

The depth profile of core energy levels: Electronic structure of buried organic/metal interfaces examined by X-ray photoemission and target factor analysis

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Abstract

We have developed a new experimental method of X-ray photoemission spectroscopy (XPS) that can map out the core-energy levels as a function of depth from the surface of the film. A series of XPS data are recorded with different detection angles and expanded to the Taylor series of angle-averaged spectra using the Target Factor Analysis. This procedure enables conversion of the measured angle variations in XPS to the core energy levels as a function of the depth from the surface. This method has been applied to profiling the electronic levels of buried interface between organic semiconductor and metal surfaces.

Keywords: buried organic/metal interface, organic semiconductor, photoemission spectroscopy, target factor analysis

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1. Introduction

The energy levels of semiconductors are of fundamental importance in science and technology. In particular, the interfacial electronic structure of semiconductor/metal substances and p-n junctions are relevant to various operations of electronic devices such as rectification, amplification, light emission, and photovoltaic effects [1].

The energy levels are usually studied by photoemission spectroscopy (PES), which measures the kinetic energies of photoelectrons ejected from the sample surface excited by monoenergetic photons. The energy levels in the material can be determined directly according to the rule of energy conservation. The probing depth of PES is usually on the order of nanometers, which is limited by the mean free path of electrons in the solid materials. Thus PES is acknowledged as a surface-sensitive technique, by which only the energy levels of the surface have been examined. In contrast, the energy levels in the inside or interface of the material often provide crucial pieces of information on the operation mechanisms of semiconductors.

Optical transitions have usually been employed to probe the relative energy levels inside the material. For example, sum-frequency generation can exclusively observe the relative energy levels at the interface [2]. However, the sum-frequency generation does not provide any information on depth. Moreover, optical transitions probe the relative energy levels, which are the differences between those of vacant and occupied states. No method has yet been reported that can directly observe the absolute energy levels of the buried interface from the reference electronic levels such as the vacuum or the Fermi levels.

We present in this letter a new experimental method that can provide the core-energy levels mapped out as a function of depth from the surface of materials. This method has been applied to hetero-junctions of metal and organic semiconductors in order to shed light on the performance of organic semiconductor devices of current interest, such as organic light-emitting diodes (OLED), organic field effect transistors (OFET), and organic photovoltaic cells (OPVC). In spite of exploding activities in this field of research, there still remains numerous unsolved problems in the interfacial electronic structures [3] [4]. In organic semiconductors, for instance, the carrier density is normally much smaller than that in silicon-based inorganic semiconductors resulting in negligible band bending at the interface [3]. Thus only a few organic layers from the interfaces are relevant to the performance of organic semiconductor devices. Since the thickness of the layers is just comparable to the probing depth of the method of our present concern, we expect that our technique can provide a substantial contribution to this problem.

The present method can be regarded as an extension of angle-resolved X-ray photoemission spectroscopy (ARXPS) [5] from the view point of the experimental setup. ARXPS is now widely used to analyze the depth profile of the concentration of elements [6]. In ARXPS, however, only the signal intensity is analyzed with different take-off angles of electrons. Thus information on the energy levels has been ignored. In contrast, the energy profiles are precisely analyzed, which gives depth resolution of XPS data allowing the depth-profiling of energy levels.

2. Theory

Fig. 1 shows the basic idea of the present method. X-ray radiation is incident on a sample, and the electron ejected from the inner shell of a constituent atom is detected. The photoelectron signals from layers with different depths are distinguished by changing the probing depth in the following scheme:

The electron flux generated by photoemission from a sample layer in the depth of z is attenuated in the course of traveling to the surface. When photoelectrons are detected at angle θ from the surface normal, the signal intensity at the detector can be approximated by $\exp(-pz)$, where $p = 1/\lambda \cos \theta$; λ denotes the inelastic mean free path (IMFP) of electrons, which ranges from 2 to 2.5 nm in XPS of organic materials [7] [8]. Thus the probing depth can be changed by a factor of $\cos \theta$, which ranges from 2 to 7 nm, by taking XPS at different detection angles. Let $f(z, E)$ denote the spectral line shape of a thin layer with the thickness of dz at z . The signal intensity observed in the experiment $I(p, E)$ is obtained by summing over the signals from the thin layer $f(z, E)$ from the surface, $z = 0$, to infinity,

$$I(p, E) = I_0 \int_0^{\infty} f(z, E) \exp(-pz) dz = \mathcal{L}[f(z, E); p], \quad (1)$$

where \mathcal{L} is the Laplace transformation of $f(z, E)$ with the kernel p . In the data analysis, therefore, the energy and angle variation in $I(p, E)$ are first identified from the experimental spectra. Then information on the intensity and energy, $I(p, E)$, is converted to the depth profile $f(z, E)$ by the inversion of Laplace transformation. It is assumed here that the sample film is sufficiently flat and the elastic scattering and surface excitations can be neglected [5] [6] [9]. They are reasonable starting assumptions widely used in ARXPS.

3. Experimental

The experimental setup for measurement of $I(p, E)$ was identical to that reported in Ref. [10]. Thin films of an organic semiconductor, bathocuproine (BCP) were vacuum deposited on polycrystalline metal surfaces with different workfunctions, such as Ca, Al and Au; the workfunctions are approximately 3, 4, and 5 eV, respectively [11]. The average film thickness was 5, 10, and 15 nm and the deposition rate was 1 nm min⁻¹. The sample films were transferred to the measurement chamber without exposed to air. The X-ray photoemission spectra were measured using a VG CLAM-2 electron analyzer with a MgK α X-ray source ($h\nu=1254$ eV) at detection angles $\theta=5-65^\circ$. The pass energy of the electron in the analyzer was set to 50 eV. The pressures during the sample preparation and the XPS measurement were about 1×10^{-4} and 2×10^{-7} Pa, respectively.

4. Results and analysis

The C1s core level spectra of a 5 nm-thick BCP film on Ca are shown in Fig. 2. When the detection angle was varied, a slight change in the spectral line shape with energy shifts of a few tens of meV was observed.

A usual analysis of photoemission spectra is made by fitting a set of mathematical functions, e.g.. Gaussian, Lorentzian or Voigt, using the non-linear least-squares method. However, decomposition of a spectral line-shape by curve-fitting with multiple functions often causes large ambiguity unless the spectrum has clearly separated peaks or at least shoulders. In addition, experimental line shapes are often asymmetric or tailing which cannot be precisely reproduced by mathematical functions. Thus it is practically

impossible to achieve a meaningful analysis from a curve-fitting procedure. For adequate derivation of the precise enough p -dependence from a series of $I(p, E)$ spectra to determine the depth profile of the energy levels $f(z, E)$, we have devised a procedure based on the target factor analysis, as discussed in the following.

We have found that the observed spectral shifts can be treated as a Taylor series. For example, a rigid shift of $f(E)$ by ΔE can be expressed as

$$f(E + \Delta E) = f(E) + \Delta E f'(E) + (1/2)(\Delta E)^2 f''(E) + \dots \quad (2)$$

If the spectral shifts can be assumed as rigid, i.e., the spectral line shape of a thin layer $f(z, E)$ is independent of z , any spectral change can be expanded into a Taylor series. This assumption is usually valid in the XPS of organic materials [3]. For example, the XPS spectrum $I(p, E)$ in Fig. 1 consists of a sum of the spectra centered at $(E + \Delta E_i)$ with intensity a_i is expanded into the Taylor series as

$$\begin{aligned} \sum_i a_i f(E + \Delta E_i) = \sum_i a_i f(E) + \sum_i a_i \Delta E_i f'(E) \\ + \frac{1}{2} \sum_i a_i (\Delta E_i)^2 f''(E) + \dots \quad (3) \end{aligned}$$

Since the spectrum of a thin layer $f(E)$ in Eq. 3 is practically undeterminable, $f(E)$ is approximated by a spectrum averaged over the angle parameter p . Note that no mathematical functions are employed in the whole procedure. This is beneficial to achieve high precision in a data analysis for the following reasons. First, possible errors imposed by the use of mathematical functions can be avoided. Second, the instrumental broadening such

as the line width of X-rays and the energy resolution of the electron energy analyzer is automatically included.

For precise determination of the coefficients of Taylor series, we have applied the target factor analysis (TFA), which was developed and is now widely used in analytical chemistry [12]. This procedure is not straightforward for an analysis of angle-dependent photoemission spectra, because TFA has been used only rarely in spectroscopy. We have developed the procedure to determine the coefficients of Taylor series which includes the following two steps. First, a series of spectra are decomposed into the eigenspectra (abstract spectra) and coefficients (score) by the process, so-called principal component analysis (PCA) as discussed in detail in Appendix. Since PCA is a purely mathematical procedure with a requirement of mutual orthogonality, no physical meaning is contained in the abstract spectra or scores. Then the PCA results are transformed to the form of Taylor expansion by the process called target transformation.

As discussed by Hasegawa [13], even a subtle difference in a series of spectral data can be detected and identified by PCA. The detection limits are principally set by the noise levels. Since the abstract spectra and the transformed spectra are both orthogonal systems, the accuracy gained in PCA is maintained in the course of the target transformation. Therefore, the coefficients of the Taylor series are precisely determined without loss of any meaningful information.

Fig. 3 shows results of the TFA analysis for the C1s core levels of a 5 nm-thick film of BCP. The angle averaged spectrum and its derivatives are shown in panel (a) by solid lines. The coefficients of the Taylor series are plotted in

panel (b) as a function of the angle parameter p for the substrates of different metals, Au (squares), Al (circles) and Ca (triangles). The uncertainties in the coefficients of Taylor expansion involved in the target factor analysis [12] are shown for BCP/Ca in Fig. 3(b). It is found that the uncertainties are much smaller than those required in the data processing of ARXPS (e.g., minimum precision of 3.5% is required to determine three parameters along the depth z [9]). The overall validity of the target factor analysis can be checked by comparison of the angle-averaged spectra $f(E)$ and their derivatives $d^{(n)}f(E)/dE^{(n)}$ with those obtained by the target transformation of the abstract spectra shown by dots. The good agreements shown in Figure 3a assure that the angle variation in the spectra $I(p, E)$ is well described by the Taylor expansion.

Now that the angle variation in $I(p, E)$ is precisely identified by the coefficients of the Taylor series, the energy levels can be determined as a function of depth z . For this purpose, we have used a layered model where the energy levels and the thicknesses of the layers are taken as fitting parameters. Since this procedure implicitly involves inverse Laplace transformation, only three or fewer parameters along the depth can be determined in a normal experimental conditions [9]. We have thus divided the organic layers into three regions. The position parameters of the interface z_i and the core-level energy of each layer E_i are defined as shown in Fig. 4(a). As the thickness of the first and third layers corresponds to one monolayer of the molecule, as shown below, the energy levels at the metal/organic interface and the surface are best approximated by these step functions rather than continuous functions. Note that a number of methods have been developed in the anal-

ysis of ARXPS data for calculating the inversion of Laplace transformation. Application of a more sophisticated method such as the maximum entropy method [14] [15] will lead to an improvement of the present method beyond the simple layered model.

In this particular condition, Eq. 1 is rewritten as

$$\begin{aligned}
I(p, E) = & \frac{1}{p} \{ (1 - e^{-z_3 p}) f(E) \\
& + [(1 - e^{-z_1 p}) E_1 + (e^{-z_1 p} - e^{-z_2 p}) E_2 + (e^{-z_2 p} - e^{-z_3 p}) E_3] f'(E) \\
& + \frac{1}{2} [(1 - e^{-z_1 p}) E_1^2 + (e^{-z_1 p} - e^{-z_2 p}) E_2^2 + (e^{-z_2 p} - e^{-z_3 p}) E_3^2] f''(E) + \dots \}.
\end{aligned} \tag{4}$$

The coefficients of $f(E)$, $f'(E)$ and $f''(E)$ in Eq. 4 are fitted to those of the TFA results to determine the parameters E_i and z_i . We made measurements on the three samples having different film thicknesses for each metal. Their energy levels and thicknesses were determined so as to consistently fit all the observed data. The reasonable agreement of the results of TFA based on the observed $I(p, E)$ data (dots) with the best-fit corresponding simulations (solid lines), shown in Fig. 3, supports that the energy levels of the buried interface can be accounted for by the three-layer model shown in Fig. 4(a).

The determined energy-level parameters are schematically shown in Fig. 4(b). The fractional depth resolution $\Delta z/z$ is normally no less than 0.8 which is limited by inversion of the Laplace transformation in Eq. 1 [9]. Although the energy E is not involved in the Laplace transformation, the energy and depth ($E_1 - E_2$ and z_1 , $E_3 - E_2$ and z_2) are found to be mutually dependent. The uncertainties in the energy differences between the surface and the bulk, $E_1 - E_2$, and those between the metal/organic interface, $E_3 - E_2$,

are estimated to be about ± 0.1 eV and ± 0.5 eV, respectively. The C1s core level at the metal/BCP interface E_3 depends on the metals with respect to the bulk region of the film. The dimension of the interface region, $z_3 - z_2$, is comparable to one monolayer of BCP.

The energy level of a metal/organic interface is usually determined by measuring that of the surface by PES as a function of film thickness increasing by repeated deposition [3]. Thus, the energy levels examined by the conventional measurement with varied thickness are shown in Fig. 4(c) to demonstrate the advantage of the present method. The dependence on the metals observed in the present study appears to be similar to that derived from the conventional method. However, the results obtained by the present method have revealed two important features that have never been attained by the conventional method. First, the thickness of the interface region has now been determined. It is hardly determinable by the thickness-dependent measurements because the energy levels shift gradually around the first monolayer with increasing film thickness. Second, the present method enables the measurement of the interfacial energy levels without changing the vacuum level of the sample during the whole measurement. The results clearly show that variation in interfacial energy levels with reference to the constant vacuum levels. In contrast, the vacuum level changes simultaneously with the valence and core energy levels with increasing film thickness during the conventional thickness-dependent experiment, which has imposed confusion in the interpretation of energy level and vacuum level at the metal/organic interfaces. A previous study on BCP/Au reports that the interfacial energy levels of the organic layer with reference to the vacuum

level was essentially unchanged [16]. These findings urge reconsideration of the concept of the vacuum level at the metal/organic interface [3].

Fig. 4 shows that the C1s level energies of BCP in contact with the metal surface depend on the metals. In the case of BCP/Ca, the electron transfer from metal to the unoccupied states of BCP has been reported [17]. The order of the metal dependent energy shift observed in the present results, however, is opposite to that predicted from the electron transfer. Similar observations were reported for other combinations of metals and organic layers [18] though the origin has not yet been clarified.

On the other hand, the core level at the surface is always $E_1 - E_2 = 0.3 \pm 0.1$ eV lower than that in the bulk film for any metal measured in the present study. The thickness of this outermost layer is also about 1 nm, indicating that only the first monolayer is largely different from the other layers. The observed energy shift agrees well with a simple electrostatic estimation, which shows that the energy difference between the first and second surface layers is about 0.2 eV [19] [20]. In contrast, a recent study of high-resolution XPS reports that the energy shift at the surface is nearly zero with the upper limits of 0.1 eV [21]. This discrepancy clearly demonstrates that the simple curve-fitting procedure used in the cited work is not accurate enough to evaluate the core-level energy difference between the surface and the bulk.

5. Conclusion

We have developed an experimental method that enables us to examine the core-energy levels as a function of depth. By changing the detection an-

gle, a series of X-ray photoemission spectra can be measured as a function of probing depth. The observed angle variations in the spectra are analyzed by Taylor expansion in terms of the angle-averaged spectrum, and the coefficients are precisely determined using the target factor analysis. The derived data are then converted to the depth profile of the energy levels at the interface by fitting the parameters to the three-layer model. Application of this method to organic semiconductors will bring a new insight into the interfacial electronic structures that have never been accessed by other existing methods.

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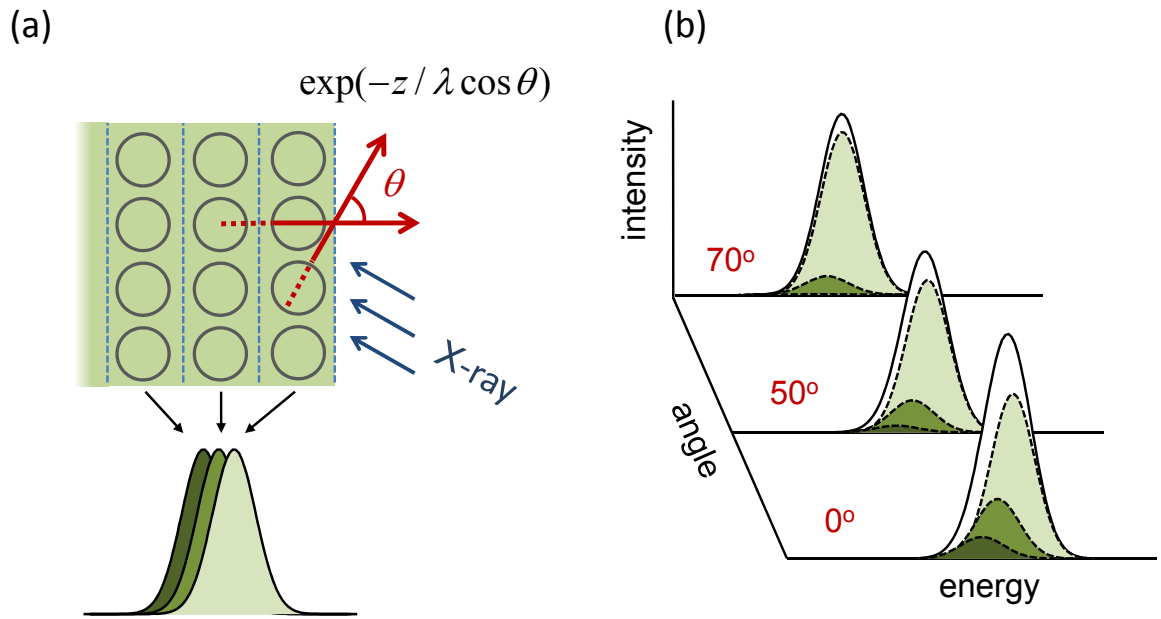


Figure 1: Principle of X-ray photoemission spectroscopy with depth z resolution. (a) XPS spectra measured at different detection angles θ contains signals from the corresponding effective probing depths, which are proportional to $\exp(-z/\lambda \cos \theta)$. (b) The energy profiles of the observed XPS spectra contain information on the core-energy levels with different z . The present method analyzes the XPS data shown in panel (b) to obtain the core-energy levels as a function of the depth z .

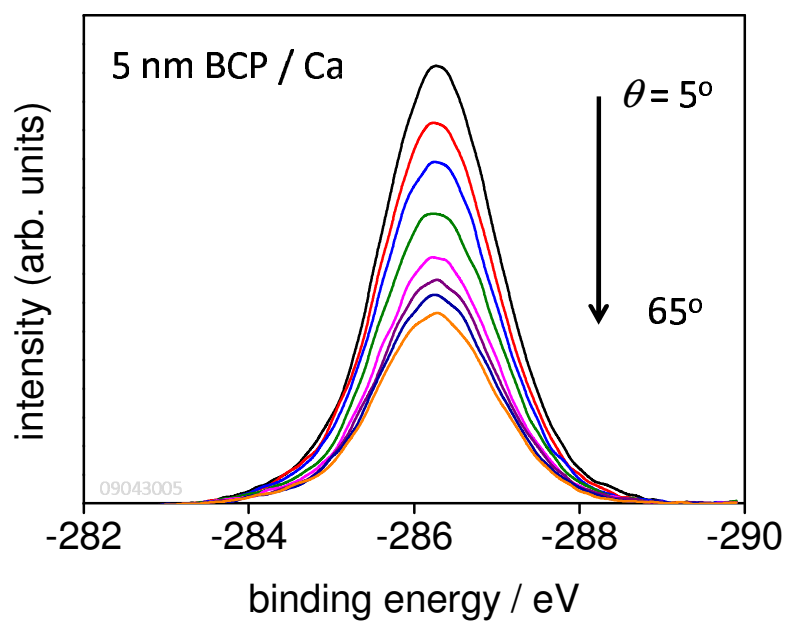


Figure 2: C1s core level spectra $I(p, E)$ of a 5 nm-thick BCP film on Ca measured at different detection angles θ .

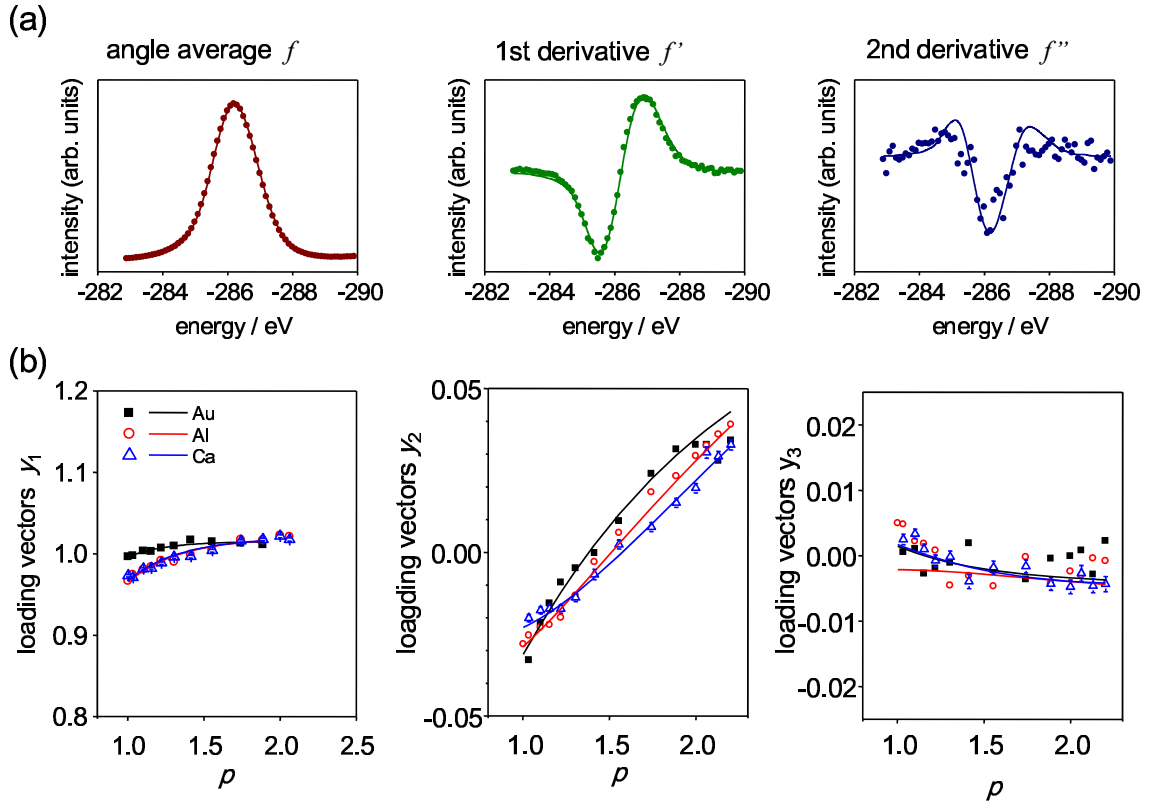


Figure 3: Results of the target factor analysis for the C1s core levels of a 5 nm-thick BCP film. (a) Angle-averaged spectrum and its derivatives, f , f' and f'' (solid lines) in comparison with the transformed abstract spectra (circles) for the film on Ca. (b) Coefficients of the Taylor expansion, a_1 , a_2 and a_3 , for the different metal substrates of Au (squares), Al (circles) and Ca (triangles) obtained by TFA. The best-fits by the three-layer model (Eq. 4 and Fig. 4b) are shown by solid lines against $p = 1/\cos\theta$.

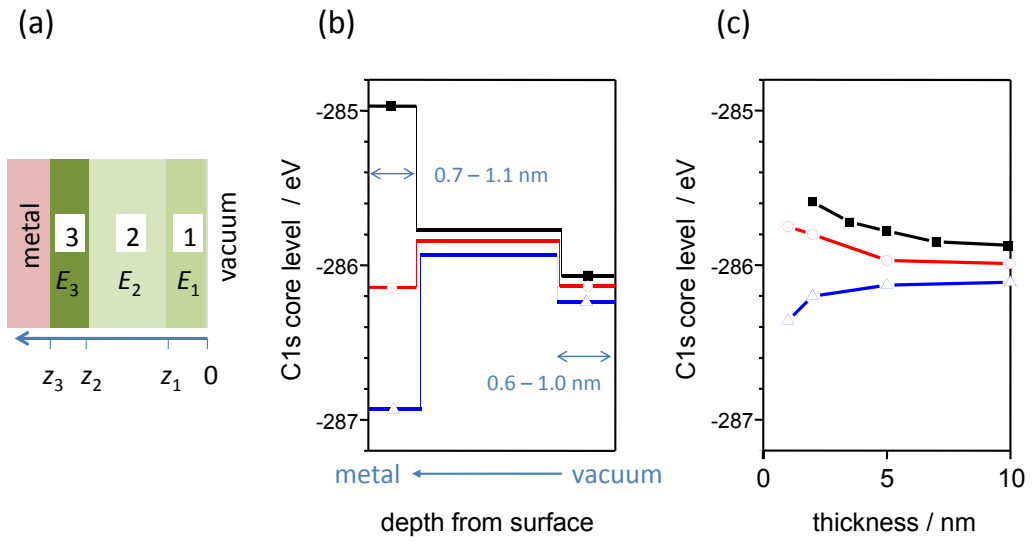


Figure 4: (a) Three-layer model structure used for the analysis (see text for details). (b) Layer thicknesses and C1s energy levels E_i determined by the present study for the substrates of Au (squares), Al (circles) and Ca (triangles). (c) Energy levels determined by a conventional measurement with varied thickness shown for comparison.

Appendix A.

The detail of the target factor analysis (TFA) to determine the coefficients of the Taylor expansion is described. We adopt the notation of a standard text book [12]. The procedure consists of the following two steps. The first step is the principal component analysis (PCA), where a series of angle-dependent data $I(p, E)$ is decomposed into the abstract spectra (eigenvectors) $\mathbf{r}_i(E)$ and the coefficients (scores) $\mathbf{c}_i(p)$:

$$\mathbf{I}(p, E) = \mathbf{r}_1(E) \cdot \mathbf{c}_1(p) + \mathbf{r}_2(E) \cdot \mathbf{c}_2(p) + \dots \quad (\text{A.1})$$

The abstract spectra $\mathbf{r}_i(E)$ are a set of orthonormal functions in the order of significance. The number of terms used in the following procedure, called the factor level, is determined using the significant factor analysis, so that the abstract spectrum of the last term is larger than the noise level. In the present study, the factor levels were determined to be 3 for the films with thickness below 5 nm, or 2 above 10 nm. The factor level corresponds to the number of independent spectral components included in the experimental spectra. Therefore, these numbers are judged reasonable, because the energy levels at the metal/organic interface and the surface may be different from that of the bulk values for thin films making three independent components, while only two components of the surface and bulk difference are expected for a film sufficiently thicker than the probing depth of about 7 nm.

In the second step, so-called target transformation is performed by introducing a transformation matrix \mathbf{T} , which transforms $\mathbf{r}_i(E)$ and $\mathbf{c}_i(p)$ into $\mathbf{x}_i(E) = \mathbf{r}_i(E) \cdot \mathbf{T}$ and $\mathbf{y}_i(p) = \mathbf{T}^{-1} \cdot \mathbf{c}_i(p)$, respectively. \mathbf{T} is determined by a linear least-squares fit to make $\mathbf{x}_i(E)$ as close as the test vectors $f(E)$ and

its n -th derivatives $d^{(n)}f(E)/dE^{(n)}$ ($n=1,2,\dots$) in the Taylor expansion of Eq. 3. In this case, Eq. A.1 yields

$$\begin{aligned} \mathbf{I}(p, E) &= (\mathbf{r}_1(E) \cdot \mathbf{T})(\mathbf{T}^{-1} \cdot \mathbf{c}_1(p)) + (\mathbf{r}_2(E) \cdot \mathbf{T})(\mathbf{T}^{-1} \cdot \mathbf{c}_2(p)) + \dots \\ &= \mathbf{x}_1(E) \cdot \mathbf{y}_1(p) + \mathbf{x}_2(E) \cdot \mathbf{y}_2(p) + \dots . \end{aligned} \quad (\text{A.2})$$

As mentioned in the text, the validity of the transformation can be checked by comparing the transformed spectra $\mathbf{x}_i(E)$, called predicted vectors, with the test vectors, i.e., the angle-averaged spectra $f(E)$ and its n -th derivatives $d^{(n)}f(E)/dE^{(n)}$ ($n=1,2,\dots$). Since the two sets of vectors agree satisfactorily as shown in Fig. 3(a), it is concluded that the coefficients of the Taylor series have been determined as $\mathbf{y}_i(p)$.