Computer programs for the calculation of x-ray intensities emitted by elements in multilayer structures

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Almost immediately after the introduction of the first electron probe microanalyzer by Castaing it was realized that the technique would be eminently suited to the analysis of thin films and the determination of concentration profiles in depth. The basic requirement for this specific application of the technique is that an accurate knowledge is available about the x-ray production as a function of depth in the specimen, a knowledge that is usually expressed in terms of so-called $\phi(pz)$ curves ($\phi$ is the number of photons and $pz$ is the product of density and linear depth in the specimen). Unfortunately, it has taken up to the beginning of the 1980s before a number of $\phi(pz)$ models became available on which a successful thin film approach could be based. Our own bulk matrix correction program "PROZA", \(^5\) with its proven excellent performance for a wide variety of applications (e.g., ultralight-element analysis and extremes in operating conditions) has been used as the basis for the development of the thin-film software package discussed here. The PROZA bulk-correction program is based on a combination of our own modifications of the surface-centered Gaussian $\phi(pz)$ approach, originally introduced by Packwood and Brown, \(^3\) and the atomic-number correction of Pouchou and Pichoir. \(^6\) Like in the Pouchou and Pichoir model, this approach guarantees that the integral of $\phi(pz)$ has at all times the value dictated by the atomic-number correction and that the $\phi(pz)$ curve displays the proper distribution. Contrary to the conventional "ZAF" approaches, this method makes it possible not only to integrate the $\phi(pz)$ curve between 0 and infinity (for bulk correction) but also between distinct limits, which is essential for thin-film applications. However, it is clear that for the extension of a bulk matrix correction program toward thin-film applications it is necessary to take the film/substrate interactions into account, and this aspect will now be discussed.

Basic Procedures

The surface-centered Gaussian $\phi(pz)$ approach is based on the use of four parameters, $\alpha$, $\beta$, $\gamma$, and $\phi(0)$, with which the $\phi(pz)$ curves are modeled. For an element in a film on a substrate one must determine how the four Gaussian parameters vary with film thickness and the nature of the substrate. In dealing with this problem the following strategy (for a single-film case) has been used.

a. The $pz$ scale in each $\phi(pz)$ curve is continuous across the interface.

b. The $\phi(pz)$ curves of the elements in the film are affected by the nature of the substrate; the curves for the substrate elements are not influenced by the presence of the film.

c. The Gaussian parameters for a particular element in the film vary between two extremes typical for either extremely thin or extremely thick layers. In the latter case the bulk parameters $P_b$ will have to be approached; in the former case the parameters can be approximated if one considers the element as being solved in the substrate $P_s$. In all intermediate cases the parameters will have to vary in a smooth and consistent way between these extremes. For the single-film case this goal has been accomplished by the use of simple exponential functions of the general form

$$P = P_b + (P_s - P_b)\exp(-ax^n)$$

in which the main parameter $x = 0.5aT \times 10^{-6}$ and $T$ is the layer thickness in $pz$ units of $\mu g/cm^2$. The exponent $n$ is unity for $\beta$ and equal to 2 for the others. The constant $a$ has the value of 6, 3, 8, or 10 for the parameters $\alpha$, $\beta$, $\gamma$, and $\phi(0)$, respectively. This empirical weighting procedure insures a smooth variation of the parameters and does justice to the fact that the backscattering of the substrate has a different effect on the various film parameters; the shortest distance of interaction is on $\phi(0)$.

For the case of a multilayer system a more complex procedure has to be followed. One obtains the composited parameters for each element by assigning specific weights to the parameters in each of the films and in the substrate, depending on the distance from the particular film examined, and finally integrating these contributions according to a fourth-degree polynomial, not unlike in the procedure followed by Pouchou and Pichoir. \(^7\) Once the four Gaussian parameters for each element in a particular film are available the generated and emitted intensities are calculated by partial integration \(^8\) of the $\phi(pz)$ curve.

Basic Structure of the Programs

The software package developed consists of two programs: one for a single film either on a substrate or unsupported ("TFA"), the other for up to 7 films ("MLA"). Basically, each program contains four options. With the first option it is possible to calculate the emitted intensities from a layer.
system with given thicknesses and compositions as a function of accelerating voltage. This option is very important to exploratory calculations to find the highest sensitivity of the system and determine the best measuring strategy.

In the second option the voltage is fixed and the calculations are performed as a function of layer thickness of (one of) the layer(s).

The third option enables the determination of layer thicknesses (for supposedly known compositions) from measured k-ratios at a fixed voltage in a single iterative and fully automatic way.

The fourth option provides the possibility of establishing both thicknesses as well as compositions from measured k-ratios at a fixed voltage in a double iterative and fully automatic way, with the obvious restriction that each element occurs only once in the system.

Performance of the Programs

The programs were extensively tested on the available thin-film data in literature and found to perform highly satisfactorily, as demonstrated in Fig. 1 on a number of measurements by Reuter et al. on two Pt films deposited on Au and Si. The agreement between the calculations (solid curves) and the measurements is excellent, which shows that the effect of the nature of the substrate is properly accounted for. The results of some of our own measurements on two Ti films on Si are shown in Fig. 2. Again the agreement between calculations and measurements is excellent, this time not only for the film but also for the substrate elements. Recently our software has been successfully used for the determination of concentration profiles in 1000 and 2500Å-thick \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) x films on \( \text{SrTiO}_3 \) substrates and the determination of N, O, and Si concentration profiles in implanted Si specimens (doses \( 10^7 \) to \( 10^8 \) at/cm\(^2\)). In the latter cases one can find the concentration profiles in an interactive way by simulating the geometry in 5-7 sublayers of the same compound with different thicknesses and compositions and comparing the calculations with the measurements, which must be available over the widest possible range in accelerating voltages.

In summary, we believe that thin-film analysis with a scanning electron microscope or microprobe is an elegant and powerful technique for nondestructive (sub)surface analysis that can now be carried out with relatively cheap and widely available equipment. Once the necessary software is commercially available the technique certainly deserves a widespread application.

References


FIG. 1.--Agreement between predictions of our program and experimental data of Reuter et al. for two Pt films of 84 and 519 µg/cm\(^2\) (392 and 2420 Å), once on Au and once on Si. X-ray take-off angle 52.5°.

FIG. 2.--Agreement between predictions of our program and our own measurements on two Ti films of 4.75 and 24.35 µg/cm\(^2\) (105 and 541 Å) on Xi. X-ray take-off angle 40°.