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Quantitative EPMA and TEM of Unsupported Films

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Abstract. Quantitative analysis can be done very accurately with the aid of computer programs based on an accurate description of the amount of X-rays generated at each depth within the specimen. These models have achieved such performance that thin layers and even multilayers can also be analyzed. In this article the next step in the development is described: the analysis of unsupported films. This technique is very well applicable in both the electron microprobe and the transmission electron microscope, but in the latter case hardware adjustments might be necessary.

Key words: $\varphi(\rho z)$ curves, thin films, transmission electron microscopy, quantitative analysis.

In the last two decades the development of more and more sophisticated computer programs for electron probe microanalysis has progressed rapidly. The widespread availability of fast and user-friendly computers, combined with the need for more reliable results, has produced a whole new generation of analysis programs capable of handling even the most difficult cases.

Most of these programs are based on an accurate description of the amount of X-ray ionisations as a function of depth within the specimen. These so called $\varphi(\rho z)$ curves have shown their merits in the analysis of homogeneous bulk specimens, not only under extreme circumstances such as heavy absorption and high overvoltages, but also as an overall improvement on the previous generation of programs, often accumulated under the name ZAF programs.

The Analysis of Layered Samples

In our laboratory we use a modified version of the surface centred Gaussian $\varphi(\rho z)$ model, which was originally developed by Packwood and Brown [1]. The overall formula which describes the $\varphi(\rho z)$ curve for the generated intensity is:

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$$\varphi(\rho \cdot z) = \gamma \cdot \left(1 - \frac{\gamma - \varphi_0}{\gamma} \cdot e^{-\beta \cdot \rho \cdot z} \right) \cdot e^{-\alpha^2 \cdot (\rho \cdot z)^2}, \quad (1)$$

in which the three parameters α , γ and φ_0 are calculated independently from fundamental parameters such as atomic number, atomic weight and edge energies, and from the accelerating voltage of the impinging electrons [2,3]. The fourth parameter β is derived by a separate calculation of the total generated intensity under the $\varphi(\rho z)$ curve. One of the advantages of this program lies in its Gaussian tail, a physically natural way to describe the decay in X-ray generation at larger depths. Over the years this model has been improved stepwise, and it has demonstrated its excellent performance especially for the analysis of the ultra-light elements boron, carbon, nitrogen and oxygen [4].

The next step in the evolution of an accurate $\varphi(\rho z)$ program is the development of a thin film analysis program, capable to determine simultaneously both the composition and the thickness of one or more layers on a substrate. In the uncomplicated case of a single film on a substrate one has to take two effects into account to calculate the intensity generated in the film: first the fact that the $\varphi(\rho z)$ curve has to be partially integrated from the surface to the film-substrate interface, and secondly the fact that the differences in atomic number between film and substrate cause the $\varphi(\rho z)$ curve of the film element to change, depending on the backscatter coefficient of the substrate. A substrate with a larger atomic number will increase the amount of backscattered electrons, compared to the number which would backscatter if the substrate were made of the same material as the film, therefore the $\varphi(\rho z)$ curve of the film will increase. The reverse is valid in case the average atomic number of the substrate is smaller than that of the film.

The four parameters of the Gaussian $\varphi(\rho z)$ curve can be modified using four simple exponential 'weighting' functions:

$$\begin{aligned} \alpha &= \alpha_b + (\alpha_s - \alpha_b) \cdot \exp(-1.5 \cdot (\alpha_b \cdot T \cdot 10^{-6})^2), \\ \beta &= \beta_b + (\beta_s - \beta_b) \cdot \exp(-1.5 \cdot \alpha_b \cdot T \cdot 10^{-6}), \\ \gamma &= \gamma_b + (\gamma_s - \gamma_b) \cdot \exp(-2.0 \cdot (\alpha_b \cdot T \cdot 10^{-6})^2), \\ \varphi_0 &= \varphi_{0b} + (\varphi_{0s} - \varphi_{0b}) \cdot \exp(-2.5 \cdot (\alpha_b \cdot T \cdot 10^{-6})^2), \end{aligned} \quad (2)$$

in which T is the film mass-thickness in $\mu\text{g}/\text{cm}^2$, and the indices s and b indicate that the parameters have been calculated as if the film element were respectively solved into the substrate or present as bulk sample. By weighting between these extremes one is assured of a smooth transition from a very thick film, in which the film parameters remain nearly unaltered, to a very thin film, in which the film elements can be treated as nearly solved in a substrate matrix.

We assume that the substrate $\varphi(\rho z)$ curves remain unchanged, so to calculate the generated substrate intensity one simply has to integrate the $\varphi(\rho z)$ curve from T to infinity. To calculate the final emitted intensity one has to bear in mind that the radiation is not only absorbed in the substrate itself, but also on its way from the interface to the surface by the film elements. This procedure can yield surprisingly good results [5].

As we have shown before, this procedure can be expanded towards the analysis of several films on a substrate. The weighting procedure has to be modified, however,

and the fourth degree polynomial weighting procedure as suggested by Pouchou and Pichoir [6] then produces satisfactory results, although the weighting coefficients have to be optimised for the Gaussian model. The number of calculations increases significantly, however, since one has to take into account the influence each film and the substrate might have on every other film present. This procedure can finally allow the analysis of even the most difficult cases, such as implantation profiles [7].

The Analysis of Unsupported Films

Mathematically the analysis of an unsupported film simply implies that one has to enter a substrate with atomic number approaching zero in the weighting procedures. But what is the $\phi(\rho z)$ curve of an element in vacuum? From the definition of the $\phi(\rho z)$ curve according to Castaing [8] and experimental evidence we assumed the following values or expressions:

- α_s is equal to α_b ,
- β_s is set to zero,
- γ_s is calculated in the usual way with the assumption of atomic number zero, and
- ϕ_{0s} is set to 1. (3)

Integration of the $\phi(\rho z)$ curve calculated in this way yields, after applying the normal absorption correction, the emitted intensity from an unsupported film, so now a single measurement at a single accelerating voltage is sufficient for the simultaneous determination of its composition and its thickness. This procedure was roughly checked by having the program calculate the emitted intensities from a fictitious film on several light and ultra-light element substrates. Extrapolating these calculated values to a substrate of atomic number zero shows good agreement with the

Fig. 1. The shape of the generated $\phi(\rho z)$ curve of Al-K α for a 100 $\mu\text{g}/\text{cm}^2$ aluminum film on top of several substrates. From the top down: Bi, Ag, Cu, Al, O, and finally a “vacuum substrate”. Accelerating voltage 10 kV

calculated values for an unsupported film. The changing shape of the $\varphi(\rho z)$ curve for Al-K α in an aluminum film on several substrates is shown in Fig. 1.

Experiments in the EPMA

To investigate possible applications we deposited 6 different layers of aluminum with nominal thicknesses of 10, 20, 40, 80, 160 and 320 nm on several substrates, among which were substrates of carbon, boron and beryllium. In the same batch the same aluminum layer was also deposited on a salt crystal. After deposition the aluminum was carefully removed from the crystal and placed on a copper grid, as often used in transmission electron microscopy. All films were analyzed in the electron probe microanalyzer at a range of accelerating voltages, using a bulk aluminum specimen as a standard. The copper grid was placed in a special holder, to prevent any of the transmitted electrons from scattering back from the holder to the film.

The measured intensity ratios and the calculated film thicknesses for the unsupported films are displayed in Table 1 for the thinnest film (10 nm), the thickest film (320 nm), and one in between (40 nm). The measurements were done in five- or tenfold, depending on the statistics. Only the results of measurements at higher voltages are displayed in Table 1, because at lower accelerating voltages the aluminium oxide skins on both specimen and standard were causing too much scatter in the results.

The results show that a rather consistent film thickness is found, although there is a slight tendency for this procedure to reduce the film thickness as the accelerating voltage increases. It is quite easy, however, to account for this phenomenon by the presence of oxide skins. A similar but less pronounced tendency was found in the calculated thickness of the aluminum films on the substrates too.

So we know the program can produce consistent results, but are they reliable, and do the approximations (3) really hold? To check this we compared the average

Table 1. X-ray intensity ratios measured in the microprobe and the mass thickness T (in $\mu\text{g}/\text{cm}^2$) as calculated by the thin film program for three aluminum films, detector take-off angle 40 degrees

Accel. voltage (kV)	Nominal thickness (nm)					
	10		40		320	
	k-ratio	T	k-ratio	T	k-ratio	T
12	0.00813	3.8	0.03608	16.5	0.29955	95.5
15	0.00539	3.7	0.02301	15.8	0.17719	94.2
20	0.00330	3.6	0.01364	15.0	0.09705	93.9
25	0.00234	3.6	0.00948	14.6	0.06369	91.9
30	0.00186	3.6	0.00740	14.5	0.04803	91.4
35	0.00153	3.6	0.00618	14.5	0.03890	90.4
40	0.001356	3.6	0.00538	14.5	0.03329	89.7
45	0.001234	3.7	0.00478	14.3	0.03061	92.0
50	0.001156	3.7	0.00435	14.0	0.02772	90.5

Table 2. Comparison of the average film thicknesses in $\mu\text{g}/\text{cm}^2$ for 6 aluminum films deposited on carbon, boron and beryllium, and for the unsupported aluminum films. Thicknesses averaged over 5 voltages, ranging from 12 to 30 kV

Substrate	Nominal thickness (nm)					
	10	20	40	80	160	320
C	3.76	7.26	13.60	24.90	48.08	84.92
B	3.94	7.56	14.06	25.62	50.50	87.56
Be	3.70	7.36	14.10	25.42	50.24	88.40
Unsupported	3.66	7.14	15.28	25.92	53.62	93.38

film thickness of the unsupported films with the thickness of the same film deposited on three of the ultra-light elements. The results are in Table 2.

A second sample we tested in the electron probe microanalyzer was an aluminum-zirconium alloy. The specimen was produced by mixing and arc melting the pure elements, and its composition was checked by EPMA and found to be Al_2Zr_3 , with some distinguishable inclusions of Al_3Zr_5 , however, those could be avoided during the analysis. From this bulk specimen a TEM specimen was produced, using grinding with a dimple machine and ion beam milling.

The TEM specimen was placed in the same special EPMA specimen holder, and a linescan was done from the edge of the hole in the centre of the specimen to a very thick part of the specimen, setting 60 points at regular intervals to cover a total distance of 150 μm . Standards used were pure zirconium and aluminum, and the measurements were done at accelerating voltages of 5, 10, 20, and 40 kV. The linescan at each accelerating voltage was started at a spot just a few micron perpendicular to the direction of the previous scan to prevent any influence from the contamination spots due to previous measurements.

In Fig. 2 the thickness is displayed as calculated by the program from the measured intensity ratios at 40 kV. In the same figure we also display the weight fractions of aluminum and zirconium as retrieved simultaneously during the analysis at 40 kV. In spite of the tremendous differences in specimen thickness it is still possible to retrieve nearly constant compositions. Note by the way that the film thickness really displays a cross section of a TEM specimen.

Of course determining the composition is not as difficult as it might seem, since hardly any correction is involved to convert the intensity ratios into weight fractions. Therefore identical work has been performed on a Cu_2O specimen. Since oxygen- $\text{K}\alpha$ radiation is considerably absorbed in copper (mass absorption coefficient of 5920 cm^2/g), a simple ratio technique is insufficient, and substantial corrections have to be applied.

The results are displayed in Fig. 3 for a linescan from the thin part in the centre to a thicker part, at 5 kV accelerating voltage. As one can see, the Cu_2O stoichiometric composition is retrieved in the thicker part of the specimen only, but this phenomenon can easily be attributed to the oxidation of the specimen during specimen preparation, which might generate a CuO skin.

Fig. 2. Calculated sample thickness for the Al_2Zr_3 specimen at 40 kV (right y-axis), and the composition of the specimen as calculated simultaneously from these results (left y-axis)

Fig. 3. Calculated sample thickness for the Cu_2O specimen at 5 kV (right y-axis). The composition of the specimen as calculated by the program is displayed too (left y-axis), together with the stoichiometric values for Cu_2O and CuO

Thin Film Analysis in the TEM

The analysis of unsupported films finds its justification in its improved spatial resolution, caused by the small electron-specimen interaction volume. To obtain an even better resolution the analysis can best be done in the transmission electron

microscope at higher accelerating voltages. Therefore it would be interesting to see if the technique described in the previous pages could be applied in TEM as well.

So far, elemental analysis in the TEM is generally done either standardless, or by using a thin standard of known composition containing the same elements as present in the specimen (Cliff-Lorimer [9] method). These techniques need complicated corrections, however, if any significant absorption is present, and especially the analysis of ultra-light elements is very difficult, unless the film thickness is known. The use of single element bulk standards has been tried before [10], but not using a sophisticated $\phi(\rho z)$ model, which severely limits the use of this method because at higher accelerating voltages an accurate absorption correction is very often needed to calculate both the standard and the specimen intensities.

Several techniques are available for the determination of the film thickness. Each has its own advantages, but it is hard to find a technique which yields an accurate answer over a wide range of thicknesses on any spot on the specimen. As we have shown before using our method would yield the film thickness as a by-product of the elemental analysis.

Many problems arise, however, when an attempt is made to apply our micro-probe technique in the TEM.

- First of all generally a lot of stray electrons and X-rays are present in all parts of the TEM microscope column, so considerable precautions have to be taken to prevent drawing premature conclusions concerning beam current and primary beam induced X-ray intensity.

- The beam current has to be measured rather accurately. A commercially available analytical specimen holder will generally do, but since these are connected to a picoampere meter, a certain minimum beam current is required to obtain sufficient accuracy. When monitoring the X-ray intensity emitted by a bulk standard specimen a minimum beam current would already cause an excessive count rate, so an X-ray detector at a variable distance from the specimen or one equipped with a variable detector aperture would be preferable. One also has to be very careful not to damage the detector by allowing it to be bombarded with too many backscattered and secondary electrons.

- The stability of the beam current can also cause serious problems. Monitoring the beam current for 24 hours might reveal substantial variations, not just over hours time, but sometimes within minutes.

- Another problem arises from the fact that often both standard and specimen have to be tilted towards the detector due to the low detector take-off angle. This is not a problem for the determination of the thickness of the specimen, since a simple multiplication of the calculated thickness with the cosines of the tilt angle would be a close enough approximation. But for the standard a more refined correction has to be used, because—although the self absorption coefficient for most elements is very low—the enormous depth at which some X-rays are generated makes absorption a significant factor. Therefore a simple “cosines approximation” will not do, and a full tilted $\phi(\rho z)$ approach has to be applied. In our program we used the procedure published first by Pouchou et al. [11], which had to be adjusted to suit the Gaussian model.

- As a final problem we would like to mention the fact that the entire $\phi(\rho z)$ theory is based on measurements in the EPMA accelerating voltage range of 2 to 50 kV.

It is unknown for many parts of the program if higher accelerating voltages can be handled. Future research will have to show at which accelerating voltage the contemporary programs start to fail, and serious high voltage adaptations will have to be applied.

In our laboratory we have tried to analyze in the TEM several unsupported aluminum films that were analyzed in the EPMA before. However, serious problems with the electron beam stability considerably reduced the accuracy and reproducibility of the results. The expected tendencies (lower intensity ratios at higher voltages, etc.) were found, but for the time being any accurate quantification could not be achieved.

Conclusions

Using $\varphi(\rho z)$ models to determine the composition and the thickness of an unsupported film can be a very simple and accurate method as the microprobe experiments show. Although this method can also be applied for quantitative analysis in the transmission electron microscope, hardware problems can easily disturb any quantification.

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