Quantitative Analysis of Thin Films and Multiple Thin Film Structures by Monte-Carlo Techniques

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Summary
Monte-Carlo techniques have been employed successfully to XRF of light elements in complex thin film structures consisting of parallel stripes. For the first time, secondary excitation by photo-electrons have been taken into account in thin films, which has not been possible so far with conventional fundamental parameter methods. Application of the MC-method to homogeneous thin films with elements of medium/high atomic numbers is possible but much slower and less accurate than conventional fundamental parameter computations.

Introduction
Analysis of thin films and multiple thin film structures is a well-developed application of XRF and supported by fundamental parameter approaches. For elements of the first decade, however, limitations must be observed, because excitation effects by photoelectrons and Auger-electrons have to be taken into account. Reasonable approximations for such interactions have been included into fundamental parameter models for bulk materials and previously reported1-5, but this is not possible in the case of thin films. The range of electrons can exceed individual film-thicknesses and even the thickness of whole structures by far, leading to complicated, curled, sometimes back-bending electron paths through several layers. Our attempt was to employ Monte-Carlo techniques to this problem.

In the first part of the paper, a more general discussion of the advantages and disadvantages of MC-methods compared to the conventional f.p. method for thin films of medium/high-Z’s is given. The second part shows an example of a complicated structure involving light elements, which cannot be described by conventional fundamental parameter methods.

Scheme of MC-computations
The developed software6 uses an 800x800 pixel “worksheet”, which contains the element map (layers of elements or any other structure) and is used to display graphically the interactions of interest (fig.1). For far reaching interactions, where the photons or electrons interact outside the worksheet, the pixel-array (or part of it, e.g. the substrate) is extended by virtual repetition. The scaling factor that converts between physical size and pixel-size can be set as input-parameter.

Thin films: computational aspects
Conventional primary and secondary (and higher order) excitation in thin films follow the same principles as for bulks, but require a more complex mathematical treatment7,8. Particularly accounting for interelement effects between layers (and with the substrate) in multilayer structures is a time-consuming computational procedure. Contributions of excitations within a thin layer and between thin layers of a structure (assuming medium Z’s and a total thickness...
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around a few 1000Å or less) are generally below 0.5% of the observed counts, but the substrate radiation can contribute up to 10%, depending on thicknesses and elements (fig. 2). In multilayer structures the interelement effects are in the same order of magnitude as in a homogeneous single thin film made of the same material.

The Monte-Carlo method is a statistical method, and the finally obtained degree of reliability of the result is a function of successfully computed counts of the interesting events (as for real photons). Following events of low probability (excitation of light elements, analysis of trace materials, analysis of thin films) may therefore be quite time consuming and is nevertheless subject to a statistical error. The conventional method, on the other hand, requires also complex mathematics and time consuming computations, but gives finally an accurate result (within the general validity of the model and except for purely numerical errors, which are limitations of all models).

Figure 1. Left: 800x800 pixel array for maps and graphics. Right: Pixel-array holding a random element map (top/middle). The virtual repetition of the array (all others) allows distant interactions to be accounted for. The same computing scheme can be used for inhomogeneous specimens.

Figure 2. Substrate/layer (example computed for Al-layer on Si-substrate), and layer/layer interactions.
For a comparative test, a multilayer structure of 40 pairs of Pd/Co layers on a bulk Si-substrate was made and measured. The nominal (total) thickness was 1050Å which is in very acceptable agreement with the result of conventional XRF using fundamental parameter computations, of 1077Å (theoretically: 40 times 12.19 Pd +14.74 Å Co). All secondary excitation effects between the 80 layers were accounted for. The number of MC-histories (initial photons) were typically in the order of $10^4$ to $10^5$ per datapoint (fig.4). Real tube-spectra were used for the initial energy distribution.

Fig. 3 shows the pixel-array of the multi-layer sample and the emitted photons. The resolution (graphical pixel size and computational step-width) is 3Å. From the silicon-substrate, only a few photon paths from a 6Å layer (2 pixel-rows) are drawn, because the abundant Si-photons would otherwise obscure the image. For the same reason only photon-paths ending at the surface (i.e. those that are counted) are shown. This includes chains of secondary interactions.

![Figure 3: 80-layer-structure on Si-substrate](image)

**Computing times:**

**Conventional fundamental parameters (per iteration step):**
- PC/PentiumPro200: 430s
- IBM PowerPC/43p: 275s

**Monte-Carlo:**
- PC/PentiumPro: 1200s $\sigma = 7\%$

**Conventional fundamental parameters without secondary enhancement:**
- PC/PentiumPro: 5s $\text{Error} \approx 10\%$
Fig. 4 shows the reason for the poor performance of the Monte-Carlo technique: The low obtained count-numbers vary considerably, and even the average of 20 data-points is uncertain (σ) by 7%. Increasing the number of computed histories would of course improve the situation but at cost of computing time.

It is interesting to compare the intensity ratios (vs. bulk) from the multilayer to those from a virtual single layer made from the same material (i.e. a Pd/Co alloy with the same masses and mass ratios):

Multilayer: \( r_{\text{Pd}} = 0.084060 \)
\( r_{\text{Co}} = 0.013647 \)

Single layer: \( r_{\text{Pd}} = 0.084438 \) \( \Delta = 0.4\% \)
\( r_{\text{Co}} = 0.013676 \) \( \Delta = 0.2\% \)

These \( \Delta \)'s are obviously the minimum computational accuracy required to simply distinguish the multilayer from a single layer. One should keep in mind, however, that analysis of thin films, particularly of the thickness, is difficult, and in most cases an error (i.e. agreement with independent methods) of 3-5% must be expected\(^9\).

As a general experience in our computed examples, we found the conventional fundamental parameter method to be faster and more accurate than Monte-Carlo computations, even with numerical parameters (particularly the integration step-widths) set to give highest precision.

**Light elements in thin structures.**

In a previous volume of Advances in X-ray Analysis, F. Weber et.al\(^10\) presented results from measurements of carbon in layer structures consisting of thin stripes of copper on a carbon substrate. One aspect of this work was to investigate the secondary excitation effect by Cu-electrons on carbon and was based on the following assumption: the average energy of photoelectrons (from copper) would increase with increasing tube-voltage and thereby cause a strongly voltage-dependent excitation effect. The actual experimental data showed however only a slow increase (of relative counts) with voltage. This chapter resumes the discussion of these data from the view-point of the Monte-Carlo computations and their results.

![Electron beam](image1)

**Figure 5.** Left: EPMA-approach (external source).
Above: Single, internal source-point
Excitation by electrons.

Excitation effects in XRF by photoelectrons and Auger-electrons have been discussed in several reports\textsuperscript{1-5}. Most models seem to be based on integral formulae giving the total number of excited photons per electron (e.g. the Green-Cosslett algorithm), which, however, cannot be used for thin films. Instead, it is necessary to follow each individual electron and describe its interaction with the sample matrix by using the actual cross-sections for the coherent and incoherent scattering events. We employ the “screened” Rutherford formula\textsuperscript{6} for coherent scattering and Gryzinsky’s algorithm\textsuperscript{7} for incoherent interactions, but it should be noted that considerable differences exist between the various existing approaches.

The initial algorithms are similar to those used for EPMA except for the fact that our computations require absolute photon-counts while in EPMA relative numbers (compared to a standard) are usually sufficient. Fig. 5 (left picture) shows the electron paths originating from an external source (electron gun), while in XRF all ionized atoms in the specimen are sources of electrons. An important consequence is that the probability for loss of electrons by emerging through the surface ("backscattering" in EPMA) is very low except for those from atoms near the surface (fig. 5, right picture; the single source-point illustrates "moving the source into the specimen" in XRF, but in reality each atom is a possible source point).

Structures of thin stripes (medium Z’s only)

In this theoretical example, the investigated structure consists of parallel copper stripes on a silicon substrate (fig. 6). A chromium interface was assumed between Cu and Si (corresponding to the design of the C/Cu structures, which were actually made and measured and are discussed in the following). The primary tube radiation illuminates the specimen almost perpendicularly ($\psi_1=85^\circ$); the spectral distribution is that of an end-window tube (Rhodium-target, 75$\mu$m beryllium-window). Primary fluorescent photons as well as secondary excitation contributions were computed.

Computed photon paths are shown in fig. 7 for tube-voltages of 30kV and 60kV. Note that the absolute numbers of photons can not be compared because of differing (and unknown) absolute calibration factors of the theoretical tube spectra. However, building ratios of (for example) Si-photons vs. Cu-photons, is correct. The effect of the higher voltage is obviously a less efficient excitation, which is made up to some extent in silicon by a deeper information depth. Shielding of SiK$\alpha$ by Cu is quite strong. Only the paths of those photons are displayed that can be counted (i.e. arrive at the top of the picture). The probability to observe a secondary excitation event (e.g. SiK$\alpha$ by CuK$\alpha$) is very low because the Cu-fluorescent photons rate from the thin structure is much lower than from a bulk.

Note that the same computational scheme can be used for specimens with rough surfaces, where shielding effects reduce the fluorescent intensity. Accordingly in the current case, the count rate increases significantly if observed from a direction parallel to the stripes.
Structures with light elements

A similar structure as that discussed above was actually made and measured, the difference being only a carbon substrate instead of silicon. Figure 8 shows the paths of electrons and photons:

Top: Excitation of copper and carbon atoms. The white paths are photoelectrons from copper and carbon, the pink lines are CKα photons. No CuKα photons are included because their large number would obscure the view. The relatively high density of electrons in Cu compared to C reflects the higher absorption coefficient for the tube photons.

The area above the specimen (black) is assumed to be vacuum. Electrons emitted from the specimen into that direction continue their paths as straight lines. A small fraction of them re-enters the specimen at some other point. In contrast to previous (and the following) graphs, all carbon photons are shown including those not reaching the “detector” (top of graph).

Middle: CKα-photons excited by tube photons (primary excitation) are drawn in violet, those excited by electron in light blue. Note that their fraction increases quite obviously with tube voltage (right graph is at 60kV, left graph is at 30kV). The relative intensity, however, compared to pure carbon remains mainly unaffected by this enhancement because the same effect dominates in both specimens.

Bottom: As above, except that CKα-photons that are excited from electrons originating from Cu are emphasized by red color and red circles for better visibility. This is an effect that should increase with tube voltage, but it’s contribution to the overall counts is too low as to affect the total count rate greatly. This is in agreement to the finding of the mentioned experiments by Weber et al.
Figure 8. Paths of photons (blue, violet, red) and electrons (white). Structure: copper (red); substrate: carbon (blue); left column: 30kV; right column: 60kV. See text.
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Literature

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