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Published in:

Journal of Vacuum Science & Technology. A: International Journal Devoted to Vacuum, Surfaces, and Films

Publication date:

2013

Document Version

Final published version

[Link to publication](#)

Citation for published version (APA):

Tougaard, S. M. (2013). Validity of automated x-ray photoelectron spectroscopy algorithm to determine the amount of substance and the depth distribution of atoms. *Journal of Vacuum Science & Technology. A: International Journal Devoted to Vacuum, Surfaces, and Films*, A31, 031503-1 to 031503-6.

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Validity of automated x-ray photoelectron spectroscopy algorithm to determine the amount of substance and the depth distribution of atoms

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(Received 12 December 2012; accepted 25 February 2013; published 14 March 2013)

The author reports a systematic study of the range of validity of a previously developed algorithm for automated x-ray photoelectron spectroscopy analysis, which takes into account the variation in both peak intensity and the intensity in the background of inelastically scattered electrons. This test was done by first simulating spectra for the Au4d peak with gold atoms distributed in the form of a wide range of nanostructures, which includes overlayers with varying thickness, a 5 Å layer of atoms buried at varying depths and a substrate covered with an overlayer of varying thickness. Next, the algorithm was applied to analyze these spectra. The algorithm determines the number of atoms within the outermost 3λ of the surface. This amount of substance is denoted $\text{AOS}_{3\lambda}$ (where λ is the electron inelastic mean free path). In general the determined $\text{AOS}_{3\lambda}$ is found to be accurate to within $\sim 10\text{--}20\%$ depending on the depth distribution of the atoms. The algorithm also determines a characteristic length L , which was found to give unambiguous information on the depth distribution of the atoms for practically all studied cases. A set of rules for this parameter, which relates the value of L to the depths where the atoms are distributed, was tested, and these rules were found to be generally valid with only a few exceptions. The results were found to be rather independent of the spectral energy range (from 20 to 40 eV below the peak energy) used in the analysis. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4795246>]

I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is one of the most widely applied methods to study the composition of surface nanostructures.^{1,2} Quantitative interpretation of XPS is often done under the assumption that the concentration of atoms in the near surface region is directly proportional to the measured XPS peak intensity. Today, it is however well known that this is only valid when the atoms are homogeneously distributed with constant concentration in the outermost $\sim 3\lambda$ of the surface, where λ is the electron inelastic mean free path. Since this is usually not the case, the results from such an analysis are often very inaccurate.³ It has been shown that a much improved XPS analysis can be obtained by making use of both the peak intensity and the peak shape. This is so because the peak shape is determined by the distribution of inelastically scattered electrons, which in turn is given by the depth distribution of the photoelectron emitting atoms since the photoelectron will lose energy on its way out of the solid.^{3–5} This analysis relies on algorithms valid for different classes of depth profiles, and it has been proven to give detailed and accurate information on the distribution of atoms in the surface region of the solid.⁵ A software package was also developed to make this analysis available for nonspecialists.⁶ This XPS-peak shape analysis method requires operator interaction because the analysis is done by changing the parameters that define the depth distribution and interactively this is compared to the measured XPS. The correct distribution has been determined when both the shape and the intensity is accounted for over a wide energy region ($\sim 50\text{--}100$ eV) of the spectrum.

There is, however, a strong and growing interest in automated XPS analysis. For an automated algorithm to work, it must be robust in the sense that small variations in the analysis procedure should not result in large changes in the analysis result. It is clear that the more information one attempts to get out of the spectra, the more important it is to make a careful analysis and the less robust will the corresponding analysis procedure be. For an automated algorithm to work in practice, it is therefore important to look for only the minimum amount of information which will still be useful for solving practical technological problems by XPS.

An algorithm was therefore developed⁷ that determines just two numbers for each spectrum: the number of atoms per unit surface area within depths $< 3\lambda$, which is denoted $\text{AOS}_{3\lambda}$ (short for the amount of substance within depths $< 3\lambda$) and a number L , which indicates approximately at what depths these atoms are distributed. This method is of course less accurate than the more elaborate XPS peak shape analysis method, but it is robust and therefore well suited for automated data analysis. This more limited amount of information is however often sufficient to solve a given technological problem.

The algorithm was developed in 2003.⁷ Its validity was tested in 2005 (Ref. 8) by comparison to experimental XPS of nanostructures that had previously been determined by more elaborate surface analysis techniques and the agreement was found to be good. The algorithm was later applied to XPS imaging, and it was found to be very effective in producing images of $\text{AOS}_{3\lambda}$ for each pixel as well as images showing those pixels for which the atoms are in certain depth intervals. This worked even for quite noisy spectra, which are typical for XPS imaging where data acquisition time for each spectrum must be kept at a minimum with corresponding high

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noise levels. Three experimental examples of 3D imaging with this algorithm have been published,^{9–11} and they were all successful and showed that subnanometer depth resolution could be reached.

With such a surprising success of this relatively simple algorithm, it is important to systematically explore its accuracy and limits of validity. This is the purpose of the present paper where we produce model spectra from three sets of nanostructures: i.e., overlayer, buried layer, and substrate with an overlayer. Subsequently, these sets of spectra are analyzed with the algorithm, and the level and range of validity are determined.

II. ALGORITHM

In this section, we summarize the algorithm derived in Ref. 7. The centroid of the peak of interest is at energy E_p , and all energies are expressed as kinetic energy. First, an energy point E_{\max} is chosen a few electronvolts above the peak structure of interest. A straight line fitted to the intensity of the spectrum from the energy E_{\max} to higher energies is then subtracted from the measured spectrum to give a spectrum $J(E)$, which represents only the contribution to the measured intensity, which is due to the peak of interest [thus $J(E_{\max}) = 0$; see Fig. 1].

The next step is to correct for inelastically scattered electrons and calculate the background subtracted spectrum, $f(E)$ (see the detailed mathematical basis of the algorithm in Ref. 7):

$$f(E) = J(E) - B_1 \int_E^{E_{\max}} J(E') K(E' - E) dE'. \quad (1)$$

Here, $K(T)dE$ is the probability for the electron to lose energy in the interval from T to $T + dE$ per unit path length traveled. The parameter B_1 is adjusted such that $f(E_p - \Delta) = 0$, where $\Delta = 30$ eV and E_p is the centroid of the peak energy (see Fig. 1). In the present paper, we will also investigate how

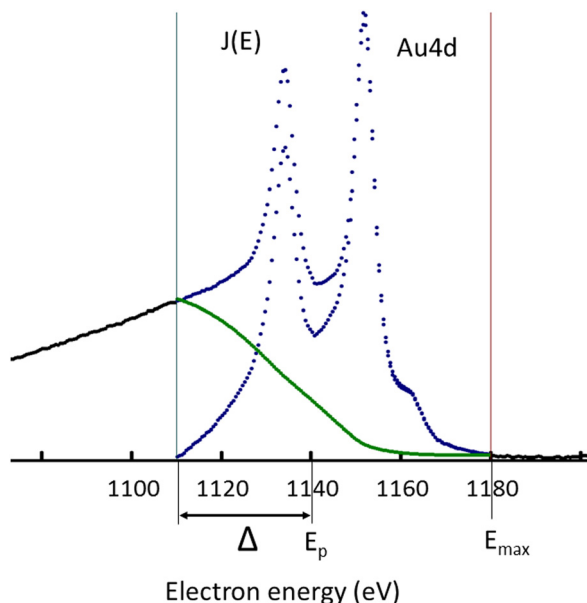


FIG. 1. (Color online) Definition of quantities used in the algorithm.

robust the algorithm is toward variations in Δ within the range from 20 to 40 eV. At the upper energy limit $f(E_{\max}) = 0$.

For $K(T)$, the following “Universal cross section” given by the expression¹²

$$B_1 \cdot K(T) = B_1 \frac{T}{(C + T^2)^2}, \quad (2)$$

with $C = 1643$ eV² is valid for most transition metals as well as for their alloys and oxides.¹² For solids such as Al, Si, SiO₂, and polymers that have a more narrow cross section, it is a better approximation to use

$$B_1 \cdot K(T) = B_1 \frac{T}{(C - T^2)^2 + D \cdot T^2}, \quad (3)$$

where C and D are constants characteristic of the solid.¹²

From $f(E)$, the peak area is determined

$$A_p = \int_{E_p - \Delta}^{E_{\max}} f(E) dE. \quad (4)$$

To make an absolute determination of the amount of substance $\text{AOS}_{3\lambda}$, it is necessary to calibrate the instrument. This may be done by analysis of the spectrum for the same XPS peak from a solid with homogeneous distribution of atoms of density c_H . Let B_0 and A_p^H denote the B_1 and A_p values obtained from analysis by Eqs. (1) and (4), respectively, of the spectrum from the homogeneous reference. If a reference spectrum is not used then $B_0 \simeq 3200$ eV² may be applied as an approximate value.

Now calculate

$$L = \frac{B_1}{B_0 - B_1} \lambda \cos \theta \quad (5a)$$

and

$$L^* = L/3, \quad (5b)$$

where θ is the angle of emission with respect to the surface normal.

The amount of substance within the outermost 3λ is⁷

$$\text{AOS}_{3\lambda} = \frac{L + \lambda \cos \theta}{1 - e^{-\frac{3(\lambda \cos \theta + L)}{L \cos \theta}}} \cdot \frac{A_p}{A_p^H} \cdot c_H \cdot (1 - e^{-3\lambda/L}). \quad (6)$$

It is often convenient to define an equivalent film thickness d by

$$d = \frac{\text{AOS}_{3\lambda}}{c_H}, \quad (7)$$

which is the thickness of the material if it is distributed as a uniform film with the same atom density as in the reference. If c_H is in (atoms/nm³) and λ is in (nm), then $\text{AOS}_{3\lambda}$ is in (atoms/nm²) and d is in (nm). Note that this is the unit in which $\text{AOS}_{3\lambda}$ is given in the rest of the present paper.

It may be instructive for the interpretation of the results to know the origin of this algorithm, which is briefly as follows.⁷ The algorithm was derived by approximating all kinds of depth distributions to an exponentially decaying or increasing function with decay length L , which can be positive or negative. So the algorithm determines that exponential profile which best accounts for the measured peak intensity and peak shape. This means that the value of L and therefore the value of L^* gives a rough indication of the in-depth distribution of atoms. In practice, it has been found that the rules in Table I may be applied.^{7,8}

The approximate validity of the rules in Table I and of the accuracy of the determined $\text{AOS}_{3\lambda}$ has so far been demonstrated by comparison to experiments in several papers,⁷⁻¹¹ but a systematic investigation of the range of validity has not been made. It is the objectives of the present paper to make a detailed test of the range of validity of the rules in Table I as well as to determine how accurate $\text{AOS}_{3\lambda}$ is determined for a wide range of atom depth distributions.

To this end, we simulate model XPS spectra corresponding to depth distributions where atoms are present as a thin film on top of a substrate, as a substrate covered by a thin layer, and as a thin layer positioned at various depths underneath a surface.

III. MODEL SPECTRA FOR DIFFERENT CLASSES OF NANOSTRUCTURES

The energy distribution in the background of inelastically scattered electrons will be more smeared out for wide than for narrow XPS peaks, and therefore, there will be less information in a wide XPS peak. We can therefore expect the accuracy of the algorithm to be worse for wide peaks. To get the most general measure for the validity of the algorithm, we will therefore explore the worst case, i.e., rather than choosing a narrow peak, we study spectra from one of the widest peak structures met in practical XPS, i.e., Au4d consisting of the Au4d5/2 and Au4d3/2 peaks, which are separated by ~ 20 eV.

Sets of XPS spectra were simulated for three classes of nanostructures: overlayers of Au on a substrate, a substrate of pure gold covered by an overlayer of varying thickness, and for a 5 \AA thick layer of Au atoms buried at varying

TABLE I. Rules to estimate the depth distribution of atoms from L .

	L^*	Depth distribution
Rule Ia	$0 < L^* \leq 1$	Most atoms are at depths $< \lambda$
Rule Ib	$-1 \leq L^* < 0$	Most atoms are at depths $> \lambda$
Rule Ic	$2 \leq L^* \leq 1$	Approximately constant
<i>If the same peak from two samples have values L_1^* and L_2^*, then</i>		
Rule II	$0 < L_1^* < L_2^*$	Atoms are surface localized in both samples and the atoms are at more shallow depth in sample 1 than in sample 2
Rule III	$L_1^* < L_2^* < 0$	Atoms are primarily in the bulk of both samples and at deeper depth in sample 2 than in sample 1

depths underneath the surface. The simulated spectra were calculated with the Quases-Generate software package⁶ using normal emission, $\lambda = 15 \text{ \AA}$ and the inelastic electron scattering modeled by the Universal cross section [Eq. (2)]. The Quases-Generate software requires an input spectrum from a homogeneous material, and we have used an Au4d spectrum recorded from a pure Au foil. We have chosen the same value of $\lambda = 15 \text{ \AA}$ for both the Au layer and the host material. This is convenient but is not a limitation to the validity of the test. For the analysis by Eq. (1), the Universal cross section [Eq. (2)] was used. In analysis of experimental spectra, this cross section is a good approximation for most transition metals, their oxides and alloys. For analysis of spectra from materials like Al, Si, SiO_2 , and polymers a three parameter Universal cross section [Eq. (3)] will be more accurate.¹² Note that in the following analysis, we give in some cases the depth measured in \AA and in other cases in units of λ .

IV. RESULTS AND DISCUSSION

In the present analysis, a simulated spectrum from pure Au was also included in the analysis. From analysis of this spectrum, the values B_0 and A_p^H were determined as described above. Each of the simulated spectra were analyzed by Eq. (1) and L^* and $\text{AOS}_{3\lambda}$ were determined from Eqs. (6a) and (6b).

A. Validity of the determined amount of substance $\text{AOS}_{3\lambda}$

Note that for convenience $\text{AOS}_{3\lambda}$ is in the following given in units of equivalent gold layer thickness [Eq. (7)].

Figure 2 shows $\text{AOS}_{3\lambda}$ determined by analysis of the simulated Au4d spectra from an Au overlayer of varying thickness d . The deviation from the true $\text{AOS}_{3\lambda}$ is quite small and amounts to less than $\sim 10\%$ over the full range of overlayer thicknesses.

Figure 3 shows the results of analysis of Au4d spectra from an Au substrate covered with an overlayer of varying thickness d . Here the true $\text{AOS}_{3\lambda}$ is $(3\lambda - d)$. The overall deviation is less than $\sim 20\%$.

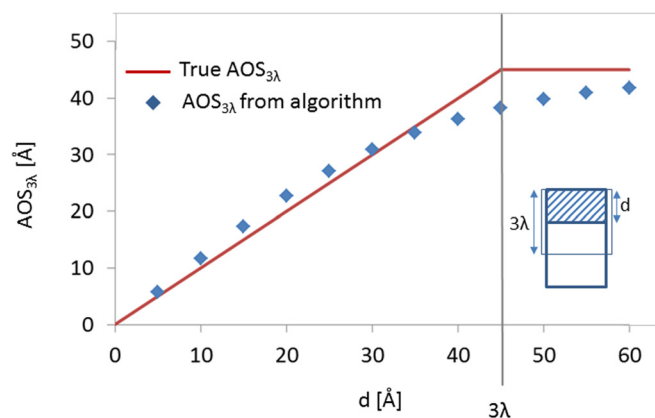


Fig. 2. (Color online) $\text{AOS}_{3\lambda}$ values resulting from analysis of Au4d spectra from overlayers of varying thickness d on a substrate. Also shown is the true $\text{AOS}_{3\lambda}$.

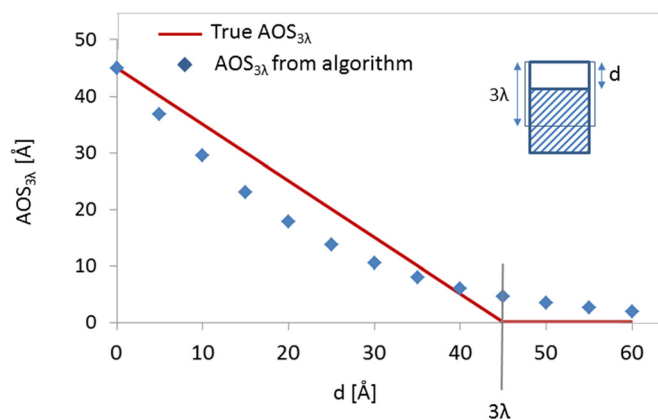


Fig. 3. (Color online) As Fig. 2 but for an Au substrate with an overlayer of increasing thickness d .

Figure 4 shows the results for a 5 Å layer of Au placed at varying depths underneath the surface. Here the deviation from the true $AOS_{3\lambda}$ is larger. For depths up to $\sim 1.5\lambda$, the deviation is less than 20%, while it is considerably larger for depths $2\lambda < d < 4\lambda$.

B. Validity of the rules for atom depth distributions

Figure 5 shows L^* values determined by analysis of the simulated spectra from an Au overlayer of varying thickness d (as in Fig. 2). The L^* values increase monotonically from ~ 0 for the thinnest layers to ~ 2 for thickness $d = 3\lambda$. Comparing this result to Table I, it is seen that it is in exact agreement with Rule II. The results are also in agreement with Rule Ia (since for all $d < 2\lambda = 30$ Å, we have $0 < L^* < 1$). For all spectra with thickness $d > 3\lambda$ (which corresponds to a constant concentration in the full $0-3\lambda$ depth range), we see from Fig. 5 that $L^* > 2$. This is in full agreement with Rule Ic.

Figure 6 shows the determined L^* values for a substrate of Au atoms covered by an overlayer of varying thickness d (as for Fig. 3). The values increase monotonically from $L^* = -2.1$ for $d = 5$ Å to $L^* = -0.57$ for $d = 45$ Å ($= 3\lambda$). This is in full agreement with Rule III in Table I. For all $d > 15$ Å ($= \lambda$), it is seen from Fig. 6 that $-1 < L^* < 0$.

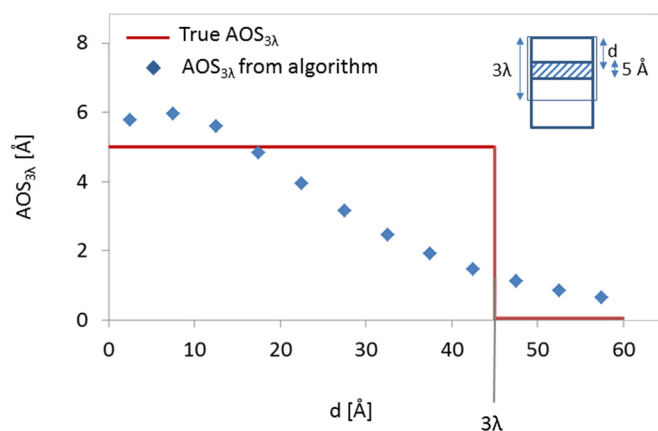


Fig. 4. (Color online) As Fig. 2 but for an Au layer of 5 Å thickness placed at varying distance d underneath the surface.

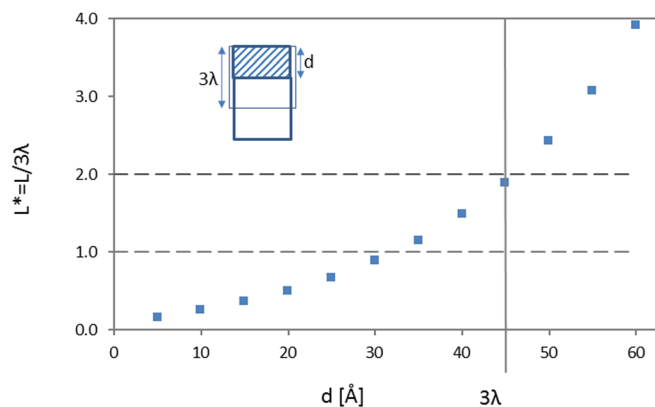


Fig. 5. (Color online) L^* values resulting from analysis of Au4d spectra from overlayers of varying thickness d on a substrate.

This is in perfect agreement with Rule Ib. For overlayer thickness $d < 5$ Å, we find that $L^* < -2$. This is in reasonable agreement with Rule Ic because in this case most of the atoms in the $0-3\lambda$ depth region are roughly homogeneously distributed.

Figure 7 shows the determined L^* values for a 5 Å Au layer, which is situated at increasing depths d in a matrix (as in Fig. 4). For $0 < d < 10$ Å, it is seen that $L^* > 0$ and it increases monotonically in agreement with Rule II and that $0 < L^* < 1$ in agreement with Rule Ia. For depths $d > 30$ Å, it is seen that $L^* < 0$ and it increases monotonically in agreement with Rule III. For all $d > 30$ Å ($= 2\lambda$), we see that $-1 < L^* < 0$, which is in agreement with Rule Ib. For 10 Å $< d < 30$ Å, the results are however in disagreement with Rule Ic.

C. Sensitivity of the algorithm to variation in the position of E_{\min}

In the above analysis, we have used $\Delta = 30$ eV; i.e., E_{\min} is chosen to be 30 eV below the centroid E_p of the peak structure. It is of interest to know how sensitive the results

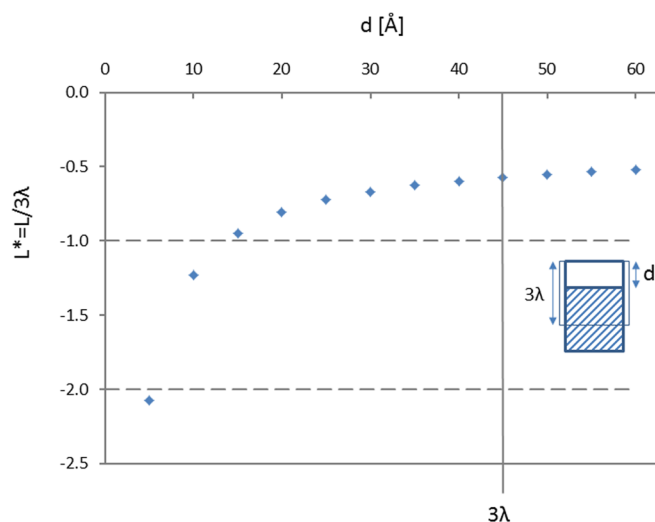


Fig. 6. (Color online) As Fig. 5 but for substrate with an overlayer of increasing thickness d .

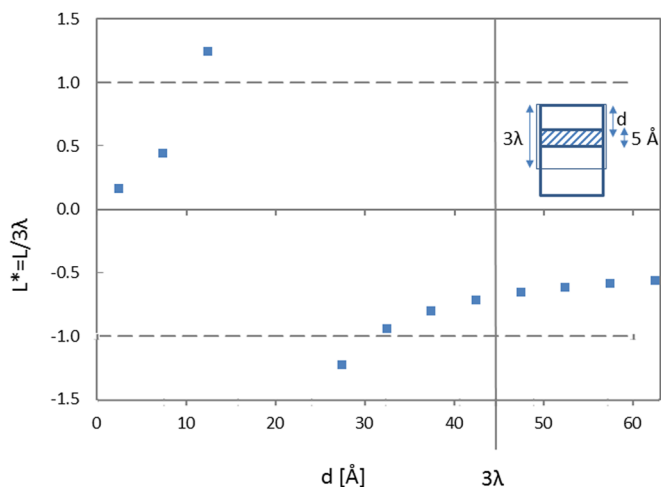


Fig. 7. (Color online) As Fig. 5 but for a layer of 5 Å thickness placed at varying distance d underneath the surface.

are to variations in the applied value for Δ . Thus, for automated data analysis, it is important to know how critical it is that an accurate value is used for the centroid E_p (a variation in E_p with constant Δ corresponds to constant E_p with a variation in Δ). It may also be a problem if there is an interfering peak ~ 30 eV below the peak in which case one could

avoid this peak by using a smaller value for Δ . On the other hand, one might be interested in knowing if the analysis is more accurate if the spectrum is analyzed over a wider energy range. To investigate these matters, we have therefore studied the result of using $\Delta = 20$ eV, 30 eV, and 40 eV, respectively.

The results for $\text{AOS}_{3\lambda}$ is shown in Fig. 8 for the three classes of depth profiles. It is seen that there is only a moderate dependence on Δ . For overlayers, using $\Delta = 40$ eV gives the smallest overall deviation from the true $\text{AOS}_{3\lambda}$ namely $\sim 5\%$ while the deviations are $\sim 10\%$ with $\Delta = 30$ eV and $\sim 15\%$ with $\Delta = 20$ eV.

For the XPS peak from an Au substrate covered with an overlayer [Fig. 8(b)], there is not much difference between the analysis using the three values of Δ and the overall error is in all cases $\sim 20\%$ although for $\Delta = 20$ eV the deviation is marginally larger than for 30 and 40 eV.

For a 5 Å Au layer placed at varying depths in a matrix [Fig. 8(c)], the results are practically the same for all $d > 15$ Å. For $0 < d < 15$ Å, the overall error is $\sim 5\%$ with $\Delta = 40$ eV and $\sim 15\%$ for $\Delta = 30$ eV and $\sim 30\%$ with $\Delta = 20$ eV.

Figure 9 shows the results for L^* . In general, the values are very similar although the exact values vary slightly with the chosen value for Δ . So the rules in Table I apply in general with the same accuracy independent of Δ . The difference is

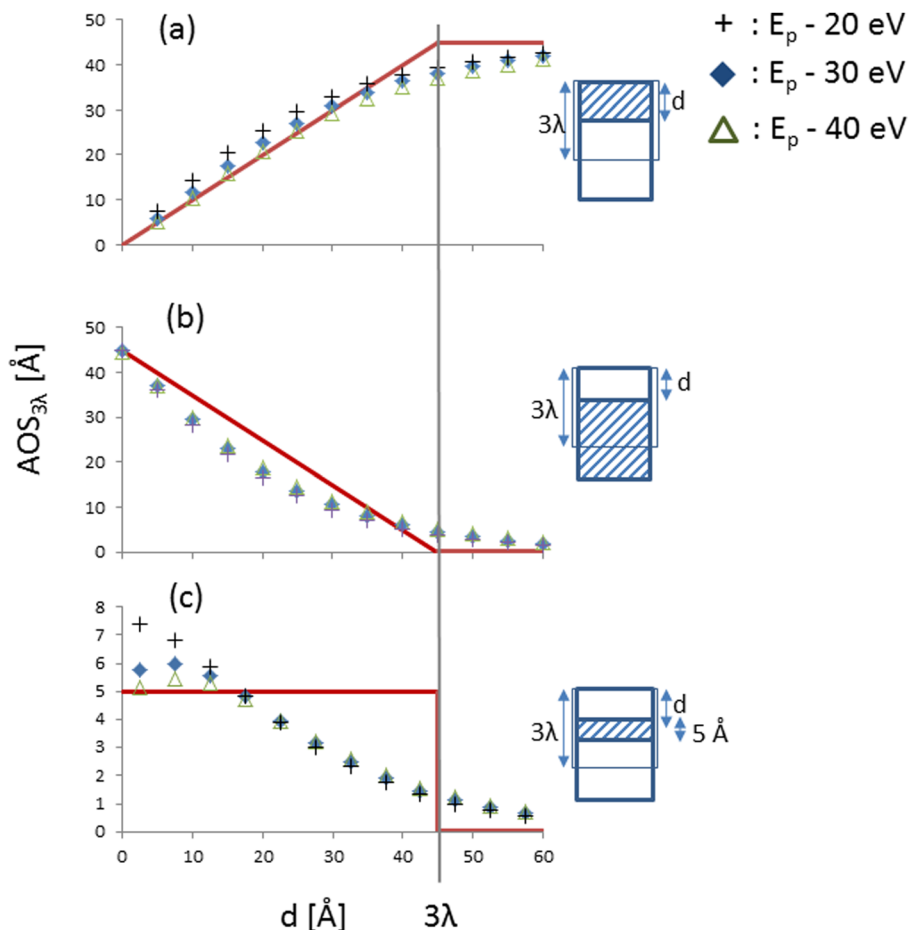


Fig. 8. (Color online) As Figs. 2-4 but for different values of $\Delta = 20$ eV, 30 eV, and 40 eV.

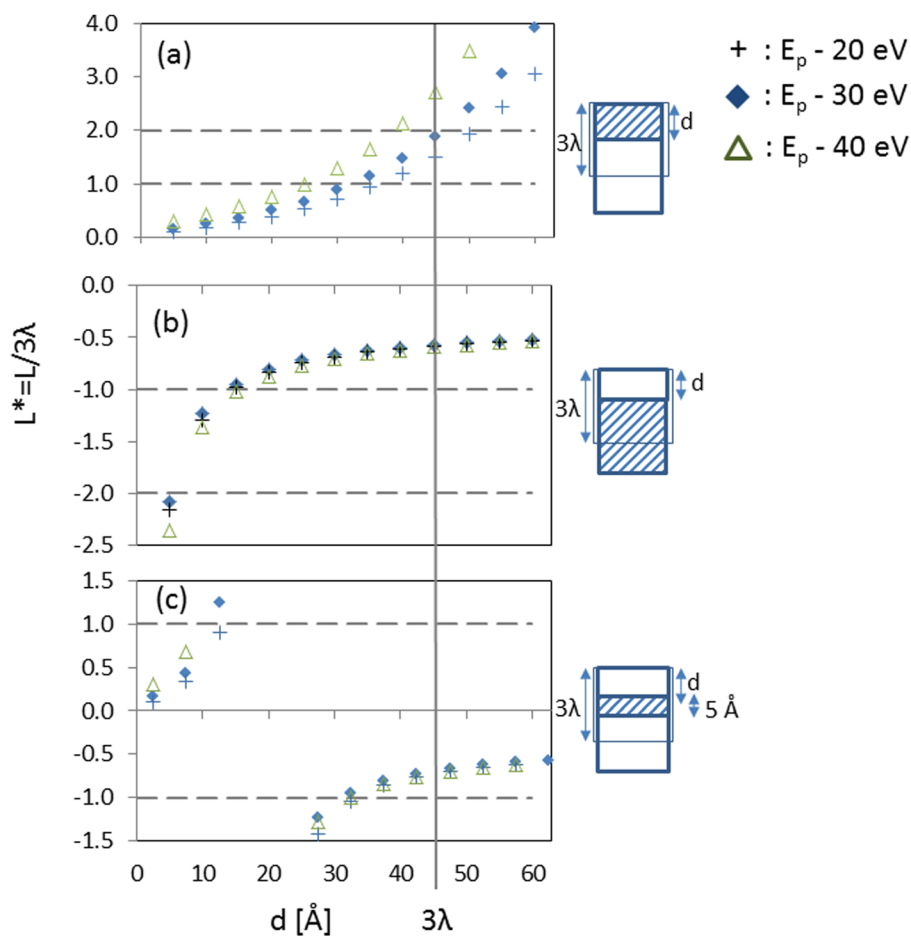


Fig. 9. (Color online) As Figs. 5–7 but for different values of $\Delta = 20$ eV, 30 eV, and 40 eV.

largest for overlayers in the upper panel in Fig. 9 where it is seen that the agreement with Rule Ia is slightly better with $\Delta = 40$ eV.

V. CONCLUSIONS

We have studied the validity of a previously published algorithm⁷ for automated XPS characterization of nanostructures, which involves the peak intensity as well as the background of inelastically scattered electrons. This was done by first simulating spectra for the Au4d peak structure with gold atoms distributed in the form of a wide range of nanostructures. The algorithm determines the number of atoms within the outermost 3λ of the surface, which is denoted AOS_{3λ}. It also determines a characteristic length L , which gives information on the depth distribution of atoms. A set of rules for this parameter were tested. In general, the AOS_{3λ} is found to be accurate within ~ 10 – 20% depending on the particular depth distribution of the atoms. The characteristic length L was also found to give unambiguous information on the depth distribution of the atoms for practically all cases and the validity of a previous postulated set of rules was confirmed. The results were found to be rather independent of

the spectral energy range (from 20 eV to 40 eV below the peak energy) used in the analysis.

ACKNOWLEDGMENT

Financial support from The Danish Research Council for independent Research—Natural Sciences was acknowledged.

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