the inelastic sampling depth (Table 1). Finally, a small peak is observed in the reference sample Ir 3s/3p/3d spectrum at ~ 2830 eV binding energy due to the Cl 1s core level; an RSF calculated using Eq. (5) gives a chlorine contamination level (calculated using Eq. (3)) of 2%.

Where depth profiling information is needed in HAXPES, an alternative to varying the photon energy is to vary the angle of photoelectron emission. We have explored use of the angle-resolved mode of the lab-based HAXPES analyser for this purpose, and here we demonstrate
that it can be used to accumulate a set of spectra at different angles of photoemission, and thus differing sample depths according to Eqs. (2) and (12), without moving the sample. 2D data of emission angle vs. electron kinetic energy are accumulated at the CCD camera after the analyser, and the emission angle may then be converted to elastic sampling depth according to Eq. (2) or to inelastic sampling depth (Eq. (12)). Spectra at a particular emission angle may then be extracted from these 2D data, and to improve the signal-to-noise ratio of these spectra, angular data may be summed to generate spectra at an average emission angle.

Here we demonstrate the use of the angle-resolved mode of the analyser using a 25 nm organic overlayer on a thin 18 nm Ir-organic complex above a 200 nm organic underlayer (the same sample as measured at Diamond Light Source; data shown in Fig. 3), and we use these data as a further test of the validity of the background analysis method since analysis of these data should yield the same ellipsometric overlayer thicknesses as those obtained from depth-profiling by varying photon energy. Fig. 7 a,b shows 2D data, where emission angle has been converted to elastic sampling depth (Eq. (2)), measured in an angle-resolved mode for two different sample positions: Fig. 7a shows data where the surface normal is tilted at 20° with respect to the analyser (Fig. 1 configuration A), meaning data are obtained from photoemission angles with respect to the surface normal of 0 (normal emission) to 40°; Fig. 7b shows data for photoemission angles with respect to the surface normal of 40° to 80° (Fig. 1 configuration B). As photoemission angle increases, the elastic sampling depth (Eq. (2)) decreases towards the surface.

The 2D plots in Fig. 7a show the Ir 3d photoelectron peaks reduce in intensity as sampling depth is reduced, and changes in the inelastic background are also clear. Summed angular spectra at photoemission angles with respect to the surface normal of 10, 30, 45, 55, 65, and 75° are shown in Fig. 7c-h. At a photoemission angle of 75° the Ir 3d core levels are lost but the inelastic background is still observed. Inelastic background modelling of these spectra, using QUASES-Generate (using a reference spectrum of the Ir 3d layer with no organic overlayer, and additionally inputting the photoemission angle) consistently gives the ellipsometric overlayer thickness (25 nm) within a ± 10% error, as listed in Table S5 in the SM §C.

5. Discussion

The application of HAXPES as a robust characterisation tool for advanced materials research requires routine protocols for elemental and chemical state depth profiling, and extraction of information beyond the traditional sampling depth (Eq. (2)) using inelastic background modelling. The resulting inelastic sampling depth may be extended up to 20λ depending on how wide a binding energy region can be measured for modelling of the core level energy loss function [8].

The spectral features associated with the inelastic background (as described in §4.2) change distinctly as overlayer thickness increases (Figs. 3, 5, 6), where the onset of the background shifts to higher binding energy/ lower kinetic energy, creating a signature for how deeply a layer is buried; these spectral features can therefore be used in an industrial application (e.g., for quality control procedures) as well as in scientific research.

Modelling of the inelastic background has been developed and refined over the last 3 decades [9,11-14,34,38,39], and here we demonstrate that overlayer thicknesses can routinely be extracted within reasonable error using the QUASES software package. However, we do use an ideal material system for these measurements: organic materials with well-known atomic concentrations, flat surfaces, abrupt interfaces, and reference samples (without an overlayer) were available. Use of organic materials with minimal elastic scattering of electrons enables confident use of angle-resolved measurements. For materials where elastic scattering influences the data more strongly, care must be taken to account for this; in addition, calculations of effective
attenuation lengths (Eq. (1)) require calculation of the single scattering albedo. However, modifications to account for this are well established and can be applied to inelastic background modelling [4,35,36]. QUASES-Analyze is effective when core level peaks of the buried layer are detected (Fig. 4 and Fig. 5, 25 and 50 nm overlayers, as well as Fig. S4 in the SM §C). QUASES-Generate, where a reference sample is used, is effective when the core level peaks are completely attenuated by the overlayer (Fig. 5, 75, 100 and 140 nm overlayers, Fig. 6, 100 and 200 nm overlayers, and Figs. S5, S6, S7 in SM §C). We demonstrate the robustness of these techniques through the accuracy and consistency of the overlayer thicknesses obtained when varying overlayer thicknesses from 25 to 200 nm, as well as by probing these layered structures with a varying sampling depth. At Diamond Light Source the photon energy was varied between 6 and 10 keV, changing the sampling depth as detailed in Table 1. With inelastic background modelling we have extracted information from a depth of 18.5 times the IMFP of the Ir 3d photoelectrons measured. We have also used an angle-resolved mode of the electron energy analyser to then reduce the sampling depth according to Eq. (12).

In the laboratory, using the world’s first high-throughput lab-based Ga Kα HAXPES system (9.25 keV), we have pinpointed layers buried beneath an overlayer up to 200 nm thick, equivalent to 15 times the IMFP of the Ir 3d photoelectrons measured. We have also used an angle-resolved mode of the electron energy analyser to then reduce the sampling depth according to Eqs. (2) and (12). The use of the angle-resolved mode with fixed photon energy in the lab-based system achieves the same effect as changing the photon energy at a synchrotron (evident when comparing the spectra in Fig. 5 with Fig. 7 c-h). Inelastic background modelling again yields the ellipsometric overlayer thickness within reasonable error as detailed in Table S5; the accuracy deteriorates at the highest emission angle, with respect to the surface normal, of 75°, likely due to the influence of surface roughness and/or elastic scattering. For the determination of an overlayer thickness, measurements at higher emission angles are not necessary, and close to normal emission is preferred for maximizing the sampling depth. However, for depth profiling using angle-resolved photoemission, it is worth noting that accuracy will diminish with increasing photoemission angle, i.e., with increasing surface sensitivity \[19,20\]. That with angle-resolved HAXPES is a suitable substitute for depth profiling in lieu of access to a HAXPES synchrotron beamline where the photon energy can be varied. Angle-resolved HAXPES can also be combined with surface-sensitive XPS (e.g., in the laboratory using Al Kα X-rays (1486 eV)) which then enables minimally-destructive profiling from the surface into a bulk of a material.

Calculated RSFs for Ir, C, O, and N have been tested by measuring core levels from each element at multiple photon energies, and comparing the intensities to the RSFs for each core level calculated according to Eq. (5) (using recent data tables of photoionization parameters \[30,31\]). For measurements at photon energies in the range 6–10 keV, the use of the calculated RSFs consistently gives close to the expected stoichiometry for a thick Ir(ppy)_2acac sample as shown in Fig. 6. A slight excess in oxygen content compared with the nominal composition is likely to be due to some surface oxidation and/or adsorption of water. Detailed comparison between expected and calculated peak intensities (SM §B) suggests that for HAXPES, where electron kinetic energy is normal, of 75°, likely due to the influence of surface roughness and/or elastic scattering. For the determination of an overlayer thickness, measurements at higher emission angles are not necessary, and close to normal emission is preferred for maximizing the sampling depth. However, for depth profiling using angle-resolved photoemission, it is worth noting that accuracy will diminish with increasing photoemission angle, i.e., with increasing surface sensitivity \[19,20\]. That with angle-resolved HAXPES is a suitable substitute for depth profiling in lieu of access to a HAXPES synchrotron beamline where the photon energy can be varied. Angle-resolved HAXPES can also be combined with surface-sensitive XPS (e.g., in the laboratory using Al Kα X-rays (1486 eV)) which then enables minimally-destructive profiling from the surface into a bulk of a material.

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energies usually exceed 3 keV, no transmission function correction is required for the EW-4000 analyser over this kinetic energy range (~7.2 – 9.0 keV, binding energy up to ~2 keV).

Application of calculated RSFs to data taken using the lab-based HAXPES instrument also show reasonable agreement with expected values, but the Ir-complex sample exhibited further oxidation due to the time delay between synchrotron beamtime and the lab system installation. The laboratory RSFs may require refinement because the transmission function may vary at lower kinetic energies, and new RSFs are required in order to quantify data taken using angle-resolved modes. However, these calculations pave the way for RSFs for all elements to establish the new Ga K-core levels in the lab-based system as a “black-box” tool that can be used in the same way as spectrometers equipped with other lab-based sources such as Al Kα and Ag Lα at lower photon energies [17,28,29].

The iridium content in the metal-organic complex used here is only ~ 3 at.%, indicating the potential for HAXPES measurements of buried layers containing heavier elements, where sensitivity factors for deeper core levels are often two orders of magnitude greater than carbon (C 1 s). As an example, in the survey spectrum of the Ir-complex measured with 10 keV X-rays in Fig. S2, SM 3 b, the Ir 3 s/3p/3d core levels clearly dominate. The success of the inelastic background modelling of the buried Ir-containing layer also shows that this modelling does not require high atomic concentrations of the elements of interest.

By measuring samples at a synchrotron hard X-ray beamline as well as using the new 9.25 keV HAXPES-lab system from ScientaOmicron GmbH, we have benchmarked the lab-based system and demonstrated its capability. Now that high-throughput HAXPES has been brought into the laboratory environment (as a standalone characterisation technique, as well as for feasibility studies ahead of synchrotron beam time), it is expected that the uptake of HAXPES will increase across a wide range of advanced materials research.

6. Conclusion

We have demonstrated the routine and accurate application of inelastic background modelling of hard X-ray photoelectron spectra by testing a large set of high-quality samples made up of metal–organic complexes buried underneath calibrated overlayer thicknesses up to 200 nm thick. Using a synchrotron source, signals from a buried layer were measured below overlayer thicknesses up to 18.5 times the IMFP of the Ir 3d photoelectrons, and using a lab-based 9.25 keV source, overlayer thicknesses up to 15 times IMFP of the Ir 3d photoelectrons were determined; these sampling depths are 5–6 times greater than achieved using core level photoelectron peaks. As the top overlayer thickness was changed, and as each layer was measured using different sampling depths (either through varying the photon energy at a synchrotron, or using an angle-resolved mode of the analyser in the lab-based system with fixed photon energy), the overlayer thickness was easily extracted within a reasonable error margin. This demonstrates the robustness of the technique as required for industrial quality control applications. Use of an angle-resolved mode in the lab-based system was used to reduce the sampling depth of the measured photoelectrons, which enables profiling from the surface into the bulk of a material, particularly when HAXPES is combined with surface sensitive XPS.

Calculations of relative sensitivity factors have been shown to be accurate for the C 1 s, O 1 s, N 1 s, and Ir 3 s, 3p3/2 – 4d5/2, 3p1/2 – 4d5/2 core levels, enabling routine extraction of atomic concentrations (using core level photoelectron peaks) with typical errors of ± 0.8 at. %. We therefore demonstrate the potential for straightforward non-destructive depth-profiling using both elastic and inelastic signals enabled by synchrotron and lab-based HAXPES.

CRediT authorship contribution statement

B.F. Spencer: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization, Project administration, Funding acquisition. S. Maniyarasu: Investigation, Writing - review & editing. B. Reed: Investigation, Resources, Writing - review & editing. D.J.H. Cant: Validation, Formal analysis, Investigation, Resources, Writing - review & editing. R. Ahumada-Lazo: Methodology, Investigation, Writing - review & editing. A.G. Thomas: Methodology, Investigation, Writing - review & editing. C.A. Murny: Methodology, Writing - review & editing. M. Maschek: Methodology, Investigation, Writing - review & editing. S.K. Eriksson: Conceptualization, Methodology. T. Wiell: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. T.L. Lee: Methodology, Investigation, Writing - review & editing. S. Tougaard: Conceptualization, Software, Validation, Formal analysis, Writing - original draft, Writing - review & editing. A.G. Shard: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing. M. Stewart: Supervision.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

Acknowledgements

This work was supported by the Henry Royce Institute, funded through EPSRC grants EP/R00661X/1, EP/P025021/1 and EP/P025498/1. We acknowledge Diamond Light Source for time on Beamline I09 under Proposal S120059. The work at NPL was supported by the “Metrology for Advanced Coatings and Formulated Products” theme of the UK National Measurement System. We would also like to thank Dr. Malvina Trzhaskovskaya and Prof. Victor Yarzhemsky for photoionization calculations at 9.25 keV, and Mr. Steve Spencer and Miss Amy Paterson from NPL for preparing the layered organic samples and performing ellipsometric analysis. The data associated with this paper are openly available from The University of Manchester Pure Data Repository at Mendeleev Data: 10.17632/8de2m5f7b.1.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2020.148635.

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