Iterative fitting method for the evaluation and quantification of PAES spectra

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Abstract. The elemental composition of surfaces is of great importance for the understanding of many surface processes such as catalysis. For a reliable analysis and a comparison of results, the quantification of the measured data is indispensable. Positron annihilation induced Auger Electron Spectroscopy (PAES) is a spectroscopic technique that measures the elemental composition with outstanding surface sensitivity, but up to now, no standardized evaluation procedure for PAES spectra is available. In this paper we present a new approach for the evaluation of PAES spectra of compounds, using the spectra obtained for the pure elements as reference. The measured spectrum is then fitted by a linear combination of the reference spectra by varying their intensities. The comparison of the results of the fitting routine with a calculation of the full parameter range shows an excellent agreement. We present the results of the new analysis method to evaluate the PAES spectra of sub-monolayers of Ni on a Pd substrate.

1. Introduction
Positron annihilation induced Auger Electron Spectroscopy (PAES) is known as an analysis method with outstanding surface sensitivity [1], [2]. Auger electrons are emitted with an element-specific energy from ionized atoms in a radiation-free transition. Low energy positrons from the positron source NEPOMUC with an energy of less than 20 eV are used to ionize an atom and induce the Auger process [3]. For this technique, the vast majority of the Auger electrons originate from the topmost atomic layer of the sample [4], allowing the investigation of the elemental composition of the surface layer. So far, there is no standard evaluation method for PAES spectra as implemented in e.g. CasaXPS for the spectra of X-ray induced photo electron spectroscopy. Hence, the evaluation of PAES spectra is of great importance for quantification and the interpretation of the results.

2. Evaluation of PAES spectra
Before going into detail of the evaluation, the main components of the PAES spectrum will be explained. A typical PAES spectrum is shown in Figure 1. In addition to the outstanding surface sensitivity of PAES using low energy positrons of some eV, a second advantage is that the Auger transitions are free from secondary electron background. Low energy Auger transitions have a FWHM of several eV, which results from the broad energy distribution of the valence band and the lifetime of the states involved. Besides, the Auger peak of the according transition shows a low energy tail of inelastically scattered Auger electrons. A very low electron background...
Figure 1. PAES survey spectrum of polycrystalline Cu showing the main contribution to a PAES spectrum: Due to the low energy of the incoming positrons of only \( \sim 20 \text{ eV} \), the Cu M\(_{2,3}\)VV-Auger transition is free from secondary electron background. The Auger transition itself shows a tail of inelastically scattered Auger electrons with lower energy. A very low electron background results from scattered Auger electrons from transitions at higher energies and appears as a constant contribution to the spectrum.

Figure 2. First approach for the quantification of PAES spectra: Energy intervals (ROIs) around the Auger peak positions are defined wherein the events are counted. For this, the spectra of the pure elements are necessary for calibration. The scattered Ni Auger electrons in the Pd ROI have to be taken into account. Therefore, this weighted fraction of scattered Ni Auger electrons is subtracted from events in the Pd ROI to not overestimate the Pd contribution in the spectra.

2.1. Counts in ROI

In a first approach to quantify the contribution of each element to the PAES spectra, the events in fixed energy Region of Interest (ROI) around the Auger peak positions were summed up. Each ROI was set to a width of 8 eV corresponding to the FWHM of a Gaussian fit of the Auger peaks. For this purpose, PAES spectra of the pure elements were recorded and used as reference spectra for calibration. For several reasons, the Auger transitions do not appear as sharp lines in the recorded spectra. Especially, the low energy tail, which stems from inelastically scattered Auger electrons, can extend to another Auger peak with a lower energy spuriously pretending a higher intensity of this transition. In the measurements discussed here, scattered electrons from the Pd N\(_{2,3}\)VV transition at 78 eV disturb the Ni M\(_{2,3}\)VV and the Pd N\(_{2,3}\)VV transitions at 61 eV and 43 eV, respectively. However, this is a rather small effect due to the low core annihilation probability for the Pd 4s electrons, so the contribution to the background is negligibly small. Further, the Ni M\(_{2,3}\)VV transition leads to a significantly increased Pd N\(_{2,3}\)VV peak. For the data analysis, the amount of the scattered electrons in the respective ROIs of the lower energy transitions originates from scattered Auger electrons from transitions at higher energies and appears as a constant contribution to the spectrum. Conventional AES uses electrons or X-rays with some keV to induce the Auger process. These high energies lead to a large secondary electron background, especially in the range of the low energy Auger transitions, which are most surface sensitive in conventional AES. For this reason, usually the derivative of an AES spectrum is shown, to make the peaks visible but a quantitative analysis of the spectra is almost impossible. The initialization of the Auger process using positrons overcomes all these disadvantages, the spectra don’t need to be differentiated and a quantification becomes possible.
2.2. Approximation by reference spectra

To overcome the special handling of scattered Auger electrons, a new approach to quantify the spectra was used. The recorded data $M$ of the compound is reproduced by the function $F$, which is a linear combination of independently scaled fractions of the reference spectra $R$ of the pure elements $X$ and $Y$ [5]:

$$F(i) = \alpha \cdot R_X(i) + \beta \cdot R_Y(i)$$

(1)

The reference spectra $R_j$ were recorded in advance with the same measurement parameters. As a figure of merit, the fit is characterized by the value $R$ which represents the difference between

peaks was determined from the reference materials and subtracted as shown for Pd in Figure 2.

Figure 3. Illustration of the first steps of the minimization algorithm using the example of 0.5ML Ni on Pd. Starting from the left, the plots show the reference spectra of pure Ni (yellow) and pure Pd (green) and the measured spectrum of the compound (black). In the first iteration step, the scaling factor $\alpha$ of Ni is varied to minimize the difference $R$ (cyan) between the measured spectrum and the fit (red). In the second step, the Pd scaling factor $\beta$ is varied, while $\alpha$ is kept constant. Subsequently, Ni is varied again, while Pd is fixed.

Figure 4. Result of the approximation of the measured data by reference spectra. Left: The measured spectrum (black) is fitted (red) by independent scaling of the spectra of pure Ni (yellow) and pure Pd (green) in order to minimize the difference $R$ (cyan) between the measured spectrum and the fit. Right: By plotting the $R$ value for all combinations of the scaling factors $\alpha$ and $\beta$ for Ni and Pd respectively with a step size of 0.01, it can be shown that the result of the new fitting procedure corresponds to the global minimum for the full parameter range. The minimum of $R$ is indicated by the red dot.
the recorded data and the fit function. This value is minimized in the fitting procedure.

$$R = \sum_i (M(i) - F(i))^2$$

(2)

It is not a requirement that the sum of the scaling factors has to be one. This condition would presuppose that the line shape of an Auger transition is not influenced by the presence of another element, or by chemical bonding. For this reason, the scaling factors are varied independently. For the fitting procedure, a constant background represented by the minimum value is subtracted from each spectrum and all spectra are normalized to one. Figure 3 illustrates the first few steps of the iteration on a 0.5 ML cover layer of Ni on a Pd substrate. Initially, the measured data and the reference spectra of pure Ni and Pd are shown. Then, the algorithm starts to vary the scaling factor \(\alpha\) for the Ni reference to minimize the difference \(R\) between data and fit. In the next step, the scaling factor \(\beta\) for Pd is varied to minimize \(R\), while the scaling factor \(\alpha\) for Ni is kept constant. After this, again the Ni fraction is varied and Pd is kept constant. Up to now, the iteration is executed 20 times, though no reduction of the \(R\) value is found any more after about ten iterations for most spectra. For a faster data evaluation, an abort criterion will be implemented, to stop the fit as soon as the variation of \(R\) between two iterations is less than e.g. 1%. The result of the minimization is shown in Figure 4. The measured data can be excellently described by a linear combination of the two reference materials over the whole energy range. By plotting the full parameter range of the scaling factors \(\alpha\) and \(\beta\), it can be shown that the result of the fitting procedure corresponds to the global minimum. The fit algorithm was also applied to Ni on Pt, Fe on Pt and Fe on Pd. Fitted and measured spectra showed a very good agreement and the resulting fractions match with the amount of cover layers deposited on the substrate. It can hence be assumed that the reproduction of the measured spectrum by a linear combination of references is possible for these systems. None of the element combinations mentioned above exhibits island growth. PAES is sensitive only to the topmost layer, and due to the three dimensional structure in case of island growth, the surface appears to have a lower coverage than the nominal value. In this case the fit might show a good agreement with the spectra, but the scaling factors differ from the amount of cover layer deposited.

3. Conclusion
In this paper we presented a new approach for quantifying PAES spectra of binary compounds by their replication with PAES reference spectra of the pure elements. The fit function is a linear combination of the reference spectra of the pure elements, each scaled with an independent factor. The quality of the fit can be quantified by the \(R\) value, representing the difference between the measured spectrum of the compound and the fit. For several combination of elements, an agreement between the measured and the fitted spectrum was achieved and the scaling factors were in good agreement with the fractions expected from the sample preparation. A comparison of the results of the algorithm with a calculation of all combinations of the scaling factor of each element proved, that the algorithm identified the best accordance between the measured spectrum and the fit.

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