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AN ITERATION PROCEDURE TO CALCULATE FILM COMPOSITIONS AND THICKNESSES IN ELECTRON-PROBE MICROANALYSIS

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Recent mathematical approximations of $\phi(\rho z)$, the depth distribution of electron excited x rays, have opened up the possibility of quantitative thin film analysis with the electron probe. Unfortunately, no published methods are currently available that solve the system of equations resulting from a thin-film system whose unknowns are the film and substrate composition and film thicknesses. The purpose of this paper is to describe an iteration procedure that solves the system of equations that result from a thin-film system (defined as a film on a buried layer on a substrate).

Quantitative Analysis by $\phi(\rho z)$ Curves

In this discussion, we consider a thin-film system with u elements in a surface film of thickness δ^{f1}, on a subsurface film (buried layer) of v elements extending from δ^{f1} to $\delta f2$, on a substrate of w elements. Packwood[1] found that $\phi(\rho z)$ can be approximated by a modified Gaussian function of the form

$$I_{i,obs} = \gamma_0 \exp[-\alpha^2(\rho z)^2] - (\gamma_0 - \phi_0)\exp[-\alpha^2(\rho z)^2 - \beta\rho z] \quad (1)$$

The general forms for the α, β, ϕ_0, and γ_0 parameters were derived from a random-walk theoretical treatment of electron trajectories.[2] Computer fitting techniques were used to optimize the functional forms of the parameters.[3,4]

Once the $\phi(\rho z)$ parameters have been calculated, the observed x-ray intensity for the ith element in a thin film system is found by multiplying $\phi(\rho z)$ by the x-ray absorption factor $\exp(-\chi\rho z)$ and integrating over the appropriate values of ρz. For the general case of an element in a subsurface film extending from $\rho z = \delta'(\delta f1)$ to $\rho z = \delta''(\delta f2)$,

$$I_{i,obs} = h_1 \int_{\delta'}^{\delta''} \phi(\rho z)\exp(-\chi\rho z)\, d(\rho z) \quad (2)$$

which can be integrated exactly:[1]

$$I_{obs} = h_2 C_i \exp[-\delta'(\chi' - \chi)]\, \gamma_0 \exp(\chi/2\alpha)^2 \cdot \{\mathrm{erf}[\alpha\delta'' + (\chi/2\alpha)] - \mathrm{erf}[\alpha\delta' + (\chi/2\alpha)]\} - (\gamma_0 - \phi_0)\exp[(\beta + \chi)/2a]^2 \cdot \{\mathrm{erf}[\alpha\delta'' + (\beta+\chi)/2a] - \mathrm{erf}[\alpha\delta' + (\beta+\chi)/2\alpha]\} \quad (3)$$

where χ' is the x-ray absorption factor for the element i radiation in the surface film and erf(x) is the error function of x. Setting $\delta' = 0$ and $\delta'' = \infty$ gives the formula for a homogeneous (semi-infinite) specimen. Setting $\delta' = 0$ and $\delta'' = \delta^{f1}$ gives the formula for a surface film of thickness δ^{f1}. Setting $\delta' = \delta^{f2}$ and $\delta'' = \infty$, with the additional absorption term $\exp[-(\chi'' - \chi)(\delta f2 - \delta f1)]$, gives the formula for a substrate covered by a surface film of thickness δ^{f1} and a subsurface film of thickness $\delta^{f2} - \delta^{f1}$. The constants h_1 and h_2 cancel in the equation which defines the experimental k-ratio for each element i.

$$k_{i,exp} = I_{i,obs}(sp)/I_{i,obs}(st) \quad (4)$$

where (sp) is the specimen and (st) is the standard.

Calculation of α, β, and ϕ Parameters for Layered Specimens

For a thin-film system, each of the parameters in $\phi(\rho z)$ will now also be a function of the electron energy, overvoltage ratio, the compositions of the films and substrate, and the film thicknesses. Packwood[5] proposed that a weighting function be based on the error function of α times the film thickness δ, or $\mathrm{erf}(\alpha\delta)$. The choice of which α to use--that from the surface film, buried layer, or substrate--is not too critical since α is not a sensitive function of atomic number. I have used a weighted value for α, $\bar{\alpha}$, based on $\mathrm{erf}[\bar{\alpha}(\delta^{f1},\delta^{f2})]$. An iterative method is required to calculate $\bar{\alpha}$ since it is not known at the start of the calculation. An initial value $\bar{\alpha}_1$ is estimated from

$$\bar{\alpha}_1 = (\alpha^{f1} + \alpha^{f2} + \alpha^{s})/3 \quad (5)$$

where α^{f1} is the α for the composition of film 1, etc. By extension of Packwood's $\mathrm{erf}(\bar{\alpha}\delta)$ weighting function to a bilayer film system, this value $\bar{\alpha}_1$ is used to calculate $\bar{\alpha}_2$:

$$\bar{\alpha}_2 = \alpha^{f1} + (\alpha^{f2} - \alpha^{f1})[\mathrm{erfc}(\bar{\alpha}_1\delta^{f1})] + (\alpha^{s} - \alpha^{f2})\,\mathrm{erfc}[\bar{\alpha}_1(\delta^{f1} + \delta^{f2})] \quad (6)$$

When $\bar{\alpha}_{n+1} = \bar{\alpha}_n$ within an error ε, the iterative solution is completed. Usually, convergence is achieved by the third iteration. A weighted ϕ_0 parameter, $\bar{\phi}_0$, is based on $\mathrm{erf}[2\bar{\alpha}(\delta^{f1},\delta^{f2})]$.[5] $\bar{\beta}$ is calculated with $\bar{Z}$ and $\bar{A}$ which are calculated in the same manner as Eq. (6).

Once the $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}_0$, and $\bar{\phi}_0$ are calculated, a

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system of equations is formed from Eqs. (3) and (4). To solve this system of equations, an iterative procedure similar to that used in the ZAF method of electron probe microanalysis of homogeneous specimens is required. An added complication in this iteration scheme is that additional variables are added in the unknown film thicknesses, which are present as the limits of the integrals in Eq. (3).

Initial Values for Film Thicknesses

Initial thickness estimates were made starting with estimates of the x-ray generation range ρz_r, which can be approximated by[6]

$$\rho z_r = 7.0\ (E_0^{1.65} - E_c^{1.65})\ \mu g/cm^2 \qquad (7)$$

where E_0 is the incident electron energy and E_c is the critical excitation energy for the x-ray line. The thickness δ^{f1} of a surface film can be thought as being comprised of the contributions from each of the u elements in the film. Treating each element individually and neglecting absorption effects we can estimate the contributed thickness ρz_i^{f1} as the thickness at which the integral from $\rho z = 0$ to $\rho z = \rho z_i^{f1}$ of the $\phi(\rho z)$ function for the specimen ratioed to the $\phi(\rho z)$ function for the pure element standard equals the k-ratio for the element, i.e., find z_i^{f1} such that

$$k_{i,exp} = \frac{\int_0^{z_i^{f1}} \phi(\rho z)^{sp}\, d(\rho z)}{\int_0^{\infty} \phi(\rho z)^{st}\, d(\rho z)} \qquad (8)$$

This equation cannot be used to calculate ρz_i^{f1} since the required function $\phi(\rho z)^{sp}$ can only be arrived at through subsequent iterations of the main iteration procedure.

This problem is avoided by use of a triangular approximation for $\phi(\rho z)^{sp}$ in Eq. (8), as in Fig. 1. $\phi(\rho z)^{st}$ is assumed equal to $\phi(\rho z)^{sp}$. Now, ρz_i^{f1} is the solution of the equation

$$q + [q - (q\rho z_i^{f1}/\rho z_{ri})]/2 = (k_{i,exp} q \rho z_{r,i})/2$$

which is

$$\rho z_i^{f1} = \rho z_{r,i}\ (1 - \sqrt{1 - k_{i,exp}}) \qquad (9)$$

$\rho z_{r,i}$ is the x-ray-generation range for the element i radiation according to Eq. (7). This solution is independent of the ordinate intercept q.

The initial thickness estimate for the surface film, δ_0^{f1}, is the sum of the contributions from each element

$$\delta_0^{f1} = \sum_i \rho z_i^{f1} \qquad i = 1, u \qquad (10)$$

The initial thickness estimate for the buried film, δ_0^{f2}, can be calculated in a similar manner:

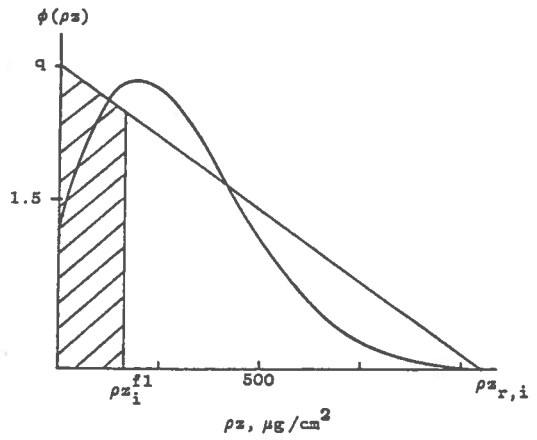

FIG. 1.--Triangular approximation for $\phi(\rho z)$ used to calculate starting film thicknesses in iteration procedure. Fractional area shaded is assumed equal to the k-ratio for the ith element.

$$\rho z_i^{f2} = \rho z_{r,i} \left(1 - k_{i,exp} - \frac{2\delta_0^{f1}}{\rho z_{r,i}} + \frac{(\delta_0^{f1})^2}{(\rho z_{r,i})^2} \right)^{1/2} \qquad (11)$$

with δ_0^{f2} calculated in the same manner as δ_0^{f1} in Eq. (10).

Initial Values for Film and Substrate Compositions

For the elements in the surface film, the normalized k-ratios are used as the starting compositions $C_{i,0}$. For the buried layer, the k-ratios are first adjusted by the x-ray absorption term of the surface film, $\exp[-\delta_0^{f1}(\chi' - \chi)]$, and then normalized. Finally, for the substrate, the k-ratios are adjusted by the x-ray absorption terms for the surface layer and buried layer and then normalized. Thus

Surface film

$$C_{i,0} = \frac{k_{i,exp}}{\Sigma k_{i,exp}}$$

Buried layer

$$C_{i,0} = \frac{k_{i,exp}}{\Sigma k_{i,exp}} \frac{\exp[-\delta_0^{f1}(\chi' - \chi)]}{\exp[-\delta_0^{f1}(\chi' - \chi)]} \qquad (12)$$

Substrate

$$C_{i,0} = \frac{k_{i,exp}\ \exp[-\delta_0^{f1}(\chi' - \chi) - (\delta_0^{f2} - \delta_0^{f1})(\chi'' - \chi)]}{\Sigma k_{i,exp}\ \exp[-\delta_0^{f1}(\chi' - \chi) - (\delta_0^{f2} - \delta_0^{f1})(\chi'' - \chi)]}$$

Film Thicknesses and Compositions for Subsequent Iterations

The initial values for the film and substrate compositions and film thicknesses are used in Eq. (4) to calculate initial theoretical k-ratios, $k_{i,1}$, for each element. The experimental k-ratios, $k_{i,exp}$, together with $k_{i,1}$, are now used to calculate new concentrations and thicknesses $C_{i,1}$, δ_1^{f1}, and δ_1^{f2}, for the first iteration. The process is repeated with $C_{i,1}$, δ_1^{f1}, and σ_1^{f2} being used to calculate new theoretical k-ratios $k_{i,2}$ for the second iteration. This process continues until no further change in concentrations are observed within a preset error ε for each element.

Of importance here is the method for calculating $C_{i,m+1}$, δ_{m+1}^{f1}, and δ_{m+1}^{f2} from $C_{i,m}$, δ_m^{f1}, and δ_m^{f2} using $k_{i,m}$ and $k_{i,exp}$. Several convergence methods were examined. The hyperbolic method of Criss and Birks used in most ZAF correction procedures for homogeneous specimens was tried first. It was not obvious that this method should work for thin films, but in fact it did produce convergence for all systems studied. The rate of convergence was slow, however, especially in the case of bilayer systems. A faster method is the relatively simple convergence method of Eq. (13), which produced solutions in 30-50% fewer iterations than the hyperbolic method:

$$C_{i,m+1} = C_{i,m} \frac{k_{i,exp}}{k_{i,m}} \tag{13}$$

For the buried layer and substrate, faster convergence is sometimes achieved when, after the $C_{i,m+1}$ are normalized, they are adjusted by:

Buried layer

$$C_{i,m+1} = C_{i,m+1} \frac{\exp[-\delta_m^{f1}(\chi' - \chi)]}{\exp[-\delta_{m+1}^{f1}(\chi' - \chi)]} \tag{14}$$

Substrate

$$C_{i,m+1} = C_{i,m+1} \frac{\exp[-\delta_m^{f1}(\chi'-\chi)] \exp[-(\delta_m^{f2} - \delta_m^{f1})(\chi''-\chi)]}{\exp[-\delta_{m+1}^{f1}(\chi' - \chi) \exp[-(\delta_{m+1}^{f2} - \delta_{m+1}^{f1})(\chi''-\chi)]}$$

This adjustment increases the rate of convergence by increasing/decreasing the $C_{i,m+1}$ in line with the increase/decrease in δ_{m+1}^{f1} and δ_{m+1}^{f2}.

The best method found for successive thickness estimates was a ratio of k-ratio sums:

Surface film

$$\delta_{m+1}^{f1} = \delta_m^{f1} \cdot \frac{\sum_i k_{i,exp}}{\sum_i k_{k,m}} \qquad i = 1,u \tag{15}$$

Buried layer

$$\delta_{m+1}^{f1} = \delta_m^{f1} \frac{\sum_i k_{i,exp}}{\sum_i k_{i,m}} \qquad i = 1,v \tag{15}$$

Implementation of the Iteration Procedure

The $\phi(\rho z)$ thin film model and correction procedure has been used on a wide variety of specimens. The iteration procedure has never failed to converge, usually within 5-10 iterations. The convergence is only slightly sensitive to the starting values for film compositions and thicknesses. In fact, a much simpler method for calculating the initial film thicknesses δ_0^{f1} and δ_0^{f2} based on Eqs. (9)-(11) is:

Surface film

$$\delta_0^{f1} = R\sqrt{1 - \Sigma k_{i,exp}} \tag{16}$$

Buried layer

$$\delta_0^{f1} = R\left[1 - \Sigma k_{i,exp} - \frac{2\delta_0^{f1}}{R} + \frac{(\delta_0^{f1})^2}{R^2}\right]^{1/2}$$

where $R = 7.0E_0^{1.65}$ in μg/cm². Convergence with these equations took at most one or two more iterations than the method described above. The step to adjust the starting concentrations of elements in subsurface films and substrates for overlayer x-ray absorption reduces the number of iterations by 1-3, but is not necessary for convergence. It is likely that even more efficient convergence schemes than these may be found.

The number of unknowns in the system of equations solved in the iteration procedure is the combined number of elements in the film and substrates, u + v + w = n, and the two film thicknesses δ^{f1}, δ^{f2}, or n + 2. The number of equations totals n. There are more unknowns than equations, which means there may be no solution. The number of unknowns can be reduced in several ways. For example, the weight fraction sums for the two films can be constrained to 1.0, which reduces the number of unknowns to n + 2 - 2 = n. The weight fraction sum for the substrate is then allowed to float freely and becomes a test of the combined analytical procedure and $\phi(\rho z)$ model. The closer the value is to 1.0, the better the $\phi(\rho z)$ model. Due to the magnified effect of uncertainties in mass absorption coefficients and the thin-film model, the largest errors in composition willl be in the substrate, whereas errors in the substrate composition will have relatively little influence on the film compositions or thicknesses. It is thus advantageous to fit the thin-film system to a model in which the film compositions are constrained to a sum of 1.0, letting errors in the model accumulate as much as possible in the substrate composition. In most specimens, the determination of film compositions and thicknesses is of more interest than the determination of substrate composition.

TABLE 1.--Concentrations and predicted k-k-ratios for 100 μg/cm² $Y_1Ba_2Cu_3O_{6.5}$ on 100μg/cm² $SrTIO_3$ on SiO_2 substrate for 15kV beam voltage and 40° take-off angle; φ(ρz) parameters of Bastin et al.[4] were used.

Layer	Element, x-ray line	Concentration in layer, Wt%	k-ratio
1	Y Lα	13.35	.0382
1	Ba Lα	41.23	.1266
1	Cu Kα	28.61	.1275
1	O Kα	16.81	.0477
2	Sr Lα	47.74	.1092
2	Ti Kα	26.10	.0825
2	O Kα	26.15	.0248
substrate	Si Kα	46.74	.1194
substrate	O Kα	53.26	.0120

TABLE 2.--Film and substrate compositions and film thicknesses at the end of each loop of the iteration procedure.

	Thickness, μg/cm²		Weight Fraction								
			Layer 1				Layer 2			Substrate	
Iteration	Layer 1	Layer 2	Y	Ba	Cu	O	Sr	Ti	O	Si	O
0(start)	81.9	90.2	.1123	.3725	.3749	.1403	.5113	.3202	.1686	.5342	.5658
1	100.3	90.4	.1643	.5117	.3501	.1987	.4819	.2707	.2488	.3661	.4447
2	99.1	98.7	.1315	.4074	.2841	.1651	.5254	.2873	.2793	.4809	.5002
3	99.7	99.5	.1341	.4154	.2885	.1682	.4823	.2647	.2614	.4811	.5461
4	99.9	99.8	.1337	.4132	.2868	.1682	.4792	.2621	.2620	.4686	.5334
5	100.0	99.9	.1336	.4125	.2863	.1681	.4781	.2614	.2616	.4680	.5324
6	100.0	100.0	.1335	.4124	.2862	.1681	.4776	.2612	.2616	.4675	.5327
7	100.0	100.0	.1335	.4123	.2861	.1681	.4775	.2611	.2615	.4674	.5326
8	100.0	100.0	.1335	.4123	.2861	.1681	.4775	.2610	.2615	.4674	.5326

TABLE 3.--Composition and thickness of Ni-Mo multilayers.

	Mo and Ni Found, μg/cm²				Composition, Atomic %				Thickness[a], nm		
	φ(ρz)		ICP		φ(ρz)		ICP		φ(ρz)	XRD	ICP
Specimen	Ni	Mo	Ni	Mo	Ni	Mo	Ni	Mo			
A	138	156	155	151	59.4	40.6	62.7	37.3	308	305	322
B	149	160	169	156	60.9	39.1	63.9	36.1	325	322	343
C	140	152	153	162	60.6	39.4	63.6	36.4	307	313	345
D	138	158	158	153	59.4	40.6	62.8	37.2	310	309	328

[a]Linear thickness, z, was calculated from mass thickness, ρz, with the formula:

$$z = \frac{\rho z}{\overline{\rho}} \qquad \text{where} \qquad \overline{\rho} = \frac{C_{Ni} \cdot A_{Ni} + C_{Mo} \cdot A_{Mo}}{\frac{C_{Ni} \cdot A_{Ni}}{\rho_{Ni}} + \frac{C_{Mo} \cdot A_{Mo}}{\rho_{Mo}}}$$

where C is the atomic fraction, A is the atomic weight and ρ is the density of each element in the film.

The combined φ(ρz) model and iteration procedure can be demonstrated on the relatively complicated model system 100 μg/cm² $Y_1Ba_2Cu_3O_{6.5}$ on 100 μg/cm² $SrTiO_3$ on SiO_2 substrate. In the actual analysis of such a material, it would not be possible to find the oxygen k-ratios for each layer and substrate experimentally. However, we have analyzed such specimens in our laboratory by fixing the oxygen weight fraction at each step of the iteration according to its stoichiometry using element valences. To illustrate the operation of the iteration procedure, I have used the set of predicted k-ratios for this system as the "experimental" k-ratios. These k-ratios can be calculated based on the procedure previously described. They are given in Table 1.

The combined φ(ρz) model and iteration procedure should be able to determine the layer thicknesses and compositions from the set of theoretical or experimental k-ratios. Listed in Table 2 is a sample output of the program execution. The stopping criterion is $C_{m+1} - C_m \leq 0.0001$ for each element.

The composition and thickness for layer 1 is determined to within 1% in only two itera-

tions and for layer 2 in three iterations. The slow part of the iteration scheme is the determination of the substrate composition, which is extremely sensitive to the compositions and thicknesses of the two overlayers. The iteration process can be speeded up considerably if the composition of the buried layer or substrate is fixed at the start of the iteration. Fixing the composition and thickness of the buried layer to 100 $\mu g/cm^2$ $SrTiO_3$ reduces the number of iterations to four as does fixing the substrate composition to SiO_2.

Application to Ni-Mo Thin Films

Table 3 shows the results of 20kV analyses of Ni-Mo multilayer arrays on SiO_2. The bilayer thicknesses of the Ni-Mo multilayers were varied from 2.1 to 20.1 nm. The mean free paths of the analytical lines used, Mo Lα and Ni Kα, and the electron range are all much larger than the bilayer thickness. The multilayers can thus be treated as if they were single homogeneous alloy films. The composition of each specimen was determined with an accuracy of ± 2% by inductively coupled plasma/atomic emission spectroscopy (ICP). The thicknesses of the films were also determined by an x-ray diffraction (XRD) technique. In the XRD technique, the bilayer thicknesses were determined from the superlattice x-ray diffraction peaks and then multiplied by the number of bilayers (80-200). Accuracy of this method is estimated as ± 2%. Fluorescence corrections are not indicated for these specimens, but could easily be incorporated into the program.

The average difference in composition between the ICP and $\phi(\rho z)$ (electron-probe) methods is 11.0% for Ni and 3.8% for Mo. The average difference in thickness determinations is 1.0% comparing the electron probe with XRD and 6.5% comparing electron probe with ICP. The difference in thickness determinations between the electron probe and ICP techniques is explained by the lower Ni found with the electron probe; however, it is not clear why the ICP thickness values found were significantly thicker than those found with the XRD technique, since both are reportedly accurate to ± 2%.

An important aspect of thin-film analysis with an electron probe is the accurate modeling of the $\phi(\rho z)$ curves. Various forms of the $\phi(\rho z)$ parameters and weighting functions can now be rapidly tested on complex systems with this iteration procedure. Databases containing experimental k-ratio and composition data for a large number of thin film systems could be constructed and used to test $\phi(\rho z)$ and weighting function models.

References

1. R. H. Packwood and K. S. Milliken, *A General Equation for Predicting X-ray Intensities from Stratified Samples in the Electron Microprobe*, CANMET Research Report PMRL 85-25(TR), May 1985.

2. R. H. Packwood and J. D. Brown, "A Gaussian expression to describe $\phi(\rho z)$ curves for quantitative electron probe microanalysis," *X-ray Spectrometry* 3: 138, 1981.

3. J. D. Brown and R. H. Packwood, "Quantitative electron probe microanalysis using Gaussian $\phi(\rho z)$ curves," *X-ray Spectrometry* 11: 187, 1982.

4. G. F. Bastin, F. J. J. van Loo, and H. J. M. Heijligers, "Evaluation of the use of Gaussian $\phi(\rho z)$ curves in quantitative electron probe microanalysis: A new optimization," *X-ray Spectrometry* 13: 91, 1984.

5. R. H. Packwood, from text of the Microbeam Analysis Society's 1986 Tour Speaker's Talk, given at Ford Motor Co., 6 May 1986.

6. K. F. J. Heinrich, *Electron Beam X-ray Microanalysis*, New York: Van Nostrand Reinhold, 1981, 419.

7. J. Criss and L. S. Birks, "Intensity formulae for computer solution of multicomponent electron probe specimens," in T. D. McKinley, K. F. J. Heinrich and D. B. Wittry, Eds., *The Electron Microprobe*, New York: Wiley, 1966, 217.