

Understanding EDXS Analysis of Nanostructures in TEM

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EDXS elemental identification and quantification is a routine practice in materials characterization. In TEM, elemental quantification through EDXS is limited by the unknown absorption process in the material. Generally Cliff-Lorimer ratio method and absorption correction has been used for quantification [1, 2], based on assumptions of column electron beam and parallel sample surface. However, for nanostructures such as nanoparticles and nanorods, parallel surface assumption is invalid, the X-ray path to the detector depends on the geometry of the nanostructures and location of the detector. In this paper, we introduce a new model for elemental quantification. As examination sample to verify the model, ZnO single crystalline nanorods are used. The ZnO nanorods are suspended on lacy carbon coated copper TEM grid. Scanning transmission electron microscopy (JEOL JEL-2100F TEM) and Bruker Quantax microanalysis system (XFlash Detector) are used in this study.

The intensity (counts) of X-ray (I) that read from detector depends on the x-ray generated (I_G) from electron beam bombardment, absorption ratio (R_A) of materials during the path to detector and detector collection factor (R_D). The intensity can thus be expressed as the following:

$$I = I_G(1 - R_A)R_D \quad (1-1)$$

The amount of x-ray generated depends on electron source, material property (how easy to be ionized to emit the specific x-ray upon the bombardment) and interaction volume. The absorption ratio depends on the x-ray absorption coefficient and the x-ray path to the detector. The ionization ratio of material to emit the specific x-ray can be defined as k . The absorption ratio R_A is a function of x-ray path to the detector t' .

$$R_A = At' + Bt'^2 + Ct'^3 + \dots \quad (\text{A, B, C are the absorption constant of a material})$$

To correlate t' to sample thickness t , we define the geometry correction $\Delta G = t'/t$. As the thickness of specimen is small, higher order absorption can be ignored. For electron probe with diameter D goes through the specimen with thickness t , Equation (1-1) can be modified as:

$$I = k \left(\frac{1}{4}D^2t\right) \cdot [1 - A(t \cdot \Delta G)] \cdot R_D \quad (1-2)$$

When the electron probe diameter and detector factor is fixed, for a specific material, the counts I read from the EDXS detector is varied by the specimen geometrical shape. Now if we use the ratio method, for x-ray with energy E_A and E_B ,

$$\frac{I_{E_A}}{I_{E_B}} = \frac{k_{E_A} \left(\frac{1}{4}D^2t\right) [1 - A_{E_A}(t \cdot \Delta G)] \cdot R_{D(E_A)}}{k_{E_B} \left(\frac{1}{4}D^2t\right) [1 - A_{E_B}(t \cdot \Delta G)] \cdot R_{D(E_B)}} = \frac{k_{E_A} [1 - A_{E_A}(t \cdot \Delta G)] \cdot R_{D(E_A)}}{k_{E_B} [1 - A_{E_B}(t \cdot \Delta G)] \cdot R_{D(E_B)}}$$

Considering E_A and E_B are the characteristic x-ray of element A and element B, the equation can be related to the composition C_A and C_B ,

$$\frac{I_A}{I_B} = K_{A,B} \cdot \frac{C_A}{C_B} \cdot \frac{[1 - A_A(t \cdot \Delta G)]}{[1 - A_B(t \cdot \Delta G)]} \quad (1-3)$$

$K_{A,B}$ is the sensitivity factor. $(t \cdot \Delta G)$ is the geometric factor (G) of the specimen. Thus,

$$\frac{I_A}{I_B} = K_{A,B} \cdot \frac{C_A}{C_B} \cdot \frac{1-A_A \cdot G}{1-A_B \cdot G} \quad (1-4)$$

Equation (1-4) indicates that the x-ray counts ratio is varied by the geometry of the specimen; it is valid even when column assumption of electron beam is inappropriate and the x-ray path to the detector is not same from the places that x-ray generated. It is therefore suitable for both material with small dimensions and bulk material.

Figure 1 (a) shows a typical line scan EDXS measurement of ZnO nanorod. As there is no compositional difference consideration, the different change in the counts of Zn K α and Zn L α lines is due to the absorption. The counts ratio of Zn K α and Zn L α can be used to determine the geometric factor based on equation (1-4). Figure 1 (b) shows the Zn:O compositional ratios calculated from Cliff-Lorimer method and absorption correction based on equation (1-4). The declination of Zn:O ratio along the scanning distance from Cliff-Lorimer method can be corrected using our model. The absorption constants A used are $A_{Zn\ K}:A_{Zn\ L}:A_{O\ K}=5400:287000:600000$, calculated from reference [3]. The ratio relationship of absorption constant A can be determined experimentally, or calculated from mass absorption coefficient. The sensitivity factors are $K_{Zn\ K}:K_{Zn\ L}:K_{O\ K}=5.557:1.561:1.695$ for Cliff-Lorimer method and $K_{Zn\ K}:K_{Zn\ L}:K_{O\ K}=5.6:4.6:2.9$ for absorption correction.

This paper introduces a new model about EDXS elemental quantification. Different from other absorption correction methods, this model need not estimate ρt of the material. The model can also be used to examine the sensitivity factor $K_{A,B}$ and the absorption constant ratio of material.

References:

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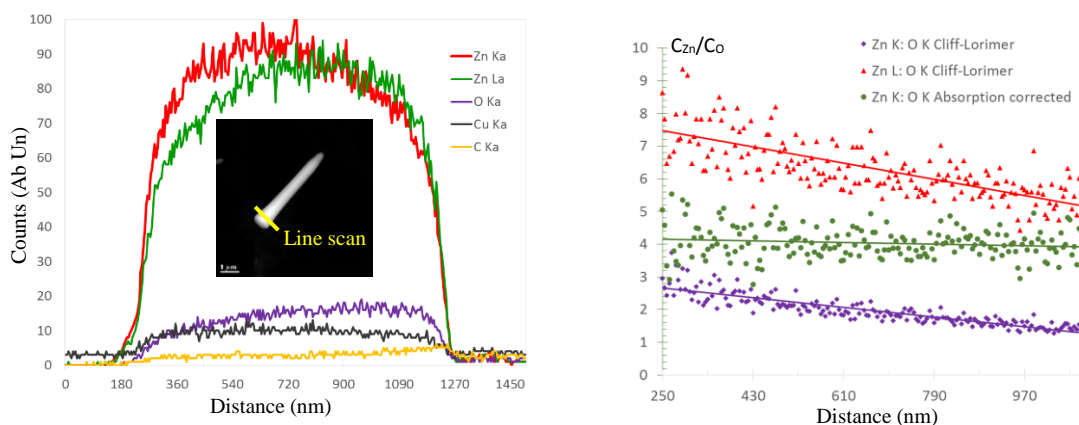


Figure 1. (a) EDXS line scan of a ZnO single crystalline nanorod, (b) Compositional ratio calculated using Cliff-Lorimer method, and through absorption correction using the model proposed in this study.