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Thin Film Quantification by EPMA: Accuracy of Analytical Procedure

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The determination of thicknesses and composition of thin films deposited on substrates is important for practical applications in semiconductor research and thin-film technology. Electron probe microanalysis (EPMA), originally developed for determining the composition of bulk samples, has become a well established technique for determining thicknesses (in the range from 1nm to 2000 nm) but also compositions of multi-elements thin films deposited on a substrate [1-3]. Measurements of thin-film thicknesses can also be performed by some others techniques such as Rutherford backscattering spectrometry (RBS), Atomic Force Microscopy (AFM), Secondary Ion Mass spectrometry (SIMS), optical interferometry (OI), x-ray fluorescence XRF etc. Beyond the microscopic aspect of the measurement, and the fact that it is a non-destructive technique, one of the advantages of the EPMA method is the possibility to have simultaneously the composition of the film and the thickness. In addition, the equipment is available in many laboratories, i.e., a scanning electron microscope with an Energy Dispersive spectrometer (EDS) or more rarely an electron probe with Wavelength Dispersive spectrometers (WDS).

The EPMA method is based on the measurement, by varying incident electrons energy, of the ratios of x-ray intensities (k-ratio) emitted by the elements in the film and substrate to those emitted from bulk standards under same experimental conditions. This k-ratio cancels some instrumental parameters (e.g., detector efficiency) and some atomic parameters (e.g., fluorescence yield). The higher the value of the incident electron energy the deeper the electrons penetrate into the specimen, and as a consequence a decrease of the k-ratio of the film elements. The observed variation of the k-ratio with incident electron energy of the film and of the substrate is the input of the EPMA quantification code, which determines the thickness of the film by fitting the experimental k-ratios with a Monte Carlo (MC) simulation code [4] or with an analytical x-ray emission model [1-3]. The first method, although more accurate, is very time consuming, even with the fastest computers available. Since quantitative results are obtained with the help of automatic iterative numerical procedures or with a manual trial and error approach, for on line determination, only analytical models are used in practice.

To convert the measured k-ratio from elements of the film and the substrate into the correct thickness and composition of the film, an analytical x-ray emission model requires an accurate description of the x-ray depth distribution ($\phi(\rho z)$) from which the emitted x-ray intensities are calculated. However, the geometry is much more complex than for bulk analysis, because discontinuities (density, elements etc.) exist at the film/substrate interface and an analytical model must take into account these various aspects. In analytical approaches, for each film element, the $\phi(\rho z)$ curves which express the physical and mathematical description of the excitation volume in a stratified specimen are empirically modified by using weighting procedures according to the specific film/substrate combination. The simplest case of a thin film/substrate combination corresponds to two elements with neighbouring atomic numbers. For this combination the electron scattering and the x-ray generation are similar as in bulk sample and the $\phi(\rho z)$ curves from film and substrate elements are identical to bulk sample. With increasing difference in atomic number the

difference in electron scattering properties between film and substrate elements increases and the change in the $\phi(\rho z)$ curves from film and substrate elements increases with regard to bulk samples. Similarly the thickness of the film relatively to the $\phi(\rho z)$ curve can vary between two extremes: extremely thin or extremely thick. In the first case, the $\phi(\rho z)$ curves from film and substrate elements correspond to a bulk with the composition of the substrate, and in the second case, to a bulk with the composition of the film. In the intermediate cases the $\phi(\rho z)$ curves vary between these two extremes. It is worth noting that we can adjust the $\phi(\rho z)$ curves between these two extremes by varying incident electrons energy. In the analytical approaches, parameters describing the $\phi(\rho z)$ curves, like the surface ionization ($\phi(0)$)[5], are empirically modified by using weighting procedures depending of the thickness of the film. For the extremely thin films, the x-ray intensity emitted by an element of the film is simply the result of the product of the thickness by the $\phi(0)$ value. For this particular case the accuracy of the thickness model is directly related to the accuracy of the analytical description of $\phi(0)$.

Depending of the instrument (EDS or WDS), the operator experience, and the nature of the film and of the substrate, the uncertainty in the thickness determination can be expected to be less than 10% [1,6] even when the difference in the atomic number of the film and of the substrate is very large. The technique is more reliable for the concentration because the uncertainty of the thickness is the same for all elements of the film and as a result, accuracy similar to bulk can be achieved. In a general way, in addition to the uncertainty of intensity measurement and of the fitting routine, deviation caused by the $\phi(\rho z)$ model must be added. Besides, calculations require the knowledge of many atomic parameters that describe the electron interaction and the x-ray emission, such as the ionization cross section, mass absorption coefficient, fluorescent yields, and others. Unfortunately, by using standards, the uncertainty of atomic parameters like mass absorption coefficient or ionization cross section is less counterbalanced in thin films than in bulk sample. Thin films determination requires a hypothesis concerning the sample structure and consequently, the operator experience is crucial for the quality of the results. The aim of this communication is to show firstly that thin film quantification by EPMA is a reliable technique, secondly the effects of various parameters on the accuracy of the results and finally as the operator experience is essential in the quality of the results, how using efficiently this technique.

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