

Plenary Lecture (Review)

# Novel Applications of Inelastic Background XPS Analysis: 3D Imaging and HAXPES

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(Received: May 3, 2017; Accepted: June 8, 2017)

Technological applications of nano-structured materials are steadily increasing and to create materials with optimized properties, it is of utmost importance to have non-destructive techniques to characterize elemental depth distributions at the *nm* scale. X-ray photoelectron spectroscopy (XPS) is ideal for this because it is sensitive on the nm depth scale and it is today widely used by industry. In the large majority of labs it is used within a formalism that relies on the measured peak intensities. In this paper we first point out the large uncertainties and the misleading results that result from such a formalism. We then review techniques that rely on analysis of a wider range of the energy spectrum around the XPS peak rather than just at the peak energy. This results in a much improved accuracy. It is first shown how a simple visual inspection of a survey XPS spectrum can be used to immediately get a rough picture of the nano-structure of the sample. For more accurate quantitative analysis, algorithms have been developed which are implemented in the QUASES (Quantitative Analysis of Surfaces by Electron Spectroscopy) software. The application of this software in practical analysis is discussed. Then it is discussed how this can be combined with synchrotron radiation at high photon energies (HAXPES) to provide analysis of structures buried more than 50 nm in a stack. Finally we discuss a newer algorithm which is less accurate but which has the advantage that it is suitable for automated XPS analysis for determination of the structure. This can be useful for routine analysis and has also been applied to 3-dimensional imaging of surface nano-structures.

## 1. Introduction

Industrial applications of nano-structured materials are steadily increasing and to create materials with optimized properties, it is of utmost importance to have non-destructive techniques to characterize elemental depth distributions at the *nm* scale. About 30 years ago it was pointed out [1] that the peak shape in X-ray photoelectron spectroscopy (XPS) depends strongly on the depth of the corresponding element in the solid. In the following years algorithms were developed to take advantage of this for improved quantitative XPS analysis of nano-structures at surfaces. The final formalism was summarized in ref. [2]. In the present paper, the limitation of traditional XPS analysis, which relies on peak areas, is first discussed. Next we illustrate how an improved analysis is obtained by analysis of both the intensity and the peak shape in a wider energy range below

the peak energy.

## 2. The problem with traditional XPS analysis

It is well established [2,3] that the measured XPS-peak intensity, which originates from excited intensity  $I_0$  of atoms at depth  $z$  measured at an angle  $\theta$  to the surface normal, is attenuated with the distance  $z/\cos\theta$  the electron travels before reaching the sample surface

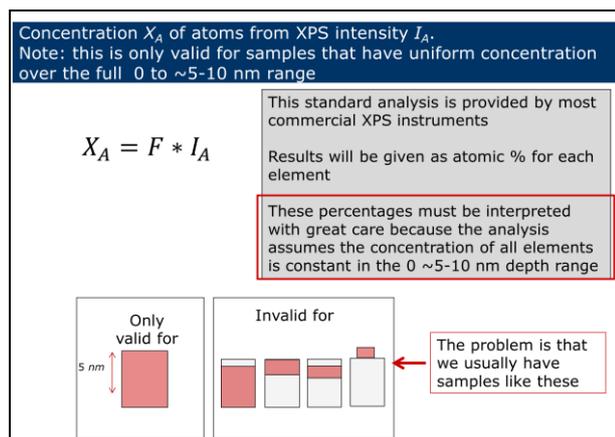
$$dI_A = I_0 * X_A(z) dz * e^{-\frac{z}{\lambda \cos\theta}} \dots\dots\dots(1)$$

Here  $X_A(z)$  is the atomic concentration of atoms  $A$  in a thin layer  $dz$  at depth  $z$ .

In traditional quantitative XPS analysis [3] it is assumed that the concentration of atoms  $X_A$  is constant in the outermost ~ 5 nm of the sample and integration of eq.(1) gives

$$X_A = F * I_A \dots\dots\dots(2)$$

where  $F$  is a factor which includes the effects of the

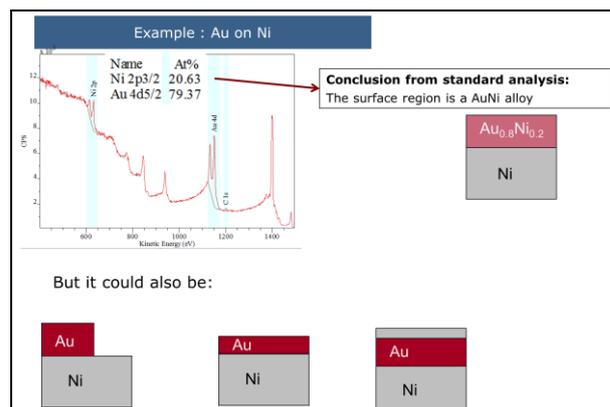


**Fig. 1** (color online) The standard XPS analysis which traditionally is used in most labs.  $F$  is defined in the text. This illustrates the limitations of the formalism for practical surface analysis since it is not valid for many samples of practical interest.

elastic and inelastic mean free path, the photoionization cross section, characteristics of the spectrometer and renormalization corresponding to the intensity from the other elements in the sample. Within this model, the surface concentration is proportional to the measured peak intensity (or peak area)  $I_A$ .

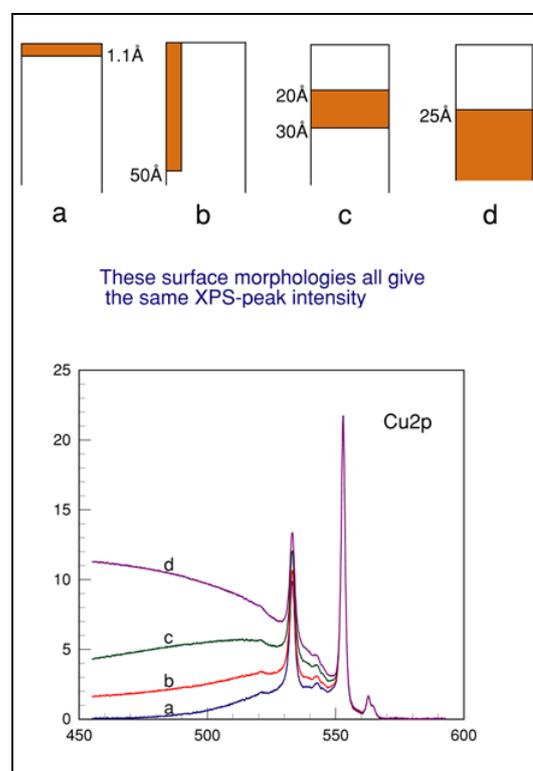
Most quantitative analysis is still today done with this method. But it is worth noting the limitations of the validity which are summarized in Fig.1. As an example that illustrates the problems with this formalism, Fig. 2 shows the spectrum of a sample which consists of Au and Ni atoms. Traditional analysis with eq.(2) (performed in this case with the CasaXPS software [4]) gives the composition table shown in the inset of Fig.2 (there is a small C contamination which has been ignored). The conclusion is that the surface region consists of an alloy with composition  $Au_{0.8}Ni_{0.2}$ . But as illustrated in Fig. 2, the same ratio of Au4d to Ni2p peak intensities could originate from other structures where the surface concentration of Au can be anywhere from 0 to 100%.

The problem with eq.(2) is that it is only valid when the surface region is homogeneous. However it is in practice very rare that the samples are homogeneous in the outermost few nm. In fact, the reason why we use XPS is that the sample composition is inhomogeneous on the nano-meter depth scale. For practical samples, the concentration varies often a lot in the topmost few nano-meters and eq.(2) is invalid for quantitative analysis of such samples. So, real samples are typically inhomogeneous in the 0-10 nm depth range.

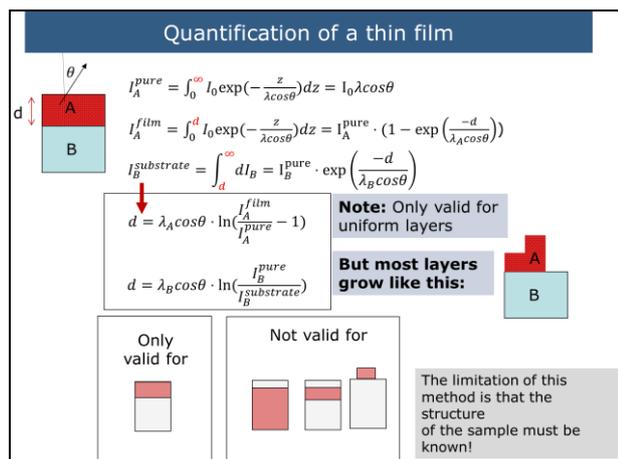


**Fig.2** (color online) Traditional XPS analysis of a sample based on peak areas.

The origin of the problem is illustrated in Fig. 3 [5] which shows model spectra with identical Cu 2p<sub>3/2</sub> photoelectron peak intensities that are obtained from four Cu/Au samples with very different morphologies. This arises because the peak intensity is attenuated with depth as in eq.(1). So the observed Cu2p peak intensity can either come from a 1.1 Å thick Cu layer on an Au substrate, from a 50 Å thick  $AuCu_4$  alloy, from a 10 Å thick layer at 20-30 Å depth or from a Cu substrate covered with a 25 Å thick Au overlayer.



**Fig. 3** (color online) Cu2p spectra from Cu atoms with different concentration distributions in a Au matrix [5] calculated with the QUASES software [6]

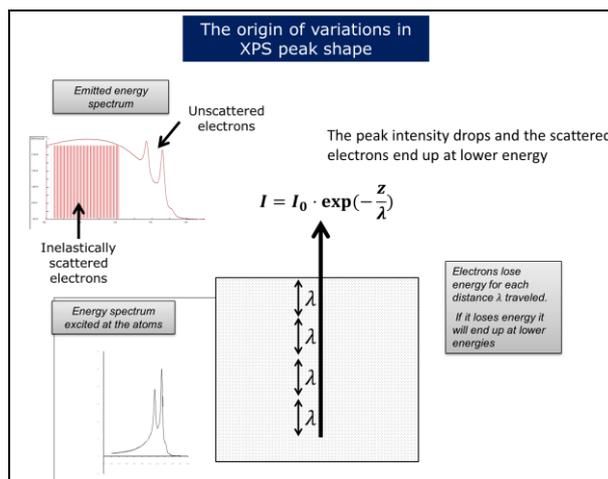


**Fig. 4** (color online) This illustrates that it is easy to correct for the attenuation effect if the structure is known. However we do the XPS because we don't know the structure. So this procedure is in general not possible.

This illustrates that a meaningful quantification based on peak intensities is not possible unless the attenuation factor is taken into account.

It is a very simple calculation to correct for this attenuation if the morphology of the sample is known. The mathematics for analysis of a thin film is shown in Fig.4. Calculations can easily be done for the other morphologies shown. The problem is however that this analysis procedure is only valid if one knows the morphology of the sample before the analysis is done.

However we never know the structure. It is exactly because we don't know the structure of the sample that we do XPS analysis. Sometimes we may think that we

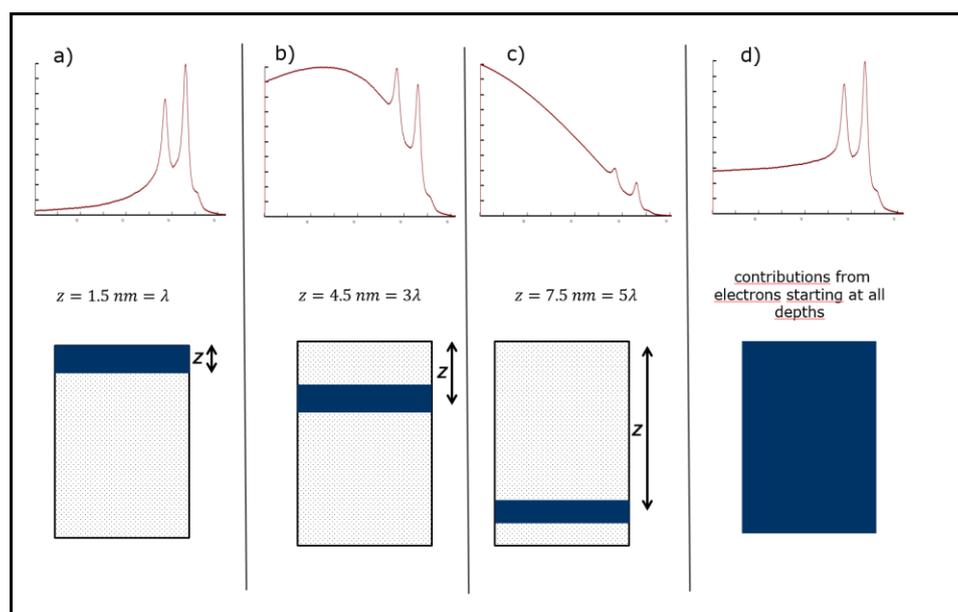


**Fig. 5** (color online) Illustrates the origin of and interplay between variations in peak intensity and peak shape.

know the structure, if e.g. atoms A are deposited on a sample consisting of B atoms. But the growth is likely to proceed with the formation of islands and we may also have diffusion or chemical reactions between the atoms. Therefore it is not possible in general to use this approach to correct for the attenuation effect.

### 3. Improved quantification by analysis of the peak shape

Looking again at Fig 3, it is clear that the XPS peak shape varies strongly with the composition. This is because the photo-excited electrons that are scattered away from the peak energy ends up at lower energies in the spectrum as illustrated in Fig. 5. This explains the varia-

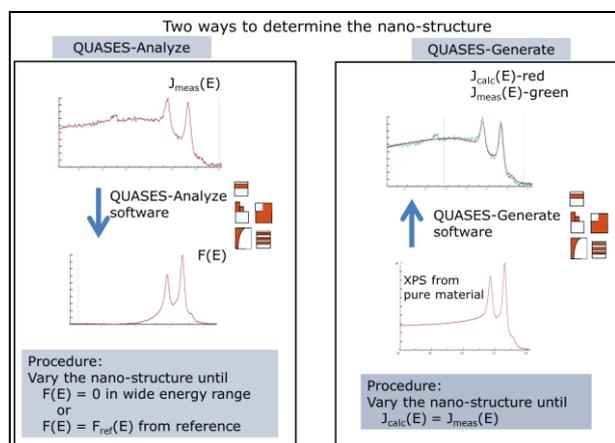


**Fig.6** (color online) Model Au4d XPS spectra calculated with the QUASES software [6] for different distributions of Au atoms. The host material has an IMFP = 1.5 nm.

tions in peak shape in Fig. 3. Another set of model spectra for different depth distributions in a fictitious sample with  $\lambda = 1.5 \text{ nm}$  are shown in Fig.6. These characteristic changes in peak shape and intensity can be used to enhance the quantitative XPS analysis tremendously. The effect is huge and the intensity say 30 eV below the peak in Fig.3 varies by orders of magnitude for different structures. So by analysis of the peak shape it is easy to distinguish between the structures in Figs. 3 and 6. This is the philosophy behind the XPS analysis which is done with the QUASES software [6]. However even a simple visual inspection of a survey spectrum gives you valuable information once you have trained your eye.

#### 4. Qualitative analysis by visual inspection of the survey spectrum

Now let us eyeball the shape of the Ni2p and Au4d peaks in the spectrum in Fig. 2 and compare to the cases in Figs 3 and 6. It is clear that Au4d has a relatively small increase in intensity below the peak energy compared to the intensity above the peak. This resembles the spectra in Figs. 3a and 6 a. The Au atoms must therefore primarily be in the top layer. In contrast, Ni2p has a large increase in intensity below the peak energy which resembles the situation in Figs. 3d and 6b and the Ni atoms must therefore primarily be in deeper layers. So this simple visual inspection gives immediately the main structure of the sample: Au is on top and Ni is below. This is exactly what is expected because this particular sample was made by depositing Au on top of a Ni substrate. But note that this qualitative analysis is totally independent of this information.



**Fig. 7** (color online) The schematics show the two different approaches for quantitative XPS analysis with QUASES software.

With some training it becomes easy to visually determine the rough structure of the sample from such a simple comparison of peak shapes to the model spectra in Figs. 3 and 6. The survey spectrum is all that is needed for such a qualitative analysis. Note that the energy resolution is not essential and the survey spectrum can with advantage be taken with a low energy resolution (high pass energy) to increase the throughput of the spectrometer and a corresponding decrease in measuring time.

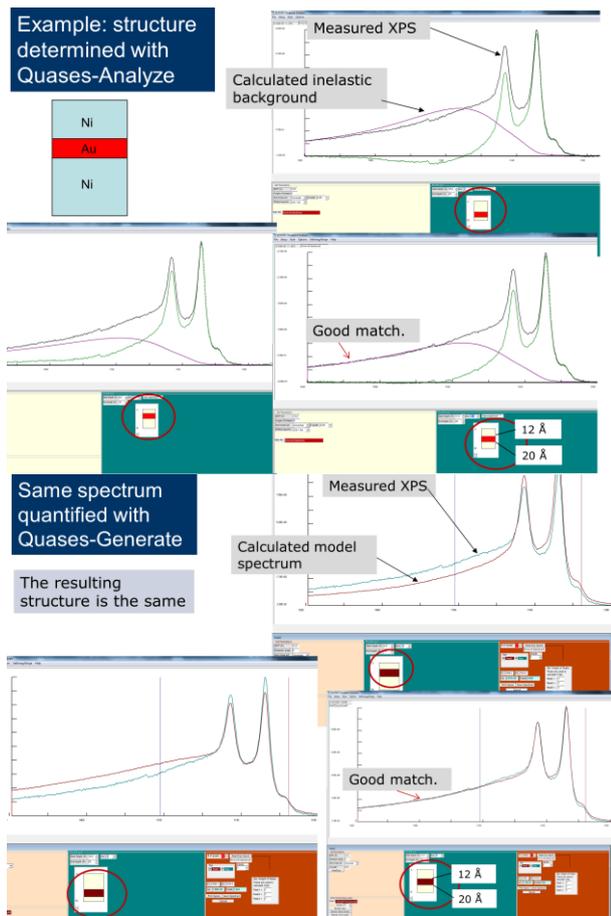
#### 5. Accurate quantification with QUASES software to model the peak shape

An accurate quantitative determination of the structure of a sample can be obtained by performing a detailed calculation of the energy loss processes. This is what is done in the QUASES-XPS software [6]. The only input in the software is  $\lambda$  and the inelastic scattering cross section. The inelastic scattering cross section can be taken from the Universality classes [7] or from cross sections for specific materials; these are included in the software. The IMFP  $\lambda$  can be taken from tables [8] or the NIST database [9] or it may be calculated from the TPP2M formula e.g. by use of the free QUASES-IMFP-TPP2M software [6].

The principle in the analysis is illustrated in Fig. 7. In QUASES-XPS, there are two ways to analyze the spectrum. With QUASES-Analyze the background corresponding to an assumed structure is calculated and subtracted from the spectrum. Thus, the structure of the sample is varied and the software calculates and displays the corresponding background. This is directly compared to the experimental spectrum. The correct structure is found when the background matches the measured spectrum in a wide energy range below the peak. If the difference spectrum is also compared on an absolute scale, to the spectrum from a reference sample then the concentration of the atoms in the structure can also be determined.

With the QUASES-Generate software, a model spectrum is calculated with an input spectrum from a pure reference sample. The structure is varied until the model spectrum fits the measured spectrum on an absolute scale.

This background analysis method is sensitive to depths of  $\sim 10 \lambda$  [10]. This is larger than the  $\sim 3\lambda$  which is usually quoted for XPS. The reason is that with



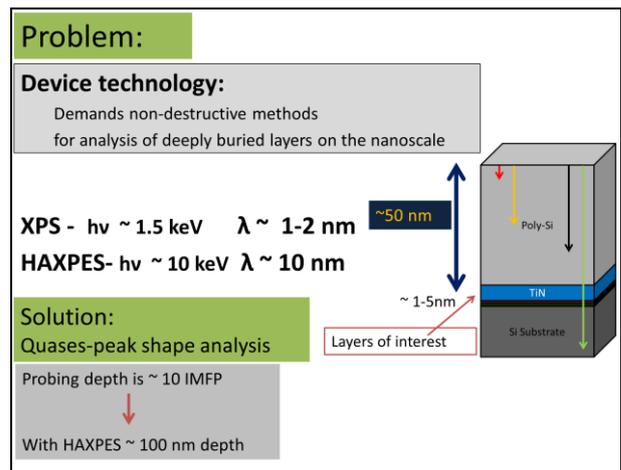
**Fig. 8** (color online) Analysis with the two softwares (see Fig. 7). The determined structure is identical as expected.

QUASES peak shape analysis we probe not only the peak intensity but also the inelastically scattered electrons. Those electrons originate from larger depths (see Fig. 5) which explains why the probing depth is considerably larger..

Fig. 8 shows an example of analysis with the two methods. They give the same result as expected. The advantage of using QUASES-Generate is that overlapping peaks (contributions from up to three peaks can be modelled simultaneously) can be analyzed which is not possible with QUASES-Analyze. The method has been applied to study numerous cases and a few are summarized in ref. [2].

## 6. Probing deeper with HAXPES

In many industrial samples the active part consists of thin nano-structures which may be buried deep in a stack as illustrated in Fig. 9. There is therefore a growing interest from industry to be able to do non-destructive analysis of layers that may be buried at depths > 50 nm

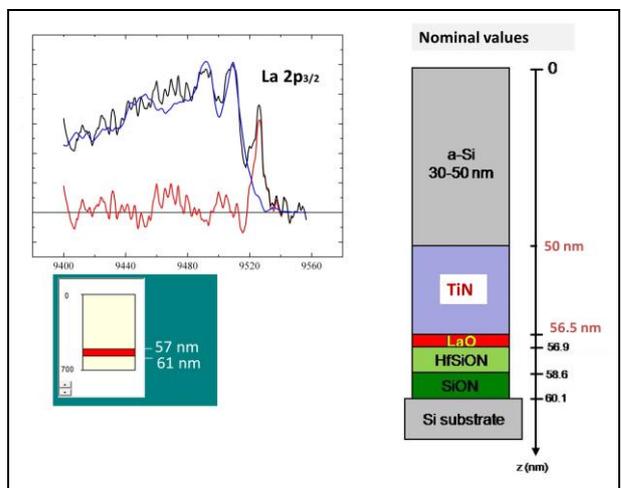


**Fig.9** (color online) There is a growing need for new non-destructive characterization techniques of nm thin layers buried deeply in a stack .ware.

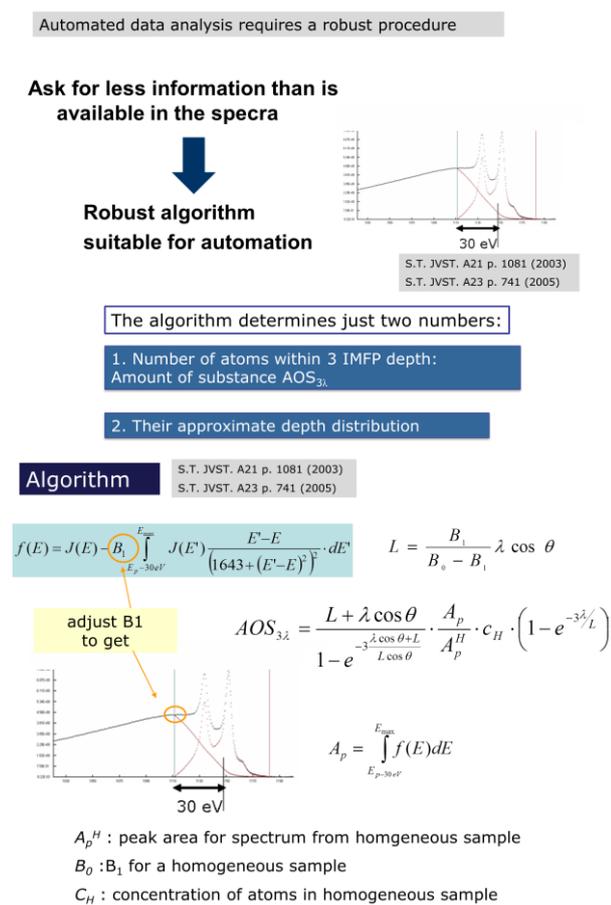
below the surface.

With traditional lab-XPS with  $AlK\alpha$  or  $MgK\alpha$  radiation sources, the kinetic energy of the emitted photoelectrons are in the range ~100 eV to 1400 eV. The corresponding IMFP ( $\lambda$ ) is in the range from 0.5 to 3 nm depending on the material and the XPS peak energy. QUASES-XPS analysis has a probing depth of  $\sim 10 \lambda$  [2,10] which gives a maximum probe depth of ~5 to 30 nm.

However with the increased availability of synchrotrons as well as high energy lab-XPS photon sources that provide high energy XPS (HAXPES) with photon energies ~10 keV or more, the inelastic mean free path for the corresponding XPS electrons is larger and this opens up for non-destructive analysis of layers at depths ~100 nm as illustrated in Fig.9. In fact it was recently shown [11] that combining QUASES with HAXPES depths up



**Fig.10** (color online) QUASES-HAXPS characterization of a La layer buried ~60 nm deep in a stack. From [12]



**Fig. 11** (color online) The algorithm for automated robust XPS analysis. The upper panel shows the idea and the lower panel the resulting algorithm [2, 13, 14].

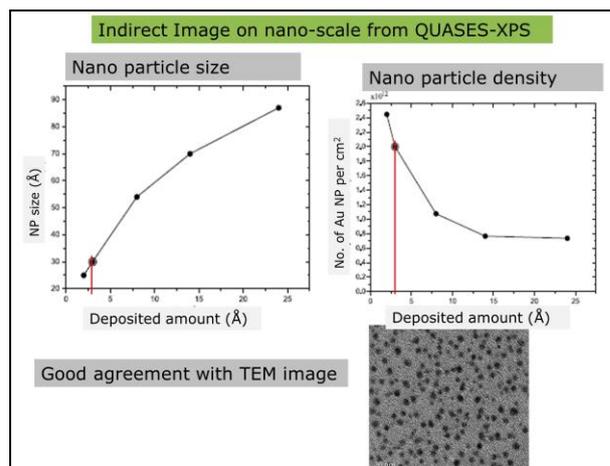
to  $20\lambda$  can be studied. The reason for the larger probing depth is that the HAXPES peaks can often be followed over an energy range of many hundred eV and the further away from the peak, the deeper is the origin of the electrons (see Figs.5 and 6).

Fig. 10 shows an example where a thin La layer buried ~60 nm in a stack has been accurately analyzed with QUASES-HAXPES analysis [12].

### 7. Algorithm for automated XPS analysis

Automated analysis is always of high interest to industry because this allows more spectra to be analyzed cheaply and fast. Automation will also allow non-specialists to do the analysis. A key quality of any automated procedure is robustness: small mistakes in the assumptions should not lead to large deviations in the result of the analysis.

With QUASES analysis it is possible to get quite detailed information on the morphology of the sample.



**Fig. 12** (color online) Indirect imaging from QUASES analysis whereby the NP size and density is determined. [15]

However to get reliable results the operator must be careful in evaluating the details. It is clear that the more details about a structure we want to determine, the more critical it is to do a careful and skilled analysis. The trick is therefore to ask for less information than what is available in the spectra. Some years ago, Tougaard developed an algorithm for that [13]. The resulting formalism is summarized in Fig. 11. As shown in the top panel of Fig. 11, rather than attempting to determine the detailed nano-structure of the sample, the ambition of this algorithm is to determine just two numbers from the peak analysis: the number of atoms within the depth  $3\lambda$  and their approximate depth distribution characterized by the value of  $L$ .

The algorithm is illustrated in the lower panel of Fig. 11 and shows the simplicity of the procedure: the background is fitted at a single energy point below the peak rather than over a large energy range (as with QUASES). This is something you can easily ask a computer to do which makes it well suited for automation.

The validity of the algorithm has been tested for both model [14] and experimental [13,15] spectra and it has been shown to give very robust results. It was even also applied for 3D imaging with very noisy spectra and proved to be useful for that (see below). It is somewhat strange that it has not yet been incorporated in commercial software systems for standard routine analysis to replace or supplement the traditional method based on peak areas.

### 8. Three dimensional imaging with XPS-background analysis.

With the smaller lateral size of industrial devices there is growing demand for non-destructive 3D-imaging of nano-structured samples. For this, automated data analysis is mandatory due to the huge number of spectra.

### 9. Indirect imaging with QUASES analysis.

With the QUASES analysis of deposited atoms on a substrate one can determine the height and coverage of the islands. If this is interpreted in terms of nano-particles (NP) where the size is the height, then it is a simple calculation to determine the NP size and density [16]. An example of such analysis of Au NP deposited on polystyrene is shown in Fig. 12. The determined NP size and density is in good agreement with the TEM image. But note that the XPS result can easily be obtained in a few minutes which is orders of magnitude faster than the time and effort involved in producing the TEM image. As shown in [16] it is also easy with QUASES XPS analysis to follow, in almost real time, the embedding of the NP into the polystyrene substrate during gradual annealing.

Pixel by pixel imaging with the automated algorithm

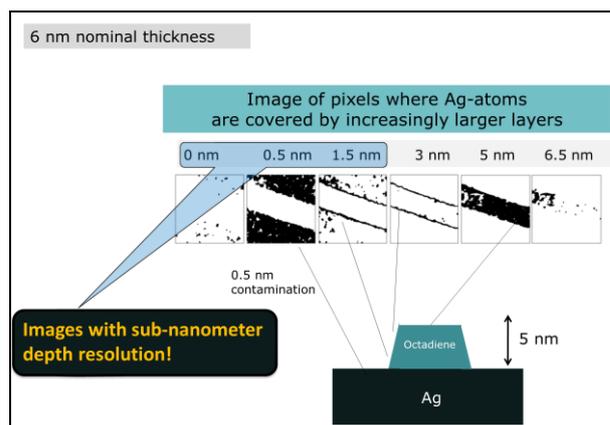
Since a surface image consists of spectra from thousands of pixels, pixel by pixel imaging is only possible with an automated procedure. The XPS-automated algorithm in Fig. 11 has been used for 3-D imaging. An example is shown in Fig. 13 where the algorithm was applied to XPS spectra taken at a lateral resolution of  $\sim 10 \mu\text{m}$  of a nominal 6 nm thick octadiene strip on a Ag substrate [2,17]. It is seen that the structure of the sample can be correctly identified layer by layer with sub nm depth resolution.

### 10. Conclusions

We have discussed different approaches to quantitative analysis of surface nano-structures by XPS. The weakness and limitations of the traditional analysis which is used in most labs were pointed out. We also showed that improved quantification is obtained when the spectrum in a wider range of energies is analyzed rather than just the intensity at the peak energy.

### 11. References

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**Fig.13** (color online) Images from pixels with different over-layer thickness for a nominal 6 nm thick octadiene strip on a Ag substrate. From [2, 16].

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## Discussions and Q&A with Reviewers

### Reviewer #1 Kyong Joong Kim (KRISS)

This is an important review paper for the useful applications of the routine XPS and HAXPES and recommended to be published without any revision. The applications of inelastic background XPS analysis will be very practical for 3-dimensional imaging of surface nano-structures.

#### [Q1\_1]

How wide range of energies at the XPS peak energy is required for analyzing the nano particle? Does the energy range depend on the analysis element or not?

#### [A1\_1]

The minimum energy range required is ~30 eV below the peak and 5-10 eV above the peak. But the accuracy is better when the range is ~60 eV below and 20 eV above the peak structure. It does not depend on the element.

#### [Q1\_2]

If the shape and the size of the Au NPs are sphere and uniform, is it possible to estimate the uncertainty in the measurement of the size of Au NPs spreaded on the surface of PS substrate?

#### [A1\_2]

Yes it is possible. The uncertainty on the height, and thereby on the size of the NP, is less than 10 %.

### Reviewer #2 Kazuhiro Yoshihara (Scienta Omicron Japan)

This is an informative review on the quantitative analysis of nano-structured surface and deeper layers (for HAXPES) by using “Tougaard background subtraction method”. This review also introduces the new automated algorithm for “Tougaard background subtraction method”, and this algorithm is useful for SASJ members to analyze three dimensional imaging of nano-structured materials. This review should be published.