Modern Thin Film Analysis by Electron Probe Microanalysis.

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The use of the electron probe microanalyzer (EPMA) to determine the thickness and composition of thin film samples using special techniques has been attempted since the 60’s. It is used in many fields to determine, for example, coating thicknesses and oxidation layers. However, it is only since the 90’s that the method drastically improved with the introduction of realistic and accurate analytical description of the X-ray production depth distribution, the so-called φ(ρz) distribution. The most used models, the PAP and XPP [1] or XPHI [2] models, are also widely used to perform quantification of bulk samples, at least 30-100 µm thick. However, sometimes a lab is asked to determine a thin film (nanometers to submicron thick) composition on top of a substrate (e.g., engineering new electronic devices). This cannot be done using the traditional EPMA software. Though, the electron microprobe’s raw data—the k-ratios—can be used, when combined with specialized software. But, availability of thin film analysis programs not common in most laboratories and, with exception of GMRFilm [3], is not free. GMRFILM is a research grade, shareware DOS program for thin film analysis created by R. Waldo at General Motors Research Labs in the beginning of the 90’s. However, modern operating systems does not readily support it anymore and its use becomes more complicated. We undertook the creation of a modern thin film analysis program, inspired by GMRFilm, with a simple graphical user interface. The program implements the PAP model as described in [1], as well as a fitting algorithm to determine film composition and thickness. The input data provided by the user are the elements present in the different layers of the studied system, plus at least one set of k-ratios for the thin film. The program calculates theoretical k-ratios and tries to match them with the experimental data by modifying the compositions and thicknesses of the studied system.

However, the predictions and quantification results obtained with the φ(ρz) models, and especially with their implementations into computer code and software, are difficult to test. Very few certified thin-film reference samples are available. The National Institute of Standards & Technology (NIST) made a thin film Mg-Si-Ca-Fe standard composed of a glass film deposited onto a 20-nm thick C film supported by a Cu grid (SRM 2063a) [4]. The standard had a certified film composition and a known glass film thickness that can be used to validate the predictions of φ(ρz) models. However, the distribution of this standard is now discontinued. NIST is also distributing a Ni/Cr Thin Film Depth Profile Standard consisting of alternating layers of Cr and Ni of known thickness (±5.2% and ±6.8% for the Ni and Cr layers, respectively) that can be used to test the models on multilayer system.

Another, less accurate, way to test the predictions of the analytical φ(ρz) models is to compare them to Monte Carlo (MC) simulations that are known to give very accurate predictions for bulk and layered sample geometries. In our implementation of the PAP φ(ρz) model, we found that using this model in conjunction with the atomic parameters (ionization cross sections, fluorescence yields, mass absorption coefficients, ...) used in the PENELOPE/PENEPMA MC code [5], resulted in calculated characteristic X-ray intensities, in absolute value, that were similar between the two methods. Characteristic X-rays emitted from pure materials, binary compounds and thin film on substrate with various compositions and thicknesses were calculated for accelerating voltages ranging from 5 to 30 kV using our “modified” PAP model and the MC code PENEPMA. Calculated absolute characteristic X-ray intensities were in excellent agreements between the two methods (Fig. 1). These results confirm the accuracy of the φ(ρz) model used.

Secondary fluorescence (SF) can play an important role in determining the thickness and composition of thin films as these values are very sensitive to the measured X-ray intensities (k-ratios). Fluorescence of the film by characteristic X-rays emitted from the substrate can increase the X-ray intensity emitted from the film by more than 30% in some cases. For example, at 25 kV, the Fe Kα X-ray intensity of a 100 nm film of FeSi2 deposited onto a substrate of Ni is increased by 9.5% due to fluorescence by the Ni Kα-Kβ X-ray lines. SF by the bremsstrahlung can also increase the measured X-ray intensity by a few percent. This phenomenon increases as the difference between the measured characteristic X-ray and the electron beam energy increases. Our thin film program considers all the characteristic X-rays with energy higher than the studied X-ray to calculate the SF due to characteristic X-rays. SF by characteristic X-rays calculated with our program is in good agreement with PENEPMA results (Fig. 2). SF by bremsstrahlung X-rays is harder to calculate as their depth distribution, a function of the X-ray energy, is not well described by analytical theories. MC simulations can be used to calculate these distributions for a given sample [6] but this adds another layer of complexity and is time consuming. An approximation method used to analytically calculate this distribution consists in calculating the φ(ρz) depth distribution emitted by a quasi-random element for X-rays corresponding to the considered bremsstrahlung energy. However, this method, which was used in GMRFilm, tends to overestimate the calculated SF. But, by applying two correction factors, depending on the element and sample studied, the SF can very well match the one calculated by PENEPMA (Fig. 2). The program, in its last stage of development, will be freely available, but is still intensively tested against experimental and MC data.

References:

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| **Figure 1.** Characteristic X-ray intensity calculated with the PAP model (lines) and PENEPMA (symbols), both using the same atomic parameters. | **Figure 2.** Fe Kα X-ray intensity excited by SF from characteristic X-rays and bremsstrahlung. PAP model: lines; PENEPMA: symbols. |