Factor analysis and advanced inelastic background analysis in XPS: Unraveling time dependent contamination growth on multilayers and thin films

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1. Introduction

Investigation and quantification of surface nanostructures are important for technological developments, such as multilayer reflection systems for application in the soft X-ray and extreme ultraviolet radiation regimes [1–4]. X-ray Photoemission Spectroscopy (XPS) provides the possibility for non-destructive analysis of surface structures [5–7]. Analysis for amorphous and perfectly flat layers is quite straightforward, whereas the data interpretation for rough surfaces is more complicated. There the XPS peak intensity varies with the angle due to shadowing effects caused by neighboring nano-clusters. The effect depends on the morphology on the surface [8]. Ways of analyzing and interpreting vast XPS data sets are crucial to understand the surface structure of the investigated materials.

Factor analysis is a mathematical technique which reveals correlations between multidimensional data sets [9,10]. In first step the common eigenvectors (spectra) and eigenvalues as the respective weights for reconstruction of the original data are obtained. Further rotation of these space coordinates identifies them with actual physical property vectors [9–11]. On close observation and quantification of these spectra, appropriate models of the investigated systems can be developed. Over the last decades this data processing method has been successfully applied for various spectroscopic methods [11–13].

An alternative method for non-destructive surface analysis relies on investigation and interpretation of the inelastic electron background in XPS according to surface morphology models [14]. The background in XPS is caused by photo-electrons that have suffered inelastic scattering in the material [14]. In various publications it has been shown that this loss tail is closely related to the depth distribution of elements in the surface region [15–17]. In the last twenty years a numerical algorithm has been developed, which has been applied to study various surface nano-structures [18–20]. In this paper we study exemplarily multilayer systems consisting of Mo/Si stacks [1] and a Ru cap layer [21] as used for soft X-ray reflection and other applications [2,3]. These multilayer mirrors (MLMs) often suffer from contamination [4] especially oxidation and carbon growth, which are of certain interest in our studies.

2. Materials and methods

All experiments were performed in ultra high vacuum (UHV) at a base pressure better than 2 · 10⁻¹⁰ mbar. In order to clean the sample surface, Ar⁺ ion sputtering at very low voltages of 50 V and a few 10 nA current was used for typically 15 min.
For the photoemission measurements the chamber is equipped with a standard twin anode X-ray source providing excitation energies of 1253.6 eV (Mg Kα) and 1486.6 eV (Al Kα), as well as a VG Clam 4 hemispherical electron energy analyzer. For all photo-electron spectra only Mg Kα was used. In order to enhance surface sensitivity and monitor angle dependent changes in the surface composition XPS measurements were taken at different electron takeoff angles with respect to the surface normal from 0° (normal emission) to 70° in 10° steps. X-ray satellite correction was achieved with a recursive numerical procedure based on line positions and intensities stated in literature [22].

3. Theory

3.1. Factor analysis

Factor analysis of a spectral data matrix leads to an ordered set of reference vectors, which are the principal components of the data set accounting for all of the data vectors [9]. They are a simpler representation of the original XPS data, where the first vector represents the data the most and the last principal component represents the data the least. Initially the principal components do not necessarily have a physical meaning. However, by rotating the principal components under specific constrains the linearly independent fundamental factors which have physical significance can be found [10]. They are the actual factors or spectra whose linear combination will reproduce all experimental spectra in the data set [10,11]. The boundary conditions for the rotation depend on the physics involved in the spectra, e.g. non-negative intensities or XPS line shape. Also all data vectors have to be a positive linear combination of these fundamental factors [10].

A set of spectra which consist of the same factors but always with different weights can be acquired by recording the spectra under various electron takeoff angles, varying the information depth of the different weights can be acquired by recording the spectra under different electron takeoff angles. A clean Ru reference is shown at 0° and a contaminated Ru capped multilayer at 0°, 30° and 60°. The red bars at 284.2 eV and 280.1 eV indicate the positions of the literature values of Ru3d3/2 and Ru3d5/2 for clean Ru, respectively [31]. The green bar at 284.4 eV indicates the position of C1s as stated in literature [30]. In the spectrum at 0° for the contaminated surface (dashed) the Ru3d5/2 excitation is located at 280.4 eV binding energy and the Ru3d3/2 at 284.6 eV. For the clean surface (solid) the 3d3/2 excitation is at 280.1 eV and the 3d5/2 at 284.3 eV, which is in accordance to the above stated literature values. This binding energy shift of ΔE = 0.3 eV observed for the contaminated sample can be related to a chemical shift evoked by partial oxidation of the ruthenium surface, which is mainly RuO2 [29]. The shift is even more pronounced for θ = 60° where it adds up to ΔE = 0.5 eV. Since the observed chemical shift due to oxidation is stronger at higher angles θ it is concluded that RuOx is located atop the metallic Ru. In the following sections this oxidized layer will be referred to as RuOx.

Furthermore, following the angular development of the peak intensities for the contaminated film it is visible that at higher angles a second very strong signal overlaps that of Ru3d3/2 which can be assigned to C1s. The C1s signal is stronger in the more surface sensitive spectra at larger θ, implying that carbon is accumulated on top of the Ru surface. Thus, it may be assumed that a metallic polycrystalline Ru film is covered by an oxidized ruthenium layer overlapping with carbon containing contaminations.

In order to establish an accurate layer model it is crucial to disentangle the various overlapping photoemission signals in the recorded XPS spectra. This can be achieved by conducting a factor analysis of the measured data array.

![Fig. 1. XPS core level Ru3d of a contaminated Ru film at θ = 0° (dashed), 30° (dotted) and 60° (dash-dotted) and a clean Ru film θ = 0° (compact). A shift in binding energy of ΔE = 0.3 eV for θ = 0° as well as an increase of the overlapping C1s at 284.4 eV signal (green arrow) is discernible.](image-url)
Fig. 2 shows the two spectral factors, which inhibit most physical significance, following from the analysis. The first factor (blue) is assigned to the signal originating from metallic ruthenium. The energy position of Ru3d5/2 at 280.1 eV and Ru3d3/2 at 284.3 eV are in very good agreement with the clean Ru reference as well as with the indicated literature values [31] in Fig. 1. The second factor (red) describes the overlayer component, which is a mixed signal of Ru3d arising from RuOx and C1s from the carbon contamination. The inset shows the factor weights for each spectrum taken at different electron emission angles \( \theta \). All measured spectra can be reconstructed with these factors by a superposition of factor 1 and factor 2 with their according weights. As an example Fig. 2 shows the original spectrum taken at 50° (circles) compared to the reconstructed signal. Again, the chemical shift of \( \Delta E = 0.5 \) eV due to oxidation is obvious when looking at the binding energy of the Ru3d5/2 peaks of the two factors.

The weights for factor 1 (metallic Ru) decrease with more grazing angle \( \theta \). Contrary, the weights for the overlayer factor rise with more grazing angle due to higher surface sensitivity. Therefore, RuOx and C are located at the surface and not in the Ru film, as already indicated by the data shown in Fig. 1.

Further attempts to separate the RuOx and C signal with factor analysis by extracting three instead of two factors were not successful. This issue might be due to the fact that the RuOx contribution and the C contribution do not change independently when the electron takeoff angle is changed. Both are located atop the metallic Ru film and their contributions change in the same way when the sample is rotated. However, this shows that the contamination layer is a mixture of both parts. If the contamination would be a film and their contributions change in the same way when the sample is rotated. However, this shows that the contamination layer is a mixture of both parts. If the contamination would be a film and their contributions change in different ways, leading to a third factor.

By taking a closer look at the development of the factor weights it is possible to extract a layer growth model for the individual contributors. For this purpose the ratio of the metallic Ru weight to the weight of the RuOx + C mixture is calculated for each electron emission angle. In Fig. 3 this ratio is plotted versus the electron emission angle and compared to the cosine of the electron emission angle \( \theta \). For an ideally flat grown overlayer the intensity from the overlayer follows

\[
I_o = 1 - e^{-z_0/\lambda_0}
\]

and the intensity from the substrate

\[
I_s = e^{-z_0/\lambda_s \cos(\theta)}
\]

where \( z_0 \) is the electron path length at \( \theta = 0° \) [22]. We have analyzed the ratio of the weight factors with the QUASES-ARXPS software [32]. This allows to use different \( \lambda \) values for the substrate and the overlayer. We have used \( \lambda = 14.1 \) Å and \( \lambda = 16.9 \) Å for the substrate Ru and the overlayer RuOx + C. The best agreement which is shown in Fig. 3 is obtained with \( z_0 = (18.4 \pm 0.5) \) Å.

4.2 Advanced background analysis

In order to cross check the model deduced from factor analysis the inelastic electron background was analyzed. The spectra were analyzed with the QUASES software [27,28,15,33–35]. This provides two sets of software which handles the analysis of the background in different ways. In one part called QUASES-Analyse, the peak is corrected for the background of inelastically scattered electrons assuming different depth distributions of atoms. The corrected spectrum is compared on an absolute intensity scale to a reference spectrum and when there is a good agreement with respect to shape and intensity then the correct depth distribution has been determined. This QUASES-Analyse method can also be applied without the use of a reference spectrum in which case the criterion for a correct depth distribution is that the background is accounted for in a wide energy range below the peak energy.

In the second part QUASES-Generate one calculates model spectra for different atom depth distributions and these are directly compared to the measured spectrum. When there is a good match on an absolute scale over the entire spectral energy range, then the correct depth distribution of the atoms has been determined. This QUASES-Generate method requires measured spectra of the pure materials because these are the input in the calculations of the model spectra.

When a peak is free from interfering peaks originating from other atoms then the QUASES-Analyse option is usually chosen. But this
analysis is not possible when peaks originating from two types of atoms overlap in energy and then the only option is to use the QUASES-Generate method.

In the present case we actually use all three methods, one for each of the analyzed peaks as follows.

The O KLL Auger peak is free from interfering peaks but we don’t have a RuO\textsubscript{x} reference spectrum so here we use QUASES Analyse without reference spectrum. For Ru3p there is the O1s peak roughly 35 eV below the Ru3p\textsubscript{1/2} peak. Therefore, we can apply QUASES-Analyse with a Ru reference spectrum in this limited energy range. Finally, for the Ru3d and C1s peaks there is a strong overlap and we have reference spectra for both the C1s and Ru3d peaks. We can therefore apply the QUASES-Generate analysis method to analyze the mixed Ru3d and C1s peaks.

Fig. 4 shows the analysis of the Ru3p peak. The reference spectrum was determined by background correcting a spectrum from pure Ru (blue curve). The red curve is the corrected Ru3p spectrum acquired from the Ru capped MLM. A stack model where the metallic Ru substrate is buried under a (18 ± 2)Å overlayer (presumably a RuO\textsubscript{x} + C mixture) gives the best fit for both the intensity and the line shape. Note that the spectra have the same peak area and therefore since the blue reference peak is more narrow its intensity at the peak energy is higher. Only the part of the spectrum below 520 eV binding energy, which has no interference with the O1s peak, was used in the analysis.

The O1s core-level signal at 531.6 eV binding energy was improper for the analysis as its loss tail is overlapping with the Ru3s core-level excitation at 587.1 eV. We have therefore analyzed the oxygen Auger signal O KLL at 515 eV kinetic energy. Various models were tested and a two island model is found to be slightly better than a single layer model. In Fig. 5 the model with the best agreement between calculated background and the actual signal is shown along with the original recorded O KLL peak (blue), the modeled background (black) and the intrinsic peak (corrected spectrum without background, red). The top layer is (15 ± 2)Å high and covers 55% of the surface. Therefore the oxidation is less in the topmost (15 ± 2)Å.

Finally the overlapping Ru3d and C1s peak region was analyzed with QUASES-Generate software and the experimental acquired spectrum was modeled using the spectrum from measured clean Ru(0001) single crystal surface and the C1s reference spectrum taken from a spectrum of HOPG. Both spectra, which are depicted in the inset in Fig. 6 (C1s (green) and Ru3d (blue)), were taken under the same conditions as that of the MLM sample. Fig. 6 also shows the measured spectrum of the MLM (red) as well as the generated model peak (black). Additionally, the buried layer model which leads to the model peak is shown. It indicates that the layer containing the metallic ruthenium is buried under a (19 ± 2)Å thick layer (presumably containing carbon and oxide). This analysis cannot tell if the Ru atoms are present as metallic or oxidized Ru. This finding agrees well with that found from analysis of Ru3p.

5. Discussion

Decomposition of the acquired Ru3d spectra from the Ru cap lead to two main factors, metallic ruthenium and a RuO\textsubscript{x} + C mixture. A further disentanglement of the oxide and carbon contribution was
not achieved because they do not change independently from each other when varying the investigation angle. This might be due to an exhausting mixing of both components in the contamination layer. From consideration of the angular behavior of the weight ratio it was concluded that the RuO$_x$ is on top of Ru and the thickness is $(18.4 \pm 0.5) \text{Å}$.

Analysis of the distribution of inelastically scattered electrons in the background of the Ru3p, Ru3d and O KLL excitations shows rather similar stack models. Comparison of the Ru3p line shape to that of a clean Ru reference showed that the Ru is buried under a closed $18 \text{ Å}$ thick of contamination layer. Modeling the overlapping spectrum of Ru3d and C1s from two reference spectra, clean Ru and C respectively, lead to the very same stack model. On the other hand the background signal of O KLL points to an islanding layer model for the O distribution, hinting that the oxidation is less in the topmost layers. The layer thicknesses following from the background analysis are in the same magnitude as that deduced from factor analysis, $(18 \pm 2) \text{Å}$ for Ru signals and islands of $(15 \pm 2) \text{Å}$ for O KLL.

Factor analysis is an adequate method to decompose data in its various components. However the investigation method must be chosen carefully to make sure that all factors change independently from each other in order to be able to disentangle them. Nevertheless, conclusions can be drawn about the layer topology even without disentangling every single spectral constituent. Inelastic background analysis is already a well established method to understand and interpret XPS signals leading to very accurate layer models. A combination of both methods as conducted above can be an expedient way to handle data from unknown sample compositions and in addition automated procedures help handling vast data volumes.

6. Summary

A multilayer mirror surface for application in the EUV radiation regime was investigated with X-ray photoelectron spectroscopy under various electron emission angles. The spectra were analyzed in two impartial ways, factor analysis and inelastic background analysis in order to get insight into the surface structure and morphology. Factor analysis proved to be a suitable way to disentangle overlapping signals and get an overall feeling for the main morphology present. The findings from this method could be successfully cross checked and expanded by inelastic background analysis. On ground of these findings a procedure can be developed to handle and analyze huge data volumes even of samples where not all corresponding factors are known.

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References