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A CALCULATION METHOD OF X-RAY EMITTED INTENSITY IN MULTI-LAYER FILMS BY MONTE CARLO SIMULATION

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Abstract

A calculation method of X-ray emitted intensity in multi-layer films is proposed in this paper. The method is based on the work developed by us: (1) a simplified physical model of electron scattering and Monte Carlo evaluations in a single medium and in multi-layer media and (2) the theories and the formulae for excitation, absorption and fluorescence of characteristic X-rays. The intensity ratio of X-rays for the known thickness films, Au/Cu/Si and Cr/Ni/Si, were calculated at 20, 25 and 30 keV. Calculated results are compared with experimental values of electron microprobe analysis for the multi-layer film specimens, and the correspondence is excellent. The work lays foundations for X-ray quantitative microanalysis of multi-layer specimens.

KEY WORDS: Multi-layer films, X-ray Quantitative microanalysis, Electron Scattering, Fluorescence correction, Monte Carlo simulation.

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Introduction

In X-ray quantitative microanalysis (XQMA), there are some special cases which are not considered by the conventional ZAF procedure. These are XQMA for the specimens of microparticles with irregular shapes, and thin films or multi-layer films. In recent years, the theoretical and experimental difficulties of XQMA for microparticles have already been solved by the authors[8] and others, such as Armstrong[1]. Some valuable contributions[5,10] have already been made in research on XQMA of film specimens.

Based on Monte Carlo calculations, using our simplified model of electron scattering, fluorescence and absorption formulae of X-rays, the intensity ratio values, k, of X-rays for multi-layer films Au/Cu/Si and Cr/Ni/Si (on substrate Si) were evaluated at the various acceleration voltages. Monte Carlo calculations show good correspondence to the experimental results of EPMA for the film specimens. This research provides a means for realizing XQMA of multi-layer film specimens.

Principle

Figure 1 demonstrates that an electron beam bombards a multi-layer film specimen on a thick substrate with normal incidence. We have derived a series of theories to treat the complex physical processes, such as electron scattering and generation, absorption and fluorescence of X-rays in a multi-layer target.

Electron scattering in multi-layer media

1) *A simplified model of electron scattering in a single medium.* Elastic scattering of electrons is calculated from[4,11]:

$$\operatorname{ctg}\frac{\theta}{2} = \frac{P \cdot E}{0.0072 \cdot Z} \quad , \qquad (1)$$

where P is the impact parameter, $P=P_o R^{\frac{1}{2}}$. R is uniform random number in the range of 0-1. If N is the scattering step number in the fixed step length model, the maximum collision parameter P_o may be expressed as follows:

$$P_o = f(N)\, Z^{0.4/E_o} \quad , \qquad (2)$$

where Z is the atomic number, and E_o is the primary energy of incident electrons. In our model N is taken as 100, then f(N) approximates to 0.85.

Inelastic scattering is represented by the Bethe equation:

$$-\frac{dE}{d\rho s} = -\frac{2e^4 N_A}{E}\cdot\frac{Z}{A}\ln\frac{1.166E}{J} \quad , \qquad (3)$$

in which N_A is Avogadro's number, A is atomic

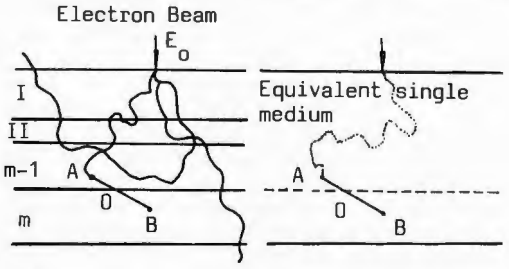

Fig. 1. Electron scattering and X-ray excitation in multi-layer media.

weight and J is the mean ionization potential. The reliability of this physical model is confirmed in our preceding papers[5,8].

2) Electron scattering in multi-layer media--'equivalent single medium scattering' calculation method. Suppose that electron i comes from medium m-1 into medium m, the scattering paths of the electron in the two media are AO and OB respectively (Fig. 1a), the step length (mass length) of electron scattering on both sides of a boundary may be approximately considered as the one in the preceding medium, we have

$$\rho_{m-1}\cdot AO + \rho_m\cdot OB = \rho_{m-1}\cdot S_{m-1} \quad , \qquad (4)$$

where S_{m-1} is the mean free path (in length units) of electron i in medium m-1, then

$$OB = \frac{\rho_{m-1}\cdot S_{m-1} - \rho_{m-1}\cdot AO}{\rho_m} \quad , \qquad (5)$$

After scattering many times, the energy of electron i at point B in medium m is E_n. The scattering path of the electron from point B only relates to the direction cosine of the vector $\overline{AB}$ and energy E_n. So all of the scatterings of electron i before point B may be regarded equivalently as those happening in medium m. Then the problem will be simplified. Based on the equal step length model, the energies $E_1, E_2, \ldots, E_k \ldots$ of the electron with the primary energy E_o at every step in medium m can be calculated by Bethe formula. By comparing E_o with $E_1, E_2, \ldots, E_k, \ldots$, the energy E_k which is the closest to E_n among the energies is obtained. Then k is regarded as the step number of scattering before electron i enters medium m. The scattering path of electron i from k+1 step in medium m is continuously simulated by using the 'equal step length' model, until the electron enters another medium or stops in medium m due to loss of all its energy. Once an electron comes into another medium, the previous scattering history is considered to be equivalent to that one happens in the 'new' medium. This is the 'equivalent single medium scattering' concept. The dotted line in Fig. 1b represents the scattering track of an electron in the 'equivalent single medium'. Electron scattering and excitation of X-ray in multi-layer media can be conveniently calculated by using the theory of 'equivalent single medium scattering' and the 'equal step length' model.

Calculation of X-ray emitted intensity in multi-layer films

1) General equation. Considering the absorption and fluorescence of characteristic X-rays, the general equation of the emitted intensity of X-rays of element i from the nth layer film of multi-layer specimens:

$$I_{n.i} = \Delta I_{n.i.f} + \int_{(n-1)\text{th layer}}^{n\text{th layer}} \varphi_n(\rho_n Z)\, d\rho_n Z \cdot \sum_{m=1}^{n} \exp(-\mu_m \rho_m d_m \csc\psi), \qquad (6)$$

where $\Delta I_{n.i.f}$ and $\int_{(n-1)\text{ layer}}^{n\text{th layer}} \varphi_n(\rho_n Z)d\rho_n Z$ are the emitted fluorescence intensity and the generated intensity of characteristic X-rays, respectively, and $\sum_{m=1}^{n} \exp(-\mu_m \rho_m d_m \csc\psi)$ is the absorption term; φ_n, $\rho_{n,m}$ and μ_m are the distribution in depth of X-rays, the density of nth (or mth) layer medium, and the mass attenuation coefficient of mth layer medium respectively, and ψ is the X-ray take-off angle.

The $\varphi_n(\rho Z)$ function can be easily evaluated by using the electron scattering model in multi-layer media mentioned above, and the excited probability of characteristic X-rays is obtained, according to Bethe as:

$$Q_{k.l} = q_{k.l}\,\frac{\ln U}{U}\,\frac{1}{E^2_{k.l}} \quad , \qquad (7)$$

in which $Q_{k.l}$ is the ionization cross-section for k or l shell electrons, $E_{k.l}$ is the minimum ionization potential, $q_{k.l}$ is a constant, and U is overvoltage ($E/E_{k.l}$).

2) Formulae for Fluorescence of Characteristic X-rays in multi-layer films. One of the most difficult problems in XQMA for multi-layer films is the calculation of the fluorescence

contribution. Castaing's equation can be used to estimate the fluorescence correction in a bulk target[2]. Cox et al. developed a correction procedure to calculate the fluorescence produced in a thin coating on a substrate[3]. In Cox's formula, the mass thickness of the film is assumed to be much less than that of excited X-ray depth in a target. So Cox's equation is suitable for the very thin film.

In this paper, formulae are presented to calculate the fluorescence intensity from an element excited by the characteristic X-rays emitted from another element in multi-layer films. The formulae are applicable whether the layer is thin or thick, and are extended to include multi-layer multi-component films. Figure 2 shows a multi-layer specimen which consists of film 1,2,..., m,..., n,.... As we know, the distribution of the X-ray photons excited by incident electrons is symmetrical to the incident direction of the electron beam[7,12], i.e. the direction of Z axis. So we suppose the characteristic X-rays of element j in film m are emitted from mid-point α of film m to simplify the calculations. Fluorescence X-rays of the film are also considered to be emitted from the mid-point of the film.

Then we derive the equations[9] for calculating the fluorescence intensity of element i in film n, ΔI_{nifmj}, produced by the characteristic X-ray of element j in film m. It is

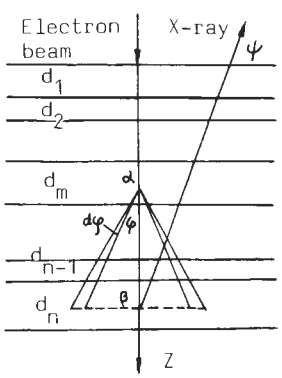

Fig. 2. Schematic diagram of calculating fluorescence correction for multi-layer films.

expressed as follows (the derivation is in reference (9)):

$$\Delta I_{nifmj} = \frac{1}{2}\,\varepsilon I_{mj}\, e^{-W_n \csc\psi} \cdot \int_0^{\frac{\pi}{2}} \sin\varphi \cdot \left[e^{-U\sec\varphi} - e^{-(U+V)\sec\varphi} \right] d\varphi \quad , \qquad (8)$$

in which $I_{m.j}$ is the intensity of the characteristic X-rays emitted from element j in film m,

$$W_n = \mu_{1,i}\,\rho_1 d_1 + \mu_{2,i}\,\rho_2 d_2 + \cdots\cdots + \mu_{n-1,i}\,\rho_{n-1}\,d_{n-1} + \mu_{n,i}\,\rho_n \frac{d_n}{2} \quad , \qquad (9)$$

$$U = \mu_{m.j}\,\rho_m \frac{d_m}{2} + \mu_{m+1,j}\,\rho_{m+1}\,d_{m+1} + \cdots\cdots + \mu_{n-1,\,j}\,\rho_{n-1}\,d_{n-1} \quad , \qquad (10)$$

and

$$V = \mu_{n,j}\,\rho_n d_n \quad , \qquad (11)$$

In the above-mentioned equations, U is the mass attenuation coefficient of film n for i radiation, $U_{m.j}$ is the m.a.c of film radiation, d_n is the thickness of the nth layer film, and the conversion efficiency factor, ε, is given by[12]

$$\varepsilon = C_{n.i}\,\frac{\mu^i_{n.j}}{\mu_{n.j}} \cdot \frac{r_i - 1}{r_i} \cdot W(i) \quad , \qquad (12)$$

where $C_{n.i}$ is the weight fraction of element i in film n, $\mu^i_{n.j}$ is the m.a.c of element i for j radiation in film n, r_i the absorption edge jump ratio of element i, and W(i) the fluorescence yield of i radiation.

Equation (8) is still applicable when film n is above film m.

If m=n, i.e. there are element i and element j in the same layer film, the form of equation (8) is:

$$\Delta I_{nifmj} = \varepsilon I_{n.j}\, e^{-W_n \csc\psi} \int_0^{\frac{\pi}{2}} \sin\varphi \left(1 - e^{-v\sec\varphi \cdot \frac{d_n}{2}}\right) d\varphi \qquad (13)$$

If layer m is very thick, e.g. it is a substrate, the assumption that j radiation concentrates on the mid-point of film m (the substrate) is unreasonable. For this case, j radiation is assumed to concentrate on the mid-point of the mean excitation depth, $d_{s.x}$ in the substrate. $d_{s.x}$ can be calculated from references (5,6). 1/2 d_m in equation (10) will be replaced with $d_{s.x}$.

Analytical Results

Results of experiment and calculation

In order to examine the reliability of this calculation method, we did the experiment of EPMA for the carefully prepared multi-layer films (Fig.3) Au/Cu/Si and Cr/Ni/Si (on substrate Si) at 20 kV, 25kV, 30kV. The X-ray intensity ratios, k of the characteristic X-ray intensity emitted from every

Multi-layer	Element	Calculated k values by M.C method			Measured k values with EPMA		
		20 keV	25 keV	30 keV	20 keV	25 keV	30 keV
	Au	0.4110	0.2382	0.1582	0.3874	0.2253	0.1487
	Cu	0.1852	0.1415	0.0986	0.1979	0.1428	0.1035
Au/Cu/Si	Si	0.1890	0.2612	0.2983	0.1893	0.2422	0.2835
	Cr	0.0627	0.0374	0.0327	0.0561	0.0341	0.0234
	Ni	0.2688	0.1517	0.0939	0.2345	0.1399	0.0930
Cr/Ni/Si	Si	0.3869	0.4448	0.4742	0.3953	0.4451	0.4702

Table 1. Comparison between the calculated k values using Monte Carlo method and the experimental results with EPMA for the multi-layer specimens Au/Cu/Si and Cr/Ni/Si. Thickness of every thin layer: Au, 0.15 mg/cm^2; Cu, 0.099 mg/cm^2; Cr, 0.034 mg/cm^2; Ni, 0.117 mg/cm^2. X-ray lines: Au, L_α ; Cu, K_α ; Cr, K_α Ni, K_α .

layer to the intensity from standard specimens. Agreement of the calculated values with the experimental results is fairly good. (table 1)

Sample preparation and thickness determination in multi-layer specimens.

The multi-layer film specimens are prepared with vacuum evaporator (Model: JEE-4X). Let us explain the preparing course with the example Au/Cu/Si films. Si substrate was finely finished, then Cu and Au films were deposited with vacuum evaporation method, and the single-layer films Au/Si, Cu/Si (on substrate Si) were deposited simultaneously for measuring thickness.

The thickness of the standard specimen, was determined by using the nuclear back-scattering method and shown in table 1.

Since nuclear backscattering method can directly give the mass thickness of specimens, the calculated error resulted from the difference between the film density and theoretical density may be avoided.

EPMA experiment of multi-layer film specimens.

The characteristic X-ray intensities Au-L_α , Cu-K_α , Cr-K_α , emitted from each layer film and substrate were determined at 20kV, 25kV, 30kV. The experimental conditions of EPMA are as follows: probe current, $2*10^{-8}$ A; probe diameter, 5 μm.

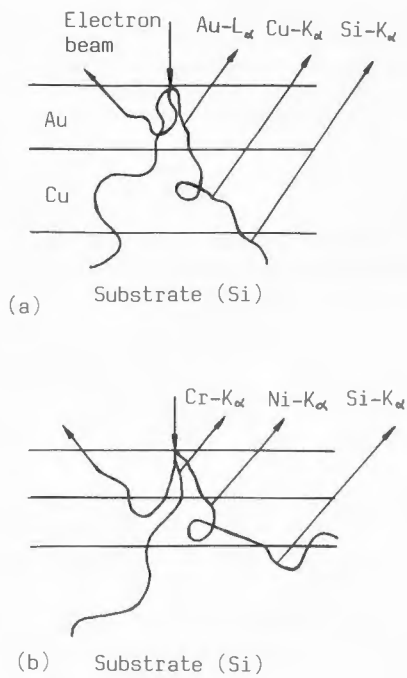

Fig. 3. Schematic diagram of X-ray excitation in multi-layer films Au/Cu/Si and Cr/Ni/Si.

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Discussion with Reviewers

G. Laudron: You have used a simplified Rutherford equation for elastic scattering and the Bethe continuous energy loss law for inelastic scattering. Have you investigated the effect of introducing more appropriate cross sections to describe electron scattering?
Authors: In the energy range of microprobe analysis, the continuous energy loss approximation and use of Rutherford equation are acceptable. But for lower beam energies, the Rutherford equation is a very poor approximation, any calculations attempting to achieve absolute accuracy will have to adopt these more precise theories such as the exact Mott elastic cross-section or the partial wave expansion cross-section.

J.A. Small: Why did the authors use so old a version of the Monte Carlo program? If the version used was dictated by the XT computer, do the authors intend to use a larger computer with an updated Monte Carlo program?
Authors: For the problem of interest in this paper, the differences between the calculated results using the Monte Carlo program based on the simplified model to be run on XT computer and the updated Monte Carlo Program based on a stricter calculation method are very small. So it is not necessary to use a larger computer in these cases.

G. Laudron: Can you describe any developments in the method of quantitative analysis of multi-layer films for non normal incident geometries? Would the calculation become more accurate?
Authors: The method of quantitative analysis of multi-layer for non normal incident geometries merits attention. Under this circumstance the X-ray intensity emitted from multi-layer can be properly increased, i.e. the accuracy of EPMA experiment is raised, since the action range of incident electrons in multi-layer films becomes larger than that for normal incidence. This method and that of normal incidence all need to be developed in the theoretical calculation and the experimental technique. First, the physical model describing electron scattering should be improved. Second, and even more importantly, the sensitivity of examining X-ray intensity should be raised to the full for XQMA of very thin multi-layer specimens.

P.J. Statham: For some combinations of film thicknesses and incident electron energy, your simulations would be entirely inappropriate. In particular, if the step length were of the same order as film thickness in any one film, choice of such a "multiple scattering" simulation would be invalid. Therefore, have you any recommendation for how the validity can be checked before one commenced a full simulation?
Authors: This is one of the important problems for Monte Carlo simulation in XQMA of film specimens. According to film thicknesses and incident electron energy, one ought to select a suitable step length so that there is enough scattering number in films to decrease the statistical error of Monte Carlo calculation. If the thickness in any one film is very thin, in order to obtain enough scattering number in the film both points need to be considered: (1) one should adopt the electron beam with lower energy to enable the average free path of electron scattering to be small enough, and (2) increase the number of simulated electrons.