Progress in electron probe microanalysis

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$5 \cdot 10^4$ mm/rad eingestellt werden. *Abbildung 9a* zeigt das winkeldispersive Spektrum in der Nähe der Kohlenstoff-K-Kante eines 60 nm dicken Kohlefilms. Deutlich erkennbar ist das erste Maximum durch Anregung von π -Übergängen sowie die Streuwinkelverteilung von Einzelelektronenstößen (Compton-Streuung) beiderseits der Hauptintensität. Im Spektrum der Al_2O_3 -Oberflächenplasmonen einer 15 nm-Al-Schicht (*Abb. 9b*) ist bei hoher Winkeldispersion die Aufspaltung der Winkelverteilung in den symmetrischen ω^+ - und den asymmetrischen ω^- -Schwingungsmoden zu beobachten.

Zusammenfassung

Die vielseitigen Einsatzmöglichkeiten eines abbildenden Energiefilters für die Untersuchung materialkundlicher Proben in einem Transmissionselektronenmikroskop (Kontrast- und Auflösungsverbesserung bei Abbildung dicker Objekte, EELS- und Mapping-Analysentechnik, die Untersuchung elastischer und unelastischer Streuprozesse in kristallinen Proben und deren Bedeutung für die Kontrastentstehung) stehen heute der materialkundlichen Forschung, die auf Beschleunigungsspannungen über 100 kV

angewiesen ist, leider nicht zur Verfügung. Es wäre wünschenswert, daß künftig auch kommerzielle Hochleistungsgeräte im Mittelspannungsbereich mit abbildenden Energiefiltern ausgestattet würden. Der hohe instrumentelle Aufwand ist sicher durch die zahlreichen Anwendungsmöglichkeiten, von denen nur einige vorgestellt wurden, zu rechtfertigen.

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Progress in Electron Probe Microanalysis

G. F. Bastin and H. J. M. Heijligers

Introduction

In the past decade some very interesting developments have taken place in the field of electron probe X-ray microanalysis which will prove to be of special interest for the research on ceramic materials.

A very important development in this respect is the introduction of new synthetic multilayer analyzer crystals, which can give 3 to more than 20 times higher count rates for the ultra-light elements Be, B, C, N, O and F, elements which are of extreme importance for ceramic materials.

No less important, however, is the strong progress that has been made in the development of new and much better matrix correction procedures (especially the so-called ϕ (ρz)-procedures) which can cope with the extreme corrections which are frequently necessary in the analysis of ultra-light element radiations.

Finally the development of programs for Thin-Film Analysis must be mentioned. Such programs require an exact knowledge of the number of X-ray photons produced (ϕ) as a function of mass depth ρz (density times linear depth) in the specimen in order to be successful. As a consequence the $\phi(\rho z)$ -models which have proved to be so

successful for bulk matrix correction provide the best possible starting position here.

New Multilayer Crystals

In the past decade techniques have been developed to deposit alternating sequences of a heavy element film (the scattering element) followed by a light element film (the spacer) with such an accuracy in the spacing (2 d-value) that they can be used as artificial crystals for X-ray detection. A number of these crystals are nowadays commercially available and most of them offer great advantages over the conventional Stearate crystal with which most microprobes are commonly equipped. In our laboratory we gained a lot of experiences with 2 of the available multilayer crystals; the first is a W/Si multilayer on a single-crystalline Si-wafer, 200 pairs of layers, 2 d-spacing 59.8 Å and optimized for the analysis of N, O and F. The second crystal is a Mo/B₄C multilayer, 2 d-spacing 149.8 Å, optimized for the analysis of Be and B. Both crystals were supplied by Ovonic Corp. (Troy, Michigan, USA).

The benefits of these crystals can be summarized as follows:

- Much higher peak intensities than the conventional Stearate crystal. The increase in intensities ranges from 2.8 (Ref. 1) for Nitrogen and Oxygen up to well over 20 for Boron.
- Strong suppression (usually) of higher order reflections. This aspect is extremely important in quantitative analysis of ultra-light elements where a correct determination of the background is crucial. The multilayer crystals usually give a much simpler and cleaner background.
- The light element emission peaks recorded with a multilayer crystal are less sensitive to peak shape alterations (Ref. 2). This must be attributed to a somewhat poorer spectral resolution of these crystals.
- The 2-d spacing of the multilayer crystals can be tailored to request. This can be important to have easy access to both sides of the peak in order to find the background.
- The multilayer crystals have a very long lifetime compared to the Stearate crystal whose surface is extremely sensitive and can never be touched.

Progress in Matrix Correction Procedures

Strong progress has been made in bulk matrix correction, especially since the introduction of the so-called $\phi(\rho z)$ -approach. This approach is based on attempts to describe accurately the number of X-rays (ϕ) produced as a function of mass depth ρz (density times linear depth) for a wide variety in experimental conditions of which the accelerating voltage, the energy of the analyzed line and the composition of the matrix are the most important.

Once such $\phi(\rho z)$ curves are available bulk matrix correction becomes a relatively straight-forward process: all that is required is the integration of the $\phi(\rho z)$ curves between the ρz values of zero and infinity in order to find the total generated intensity in standard and specimen. Likewise, the emitted intensity can be found after an appropriate correction for absorption in the matrix, for which an exact knowledge of the $\phi(\rho z)$ curve is equally essential.

It will be evident that the advantages of this approach will be most pronounced in the most difficult cases of bulk matrix correction: i.e., the analysis of ultra-light elements which is usually characterized by very extreme conditions in terms of overvoltage (accel. voltage/critical excitation voltage) and magnitude of the absorption correction. The latter can easily be an order of magnitude larger than in the analysis of heavier elements. In such cases the value of the surface ionisation $\phi(0)$ and the first part of the $\phi(\rho z)$ -curve play a crucial role in the correction procedure. It is interesting to point out here that the first part of the $\phi(\rho z)$ -curve has always been neglected in the conventional „ZAF“ approach. In recent years it has been demonstrated (Ref. 3) that the newer matrix correction procedures offer a much superior performance over the conventional „ZAF“ procedure.

At the same time, however, it must be mentioned that the analysis of ultra-light elements is *not* only a matter of using a better correction program; items like the correct measuring procedures and the use of consistent mass absorption coefficients are equally important. Regarding the former aspect it is imperative to carry out the intensity measure-

ments in an integral fashion or use the Area/Peak Factor concept (Ref. 2, 3) in order to take the effects of peak shape alterations into account. As far as the mass absorption coefficients are concerned it is frequently possible, using the new $\phi(\rho z)$ models (Ref. 2-4) to determine better and more consistent values from a series of measurements carried out over a wide range in accelerating voltage.

The benefits of the new $\phi(\rho z)$ approaches are not limited to their use in ultra-light element analysis; they also enable the use of longer-wavelength radiations of heavier elements which are increasingly being used for measurements at extremely low voltages (below 5 kV) and in the analysis of thin films which is a rapidly growing field of interest (e.g., for the semiconductor industry).

Thin Film Analysis

As has been stated before the analysis of thin films requires an exact knowledge of the number of ionisations as a function of depth in the specimen. Fig. 1 gives a number of $\phi(\rho z)$ -curves for the case of Al-K α radiation in Al at various voltages. It is immediately obvious that the variation in accelerating voltage in combination with an exact knowledge of the $\phi(\rho z)$ -curves gives full control over the X-ray excitation range in the specimen. As a consequence the emitted X-ray signals which carry information about the successive layers in depth can be used in order to find both the compositions as well as the thicknesses of the various layers.

The specific advantage of this approach is that it makes non-destructive in-depth profiling possible with equipment which is widely available. For a film with thickness T one could, as a first approximation, integrate the $\phi(\rho z)$ -curve of the film element between $\rho z = 0$ and $\rho z = T$ and that of the substrate element between T and infinity in order to find the generated intensities. However, this simple approach only works when the atomic number of film and substrate do not differ too much. When large differences do exist a correction for the changes in backscattering of the electrons caused by the substrate has to be made. As it turns out this is perfectly possible in practice (see e.g., Ref. 5).

The thickness range which can be investigated with this technique is between 0 (less than 1 nm) and a few μm ,

Fig. 1. Some $\phi(\rho z)$ -curves for Al-K α radiation in Al at various accelerating voltages.

dependent on the density of the material. Apart from the thickness it is also possible to find at the same time the composition of the film in a double iterative procedure.

If all the elements involved are only confined either to the film or to the substrate then both the thickness *and* the composition of a film can be determined from intensity measurements carried out at only one accelerating voltage. In practice, however, it is wiser to repeat the measurements at a number of accelerating voltages in order to make sure that no additional interaction layers are overlooked.

An extension towards multilayer systems is also perfectly possible (Ref. 5). It will be clear though that the more complicated the system becomes the more measuring efforts will be necessary in order to arrive at consistent results. We ourselves have recently completed a Thin Film Program which can handle up to 5 different layers on a substrate. This program will soon be available through commercial channels.

Under the restriction that no overlap of elements occurs it is possible to find the thicknesses and the compositions of these 5 layers from measurements taken at only one accelerating voltage. If overlap occurs one can still find the correct answers; however, only by using measurements taken over a range of accelerating voltages.

Concluding this brief review of progress in electron probe X-ray microanalysis it can safely be stated that as a result of the strong improvements in matrix correction procedures, especially those based on an exact description of $\phi(\rho z)$ -curves, new and exciting tools have come into the hands of

people operating scanning electron microscopes and electron probe microanalyzers; tools which can be used for the investigation of (sub) surface layers which would normally be much too thin for the usual examination in a cross-section.

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Note: A lot of information on "The State of the Art" in electron probe microanalysis can be found in the Proceedings of the First European Workshop on "Modern Developments and Applications in Microbeam Analysis", which was organized by the European Microbeam Analysis Society and the University of Antwerp (UIA) in Antwerp (Belgium) on 8–10 March 1989.

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