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Evaluation of Two Methods for Determining Shell Thicknesses of Core-Shell Nanoparticles by X-ray Photoelectron Spectroscopy

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Abstract

We evaluated two methods for determining shell thicknesses of core-shell nanoparticles (NPs) by X-ray photoelectron spectroscopy (XPS). One of these methods had been developed for determining thicknesses of films on a planar substrate while the other was developed specifically for NPs. Our evaluations were based on simulated Cu 2p_{3/2} spectra from Cu-core/Cu-shell NPs with a wide range of core diameters and shell thicknesses. Copper was chosen for our tests because elastic-scattering effects for Cu 2p_{3/2} photoelectrons excited by Al K α X-rays are known to be strong. Elastic scattering could also be switched off in our simulations so that the two methods could be evaluated in the limit of no elastic scattering. We found that the first method, based on both core and shell photoelectron intensities, was unsatisfactory for all conditions. The second method, based on an empirical equation for NPs developed by Shard, also utilized both core and shell photoelectron intensities and was found to be satisfactory for all conditions. The average deviation between shell thicknesses derived from the Shard equation and the true values was -4.1% when elastic scattering was switched on and -2.2% when elastic scattering was switched off. If elastic scattering was switched on, the effective attenuation length for a Cu film on a planar substrate was the appropriate length parameter while the inelastic mean free path was the appropriate parameter when elastic scattering was switched off.

Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful method for studying the physical and chemical properties of surfaces and interfaces, and its use has grown rapidly over the past 20

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years. XPS has been frequently utilized for the analysis of planar samples (e.g., multi-layer thin-film structures on a substrate) consisting of many different types of materials for a great variety of scientific and technological applications. Development of XPS data analysis methods and experimental protocols for characterizing supported nanoparticle (NP) catalysts (particle size, chemical composition, chemical state, etc.) also has a long history (e.g., see references 1-3). As nanomaterial usage has expanded into new areas such as biomedical applications that involve unsupported NPs in complex environments, this growth has presented new challenges and opportunities for XPS that require the development of new data analysis methods and experimental protocols.⁴ Thus, there is now increasing interest in using and developing XPS methods for determining the chemistry, structure, and size of core-shell NPs as well as other types of nanostructures.⁵⁻¹²

We consider here the use of XPS for determining shell thicknesses of core-shell NPs. We also consider the ideal case of NPs consisting of a spherical core and a concentric spherical shell. Real NPs, however, may be non-spherical and the core and shell may be excentric.^{13,14} Nevertheless, the ideal case should be satisfactorily understood before more complex structures are considered.

We report evaluations of two methods that have been used to determine shell thicknesses of core-shell NPs. One of these methods, designated Method 1, was developed for measuring thicknesses of overlayer films on planar substrates and depends on measurements of the intensities of substrate and overlayer-film photoelectron signals. In its application to core-shell NPs, both core and shell photoelectron intensities are used in place of the substrate and film signals, respectively. There is no obvious reason why Method 1 should be valid for NPs but it has been used for this purpose. In fact, depending on the structural details of the NP, using Method 1 can lead to large errors in the calculated overlayer thickness.³ The second method, designated Method 2, is an analytical expression developed by Shard¹⁵ from which the shell thickness is determined from the core radius and the ratio of photoelectron intensities from the core and shell materials (normalized to the corresponding intensities for planar materials). Both methods require knowledge of “attenuation lengths” (ALs) for designated photoelectrons in the shell material and, for Method 2, also in the core material.

The attenuation length and, more recently, the effective attenuation length (EAL) are parameters introduced to make empirical corrections for the effects of elastic scattering on the inelastic attenuation of photoelectron signal intensities.¹⁶⁻¹⁸ The EAL is now the preferred term for this purpose.¹⁶⁻¹⁸ The procedure for measuring the thickness of an overlayer film on a planar substrate based on attenuation of a substrate signal by the overlayer is now well established, and EALs for this purpose are available from a National Institute of Standards and Technology (NIST) database¹⁹ or from predictive formulae.²⁰⁻²² Recent work, however, has shown that EALs for the latter approach could be different from those for our Method 1 when both methods were again used to measure film thicknesses on a planar substrate.¹⁸ The EALs could also depend on the instrument configuration.¹⁸ We will examine the possible validity of EALs developed for describing attenuation of a substrate signal by a planar overlayer film when applied to core-shell NPs.

Our evaluations of Methods 1 and 2 for determining shell thicknesses of core-shell NPs are based on simulations of XPS spectra for arrays of Cu-core/Cu-shell NPs on a silicon substrate, as schematically illustrated in Fig. 1. These simulations were performed with the NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA).^{23,24} We chose copper for our tests since elastic-scattering effects for the Cu 2p_{3/2} photoelectron signal excited by Al K α X-rays are known to be strong.²⁵ It is possible for elastic scattering to be switched off in SESSA, and we could then evaluate Methods 1 and 2 in the limit of no elastic scattering. We could then infer that if a particular method was satisfactory for both limiting cases (strong elastic scattering and negligible elastic scattering), it would likely to be satisfactory for intermediate cases. It was convenient to use copper as both the core material and the shell material since the analysis was simplified. We note here that SESSA can provide separate measures of Cu 2p_{3/2} signal intensities from the core and the shell (i.e., without any need for spectral decomposition).

Our analysis also extends and corrects the recent report of Chudzicki *et al*²⁶ who investigated the validity of Method 2 for two types of NPs.

Materials and Methods

SESSA

SESSA^{23,24} is a NIST database that can be used to simulate XPS spectra [and also Auger-electron spectra (AES)] of nanostructures such as islands, lines or rods, spheres, and layered spheres on surfaces. Similar simulations can be performed for multilayer films. Users can specify the compositions and dimensions of each material in the sample structure as well as the measurement configuration, and the simulated spectra can be compared with measured spectra. Compositions and dimensions can then be adjusted to find maximum consistency between simulated and measured spectra.

The SESSA database has been designed to facilitate quantitative interpretation of AES and XPS spectra and to improve the accuracy of quantitation in routine analysis.^{23,24} SESSA contains physical data needed to perform quantitative interpretation of an AES or XPS spectrum for a specimen of given composition and morphology (differential inverse inelastic mean free paths, total inelastic mean free paths, differential elastic-scattering cross sections, total elastic-scattering cross sections, transport cross sections, photoionization cross sections, photoionization asymmetry parameters, electron-impact ionization cross sections, photoelectron lineshapes, Auger-electron lineshapes, fluorescence yields, and Auger-electron backscattering factors). Retrieval of relevant data is performed by a powerful expert system that queries the comprehensive databases. A simulation module provides an estimate of individual peak intensities as well as the peak spectra.

The design of the SESSA software allows the user to enter the required information in an intuitive way. The modular structure of the user interface closely matches that of the usual controls on a real instrument. A command line interface can also control the software; this feature allows users to load sequences of commands that facilitate a series of simulations for similar conditions (i.e., batch runs).

The capabilities of the present SESSA Version 2.0 for simulating XPS spectra of samples consisting of selected nanomorphologies on a planar substrate are based on the PENGEO package, a general-purpose geometry package that allows one to define quasi-arbitrary sample structures using quadric surfaces.²⁷ PENGEO is a part of the PENELOPE code which is widely used for simulation of electron and photon transport in matter.²⁸ From information provided by a user, a geometry file is created by SESSA and internally passed to PENGEO which initializes the geometry, stores it in memory, and provides various functions for tracking an electron trajectory. The geometry is based on a simple syntax with which surfaces such as planes, spheres, hyperboloids, etc. can be defined and subsequently used to delimit phases of a material.

The layered-sphere morphology in SESSA allows simulations for a spherical particle (the core) with an arbitrary number of “overlayer” shells. In our work, there was a single concentric shell. Our simulations were performed for Cu-core diameters, D , of 0.5 nm, 1 nm, 2 nm, 5 nm, and 10 nm, and for Cu-shell thicknesses, T , between 0 and 3.75 nm in increments of 0.25 nm. All nanomorphologies in SESSA reported in this manuscript are simulated as periodic, rectangular arrays on a substrate where the periodicities $P(X)$ and $P(Y)$ in the X and Y directions were both 20 nm. Test simulations performed where the periodicities were varied from 10 to 40 nm exhibited only minor variations, and thus a periodicity of 20 nm was selected for the full set of simulations. Our simulations were performed for Cu-core/Cu shell NPs on a Si substrate, as shown schematically in Fig. 1.

SESSA allows a user to place distinguishing tags on photoelectron peaks that arise from the same element, which could be present in two or more phases of the sample. This capability is very convenient for separating the photoelectron intensities for an element that might be present in two or more different chemical states. For example, it is useful to be able to separate the Si 2p signals from an SiO₂ film on an Si substrate as well as from the substrate. Appropriate chemical shifts can also be applied to the photoelectron signals from the different phases. In our simulations, we placed a tag on the Cu 2p_{3/2} photoelectron intensity from the NP core to distinguish it from the Cu 2p_{3/2} intensity from the shell. SESSA could thus provide measures of the Cu 2p_{3/2} photoelectron intensities from both the core and the shell of the NPs without any necessity for selection of and then subtraction of a background intensity.

Our simulations were performed for Al K α X-rays that were incident on the NP arrays at an angle of 55° to the surface normal. We determined the intensities of the Cu 2p_{3/2} photoelectrons that were emitted within 5° of the surface normal. That is, the entrance axis of the analyzer was normal to the surface.

The Monte Carlo simulations in SESSA are based on the trajectory-reversal approach of Gries and Werner.²⁹ In contrast to conventional Monte Carlo codes in which electrons are tracked from the source to the detector, the trajectory-reversal method tracks electrons in the opposite direction, starting from the detector and following a trajectory back to the point of origin. All of the electrons thus contribute to the accumulated signal which results in significantly shorter simulation times. A simulation may typically take between about 10

seconds and several minutes, depending on the number of peaks to be simulated and the precision desired in the intensities.

Method 1

Method 1 for determining the thickness of a NP shell is based on an algorithm for determining the thickness of an overlayer film on a planar substrate.^{30,31} It is assumed, without any justification, that this algorithm could be satisfactory for NPs. The algorithm is based on measurements of two photoelectron intensities, one from the substrate (or core), I_s , and the other from the overlayer film (or shell), I_f . If (for the moment) we neglect elastic-scattering effects, the ratio of intensities from the film and the substrate is^{31,32}

$$\frac{I_f}{I_s} = \frac{I_f^\infty}{I_s^\infty} \frac{[1 - \exp(-T/\lambda_f \cos\theta)]}{\exp(-T/\lambda_s \cos\theta)}, \quad (1)$$

where I_f^∞ and I_s^∞ are the intensities from an infinitely thick film and an uncovered substrate, respectively, λ_f and λ_s are inelastic mean free paths (IMFPs) of photoelectrons from the film and the substrate, respectively, in the film material, T is the film thickness, and θ is the mean angle of photoelectron emission with respect to the surface normal. If the photoelectron signals from the substrate and the film have nearly the same kinetic energies (e.g., as for the classic case of Si 2p_{3/2} photoelectrons from an Si substrate and an SiO₂ overlayer film), $\lambda_f \approx \lambda_s \equiv \lambda$ where λ here is the average IMFP for the film and substrate photoelectrons in the film. Equation (1) can then be rewritten³⁰

$$T_1 = \lambda \cos\theta \ln(1 + R_2), \quad (2a)$$

where T_1 designates a film thickness from Method 1 and $R_2 = I_s I_s^\infty / I_f I_f^\infty$. This film thickness can thus be determined from Eq. (2a) if the IMFP is known. The kinetic energy of Cu 2p_{3/2} photoelectrons excited by Al K α X-rays is 554 eV, and the IMFP for these electrons in Cu has been calculated to be 1.12 nm.³²

For the more realistic case where elastic-scattering effects are considered, Eq. (2a) can still be utilized by replacing the IMFP by the corresponding EAL,

$$T_1 = L_{film} \cos\theta \ln(1 + R_2), \quad (2b)$$

where L_{film} in Eq. (2b) indicates the average EAL for photoelectrons from the substrate and the film in the film.¹⁶⁻¹⁸ In general, L_{film} will depend on the film thickness, photoelectron emission angle, and instrument configuration.¹⁸ Nevertheless, Eq. (2b) is empirically useful for emission angles between 0 and 60°. In such cases, values of L_{film} can be estimated from a NIST database¹⁹ or from predictive formulae,²⁰⁻²² thereby enabling determinations of film

thicknesses from Eq. (2b). In our work, we determined L_{film} for Cu 2p_{3/2} photoelectrons in Cu from the EAL predictive formula of Jablonski and Powell²⁰ [Eq. (5) below] to be 0.80 nm. This EAL is about 29 % less than the corresponding IMFP.

We emphasize that Eqs. (1) and (2) were derived for a film on a planar substrate, and are not necessarily valid for NPs. In addition, the EALs for Method 1 can be different from those used to describe attenuation of substrate photoelectrons by an overlayer film.¹⁸

Method 2

Shard¹⁵ proposed a series of analytical expressions that can be used to determine the shell thickness, T_2 , of a core-shell NP of core radius R from Method 2. With his notation, these equations are:

$$T_2 = \frac{T_{R \sim 1} + \beta T_0}{1 + \beta}, \quad (3a)$$

where

$$T_{R \sim 1} = \frac{T_{R \rightarrow \infty} R}{R + \alpha}, \quad (3b)$$

$$T_0 = R[(ABC + 1)^{1/3} - 1], \quad (3c)$$

$$T_{R \rightarrow \infty} = \frac{0.74A^{3.6} \ln(A) B^{-0.9} + 4.2AB^{-0.41}}{A^{3.6}} + 8.9 \quad (3d)$$

$$\alpha = 1.8 / (A^{0.1} B^{0.5} C^{0.4}), \quad (3e)$$

$$\beta = 0.13 \alpha^{2.5} / R^{1.5}, \quad (3f)$$

$$A = I_1 I_2^\infty / I_2 I_1^\infty, \quad (3g)$$

$$B = L_{1,a} / L_{2,a}, \quad (3h)$$

and

$$C = L_{1,a} / L_{1,b}. \quad (3i)$$

In Eq. (3g), I_1 indicates the photoelectron intensity from the shell and I_2 the photoelectron intensity from the core. The quantities, I_1^∞ and I_2^∞ , represent the corresponding intensities from planar semi-infinite materials. Equations (3h) and (3i) show ratios of effective attenuation lengths $L_{i,j}$, where i represents the material from which the photoelectrons originated ($i = 1$ for the shell material and $i = 2$ for the core material) and j indicates the material through which the photoelectrons are traveling ($j = a$ for the shell and $j = b$ for the core). For example, $L_{1,a}$ represents an EAL for photoelectrons from the shell traveling in the shell. Shard found that the fourth EAL, $L_{2,b}$, could be estimated from $L_{2,b} = L_{1,a} / BC$. Both R and T_2 are expressed in units of $L_{1,a}$. For our SESSA simulations with Cu-core/Cu-shell NPs, Eq. (3g) becomes $A = I_1 / I_2$ and $B = C = 1$.

Shard utilized what is often called the straight-line approximation in his analysis (in which the effects of elastic scattering are neglected) and introduced EALs as an empirical means for describing these effects. It was implicit in Shard's paper that EALs developed for films on a planar substrate could be used in Eqs. (3h) and (3i). That is, for our evaluation of Eq. (3), $L_{1,a} = L_{film} = 0.80$ nm. This usage will be discussed later.

Results

Evaluation of Method 1

Figure 2 shows comparisons of shell thicknesses, T_1 , derived from Eq. (2b), the Method 1 algorithm, and SESSA simulations of Cu $2p_{3/2}$ photoelectron intensities from the Cu core and the Cu shell as a function of Cu-shell thickness for Cu-core diameters of 0.5 nm, 1 nm, 2 nm, 5 nm, and 10 nm. In these simulations, elastic scattering was switched on. We assumed $\cos\theta = 1$ in our use of Eq. 2(b) since the minimum value of $\cos\theta$ for our conditions was 0.997.

The dashed line in Fig. 2 indicates perfect correlation between T_1 and the actual shell thicknesses. However, the derived T_1 values are systematically larger than the actual shell thicknesses by between 40 % and 86 % for the 10 nm Cu-core diameter and by between factors of 2.4 and 7.1 for the 0.5 nm Cu-core diameter. Method 1 is clearly not satisfactory for determining shell thicknesses of Cu-shell/Cu-core NPs with the EAL for a Cu film on a planar Cu substrate

Figure 3 shows similar comparisons based on SESSA simulations with elastic scattering switched off. In the limit of negligible elastic scattering, we now use Eq. (2a) to determine shell thicknesses. The derived values of T_1 are again systematically larger than the actual

shell thicknesses by amounts varying between factors of 1.5 and 2.1 for the 10 nm Cu-core diameter and between 3.1 and 9.8 for the 0.5 nm Cu-core diameter. Method 1 is also unsatisfactory for these conditions.

Evaluation of Method 2

Figure 4 shows comparisons of shell thicknesses, T_2 , from Eq. (3) and the simulated Cu $2p_{3/2}$ photoelectron intensities from the Cu core and the Cu shell of 10 nm Cu-core NPs as a function of Cu-shell thickness. Elastic scattering was switched on for the results in panels (a) and (b) and switched off for the results in panels (c) and (d). We used the EAL for a Cu film on a planar Cu substrate ($L_{\text{film}} = 0.80$ nm) for $L_{1,a}$ in Eq. (3) in the results shown in panels (a) and (c) while the IMFP ($\lambda = 1.12$ nm) was used for $L_{1,a}$ in Eq. (3) for the results in panels (b) and (d). The dashed lines in Fig. 4 indicate perfect correlation between the T_2 values and the shell thicknesses, T_{shell} , used in the simulations. We quantify the degree of correlation between the values of T_2 and T_{shell} by calculating the average percentage difference, T , for each set of conditions in Fig. 4:

$$\Delta T = \frac{100}{n} \sum_{i=1}^n \frac{(T_2)_i - T_{\text{shell}}}{T_{\text{shell}}}, \quad (4)$$

where $n = 15$ is the number of Cu-shell thicknesses in each comparison.

Figure 4(a) shows good agreement between the T_2 values and the corresponding values of T_{shell} when elastic scattering was switched on and the EAL was used in Eq. (3), with $T = -3.6$ % from Eq. (4). There was similarly good agreement in Fig. 4(d) between the T_2 values and the corresponding values of T_{shell} when elastic scattering was switched off and the IMFP was used in Eq. (3), with $T = -1.5$ % from Eq. (4). There is obviously much poorer agreement in Figs. 4(b) and 4(c) between the T_2 values and the corresponding values of T_{shell} when inappropriate choices are made for $L_{1,a}$ in Eq. (3). If the IMFP is used for $L_{1,a}$ in Eq. (3) when elastic scattering is switched on, $T = 28.1$ %, while if the EAL is used for $L_{1,a}$ in Eq. (3) when elastic scattering is switched off, $T = -25.6$ %. Our results in Fig. 4(b) are qualitatively similar to those in Fig. 3(d) of Chudzicki *et al.*²⁶ who inappropriately used an IMFP instead of an EAL for a shell material that exhibited strong elastic-scattering effects.

Similar results to those in Fig. 4 were obtained for Cu-core diameters of 0.5 nm, 1 nm, 2 nm, and 5 nm. Figure 5 shows comparisons of values of T_2 and the corresponding values of T_{shell} for Cu-core diameters of (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 5 nm when elastic scattering was switched on and the EAL for a Cu film on a planar Cu substrate (0.80 nm) was used for $L_{1,a}$ in Eq. (3). Values of T from Eq. (6) range from -3.1 % to -4.9 % in these comparisons, and the average value of T for the comparisons in Figs. 4(a) and 5 was -4.1 %.

Figure 6 shows comparisons of values of T_2 and the corresponding values of T_{shell} for Cu-core diameters of (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 5 nm when elastic scattering was

switched off and the Cu IMFP (1.12 nm) was used for $L_{1,a}$ in Eq. (3). The T values in these comparisons range from -0.9% to -4.0% , and the average value of T for the comparisons in Figs. 4(d) and 6 was -2.2% .

The comparisons in Figs. 4(a) and 5 show satisfactory agreement between Cu shell thicknesses from the Shard formula [Eq. (5)] and the Cu shell thicknesses used in the SESSA simulations when elastic scattering was switched on and the Cu EAL was used for $L_{1,a}$. There is similar agreement between Cu shell thicknesses from the Shard formula and the actual shell thicknesses from the comparisons in Figs. 4(d) and 6 when elastic scattering was switched off and the IMFP was used for $L_{1,a}$. We then infer that there should also be a similar degree of agreement for other materials that are intermediate in the magnitude of elastic-scattering effects from negligible (Cu with elastic scattering switched off) to relatively large (Cu). That is, values for the EALs in the Shard formula can be obtained from data¹⁹ or predictive formulae²⁰⁻²² for thin films on a planar substrate and are useful for determining shell thicknesses of NPs. Shard¹⁵ found in his analysis that the mean relative error in his formula was a minimum when $B = 1$ (i.e., when photoelectrons from the core and the shell had the same EALs in the shell material) and when $C = 1$ (i.e., when the shell photoelectrons had the same EALs in the core and shell materials), as in our work. It is thus likely that larger differences could occur between T_2 values and actual shell thicknesses for other core-shell material combinations than found in our comparisons with Cu-core/Cu-shell NPs. Since the uncertainty of calculated IMFPs has been estimated to be about 10% ,³⁴ differences between T_2 values and actual shell thicknesses of up to 10% could be tolerated. Shard's analysis indicates that satisfactory results should be obtained for $0.5 \leq B \leq 2$ and $0.5 \leq C \leq 2$.

Discussion

General remarks

SESSA has been used previously for determining EALs for photoelectrons in thin films on planar substrates.^{18,34} There can be small but significant systematic differences between these EALs and careful measurements.³⁵ These differences have been attributed to the effect of film thickness or photoelectron emission angle on the fraction of intrinsic or shakeup intensity accompanying photoionization and/or on the inelastic-scattering probabilities in the vicinity of the substrate-film and film-vacuum interfaces.^{18,34} Neither of these effects is included in the SESSA simulations for thin films on planar substrates or for nanostructures on surfaces.

Method 2 based on the Shard¹⁵ equation [Eq. (3)] was found to be satisfactory for determining shell thicknesses of Cu-core/Cu-shell NPs if an appropriate EAL or IMFP was utilized for $L_{1,a}$. When elastic scattering was switched on in our SESSA simulations, we identified $L_{1,a}$ with L_{film} from the Jablonski-Powell²⁰ EAL predictive equation [Eq. (5) below]. Similar results would be expected with use of two other EAL predictive equations.^{21,22} When elastic scattering was switched off in the simulations, we identified $L_{1,a}$ with the IMFP. Further tests of the Shard equation should be made with dissimilar materials in the core and shell, particularly for materials with weaker elastic-scattering

effects than in Cu and for material combinations where the parameters B and C in the Shard equation depart appreciably from unity.

EAL definitions and usage

Shard optimized his equation so that elastic-scattering effects in core-shell NPs could be effectively represented by EALs obtained from attenuation measurements or calculations for overlayer films on planar substrates. While this approach is useful, there is a logical difficulty in that Technical Committee 201 on Surface Chemical Analysis of the International Organization for Standardization (ISO) has defined the EAL as the “parameter which, when introduced in place of the inelastic mean free path into an expression derived for Auger electron spectroscopy and XPS on the assumption that elastic-scattering effects are negligible for a given quantitative application, will correct that expression for elastic-scattering effects”.³⁶ This definition has two explanatory Notes that provide additional information. First, the EAL may have different values for different quantitative applications of AES and XPS. However, the most common use of EAL is the determination of overlayer-film thicknesses from measurement of the changes of substrate Auger-electron or photoelectron signal intensities after deposition of a film or as a function of emission angle. For emission angles of up to about 60° (with respect to the surface normal), it is often satisfactory to use a single value of this parameter. For larger emission angles, the EAL can depend on this angle. Second, since there are different uses of EAL, it is recommended that users specify clearly the particular application and the definition of the parameter for that application (e.g., by giving an equation or by providing a reference to a particular source).

We have already described one approach for measuring thicknesses of an overlayer film on a planar substrate (our Method 1) and noted that EALs can also be determined from attenuation of substrate photoelectrons by an overlayer film on a planar substrate. However, EALs from these two approaches can differ numerically.¹⁸ It is also possible to define an EAL for quantitative analysis in which this EAL represents the combined effects of elastic scattering on the effective differential photoionization cross section (for XPS) and the yield of photoelectrons or Auger electrons.^{16,17} This diversity in EAL applications makes it clear that the EAL should not be regarded simply as a material parameter like the IMFP, that is, a parameter that has a well-defined value for a given material and electron energy.

The ISO definition for EAL clearly indicates that this is a term that is to be used in an equation in place of the IMFP to account for elastic-scattering effects. Simple equations have been developed for quantitative XPS analyses or for determining thicknesses of films on planar substrates in which elastic-scattering effects were either not considered (in the early days of XPS when these effects were unknown) or neglected (for simplicity). Equation (1) is such an equation for determining film thicknesses in which elastic-scattering effects were neglected and in which the IMFP is the key length parameter. After consideration of elastic-scattering effects, this equation is still empirically useful if the IMFP is replaced by an appropriate EAL [as shown in Eq. (2)].¹⁶⁻¹⁸ It is still necessary, however, to specify the ranges of film thickness and photoelectron emission angle over which the equations provide satisfactory results.¹⁶⁻¹⁸ Further, an EAL developed for one application or algorithm should not be used for another application or algorithm unless this use has been validated.

The ISO definition for EAL can be applied for use of the Shard equation with the following considerations. Unlike the situation with Method 1 in which the IMFP was replaced by an EAL to account for elastic-scattering effects, the Shard equation was developed directly using EALs to account for these effects, and our work with Cu-core/Cu-shell NPs has validated this approach. We can, however, consider a modified Shard equation in which each EAL is replaced by a corresponding IMFP. That is, we define

$$B = \lambda_{1,a} / \lambda_{2,a}, \quad (3h')$$

and

$$C = \lambda_{1,a} / \lambda_{1,b}, \quad (3i')$$

where, with use of Shard's notation, $\lambda_{1,a}$ is the IMFP for shell photoelectrons in the shell material, $\lambda_{2,a}$ is the IMFP for core photoelectrons in the shell material, $\lambda_{1,b}$ is the IMFP for shell photoelectrons in the core material, and $\lambda_{2,b}$ (the IMFP for core photoelectrons in the core) can be estimated from $\lambda_{2,b} = \lambda_{1,a} / BC$. Both R and T in the modified Shard equation are now expressed in units of $\lambda_{1,a}$. The modified Shard equation, with use of Eqs. (3h') and (3i') in place of Eqs. (3h) and 3(i), has also been validated in our work when we replaced the EAL for Cu-core/Cu-shell NPs by the corresponding Cu IMFP. However, further tests of the modified Shard equation should be made for material combinations where the parameters B and C in the Shard equation depart appreciably from unity.

Subcommittee 1 on Terminology of ISO Technical Committee 201 is currently considering revised text for the explanatory Notes accompanying its EAL definition in order to provide better guidance and better clarity on how this term should be used. The proposed new Notes are:

1. The effective attenuation length can have different values for different quantitative applications of AES and XPS. However, the most common use of effective attenuation length is in the determination of the thicknesses of overlayer films on flat substrates from measurements of the changes of overlayer and substrate Auger-electron or photoelectron signal intensities as a function of film thickness or of electron emission angle. For emission angles of up to about 60° (with respect to the surface normal), it is often satisfactory to use a single value of this parameter. For larger emission angles, the effective attenuation length can depend on this angle. Effective attenuation lengths have also been used in equations for determining the shell thicknesses of core-shell nanoparticles and for quantitative analysis (to describe the changes in AES and XPS signal intensities due to elastic scattering).
2. Since there are different uses of this term, it is recommended that users specify clearly the particular quantitative application and the definition of the parameter

for that application (e.g. by giving a formula or by providing a reference to a particular source). Effective attenuation lengths developed for one application should not be used for another application unless this usage has been validated.

EAL Data for Methods 1 and 2

As mentioned earlier, EALs for Method 1, L_{film} , can be estimated from a NIST database¹⁹ or from predictive formulae.²⁰⁻²² We chose here to determine the L_{film} value for Cu 2p_{3/2} photoelectrons in Cu at an energy of 554 eV from the earlier Jablonski and Powell formula as that equation was determined using similar electron energies:²⁰

$$L_{film} = \lambda(1 - 0.735\omega), \quad (5)$$

where ω , the single-scattering albedo, is given by

$$\omega = \lambda / (\lambda + \lambda_{tr}) \quad (6)$$

and λ_{tr} is the transport mean free path (TMFP). The TMFP is related to the transport cross section of an elemental solid, σ_{tr} , by $\lambda_{tr} = 1 / N\sigma_{tr}$ where N is the density of atoms in the solid. Values of transport cross sections are available from the NIST Electron Elastic-Scattering Cross-Section database³⁷ or from an analytical formula³⁸ while TMFPs are available from the NIST SESSA database.²³ For an alloy or compound, TMFPs can be determined from transport cross sections for the constituent elements weighted by their atomic fractions.³³

The single-scattering albedo, a useful measure of the strength of elastic-scattering effects in a solid, is related to electron energy and atomic number via the IMFP and the TMFP [Eq. (6)].^{31,33} For XPS with Al or Mg K α X-rays and photoelectron kinetic energies between 200 eV and 1.45 keV, ω can vary between about 0.05 (weak elastic-scattering effects) and about 0.45 (strong elastic-scattering effects).³³ For Cu at an energy of 554 eV, $\omega = 0.387$.

Summary

We evaluated two methods for determining shell thicknesses of core-shell NPs by XPS. One of these methods was developed for measuring thicknesses of overlayer films on planar substrates while the second was developed specifically for NPs. We used intensities of Cu 2p_{3/2} photoelectrons from Cu-core/Cu-shell NPs that were simulated by the NIST SESSA database. Our simulations were performed for Cu-core diameters of 0.5 nm, 1 nm, 2 nm, 5 nm, and 10 nm, and for Cu-shell thicknesses between 0 and 3.75 nm in increments of 0.25 nm.

Copper was chosen for our tests because elastic-scattering effects for Cu 2p_{3/2} photoelectrons excited by Al K α X-rays are known to be strong. It is also possible for elastic scattering to be switched off in SESSA so that the two methods could be examined in the

limit of no elastic scattering. We could thus infer that if a particular method was satisfactory for both limiting cases (strong elastic scattering and weak elastic scattering), it would likely be satisfactory for other cases of practical interest. The relevant length parameter in the latter case is the IMFP while in the former case it is the EAL. It has been unclear, however, whether EALs determined for an overlayer film on a planar substrate are valid for core-shell NPs.

Our derived shell thicknesses from Method 1 were considerably different from the actual Cu-shell thicknesses used in the simulations. The differences varied between 40 % and a factor of 9.8, depending on Cu-core diameter, Cu-shell thickness, and whether or not elastic scattering was switched on or off. It is clear that Method 1 is not satisfactory for the determination of NP shell thicknesses, as found by Belsey *et al.* in a recent interlaboratory comparison (private communication).

Method 2 based on the Shard¹⁵ equation was found to be satisfactory for determining shell thicknesses. If elastic scattering was switched on, the EAL for a Cu film on a planar substrate was the appropriate length parameter while the IMFP was the appropriate parameter when elastic scattering was switched off. The average deviation between shell thicknesses derived from the Shard equation and the true values was – 4.1 % when elastic scattering was switched on and – 2.2 % when elastic scattering was switched off. We thus inferred that Method 2 should be satisfactory for other materials that are intermediate in the magnitude of elastic-scattering effects from negligible (Cu with elastic scattering switched off) to relatively large (Cu). That is, values for the EALs in the Shard formula can be obtained from data¹⁹ or predictive formulae²⁰⁻²² for thin films on a planar substrate and then used in the Shard equation for determining shell thicknesses of NPs. Further tests of the Shard equation are planned with dissimilar materials in the core and shell and with weaker-elastic scattering effects than for Cu.

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Fig. 1. Schematic representation of a rectangular array of Cu-core/Cu-shell nanoparticles, each with a diameter D and a shell of thickness T , on a Si substrate with periodicities $P(X,Y)$ in the X and Y directions.

Fig. 2.

Comparisons of shell thicknesses, T_1 , derived from Eq. (2b), the Method 1 algorithm, and SESSA simulations of Cu 2p_{3/2} photoelectron intensities from the Cu core and the Cu shell as a function of Cu-shell thickness for Cu-core diameters of 0.5 nm, 1 nm, 2 nm, 5 nm, and 10 nm. In these simulations, elastic scattering was switched on. The dashed line indicates perfect correlation between T_1 and the shell thickness. Equation 2(b) was evaluated with EAL $L_{film} = 0.80$ nm.

Fig. 3.

Comparisons of shell thicknesses, T_1 , derived from Eq. (2a), the Method 1 algorithm, and SESSA simulations of Cu 2p_{3/2} photoelectron intensities from the Cu core and the Cu shell as a function of Cu-shell thickness for Cu-core diameters of 0.5 nm, 1 nm, 2 nm, 5 nm, and 10 nm. In these simulations, elastic scattering was switched off. The dashed line indicates perfect correlation between T_1 and the shell thickness. Equation 2(a) was evaluated with IMFP $\lambda = 1.12$ nm.

Fig. 4.

Comparisons of shell thicknesses (symbols), T_2 , from Eq. (3), the Method 2 algorithm, and SESSA simulations of Cu $2p_{3/2}$ photoelectron intensities from the Cu core and the Cu shell as a function of Cu-shell thickness for a Cu-core diameter of 10 nm. In these simulations, elastic scattering was switched on for the results in panels (a) and (b) and switched off for the results in panels (c) and (d). The EAL for a Cu film on a planar Cu substrate (0.80 nm) was used for $L_{1,a}$ in Eq. (3) for the results in panels (a) and (c) while the IMFP (1.12 nm) was used for $L_{1,a}$ in Eq. (3) for the results in panels (b) and (d). The dashed lines indicate perfect correlation between the T_2 values and the shell thicknesses used in the simulations. Values of the average percentage difference ΔT were calculated from Eq. (4).

Fig. 5.

Comparisons of shell thicknesses (symbols), T_2 , from Eq. (3), the Method 2 algorithm, and SESSA simulations of Cu $2p_{3/2}$ photoelectron intensities from the Cu core and the Cu shell as a function of Cu-shell thickness for Cu-core diameters of (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 5 nm. Elastic scattering was switched on for these simulations. The EAL for a Cu film on a planar Cu substrate (0.80 nm) was used for $L_{1,a}$ in Eq. (3). See caption for Fig. 4.

Figure 6.

Comparisons of shell thicknesses (symbols), T_2 , from Eq. (3), the Method 2 algorithm, and SESSA simulations of Cu $2p_{3/2}$ photoelectron intensities from the Cu core and the Cu shell as a function of Cu-shell thickness for Cu-core diameters of (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 5 nm. Elastic scattering was switched off for these simulations. The Cu IMFP (1.12 nm) was used for $L_{1,a}$ in Eq. (3). See caption for Fig. 4.