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Computational Method for Composition Determination of Multilayer Epitaxial Semiconductor Structures Using Standards-Based Energy-Dispersive X-Ray Spectrometry

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Accurate measurements of composition provide critical information in understanding and optimizing epitaxial growth of compound semiconductors and alloys particularly used in optoelectronic devices. Energy-dispersive X-ray spectrometry (EDX) is widely used technique in transmission electron microscopy (TEM) to rapidly identify compositions of multilayer structures. It is easy to derive qualitative conclusions instantly with this method, quantitative analysis of the generated data remains a challenge that requires specialized software tools.

We have developed Igor Pro procedures for analysis of both EDX data, using reference standards for calibration. For EDX, spectra acquired from known-composition standards allow extraction of the spectral generation rates weighted by the detector response. It is required that the standards data are obtained from the same electron-lens configuration (TEM) and all the reference and unknown samples are of same crystal structure. The standard data set can be obtained once and used multiple times with different unknown samples.

Our EDX algorithm uses multivariate statistical analysis combined with a generalization of the ζ-factor method of Watanabe and Williams. For a thin specimen, after correcting for absorption, the detected spectral intensity (number of counts per unit energy-time) at energy E can be written

$$d(E) = \sum_k \left(n \cdot D_e \cdot T \cdot w_k\right) \cdot x_k(E) \qquad (1)$$

The sum is over constituent elements. The coefficients are the products of atomic concentration n, electron dose D_e, and foil thickness T with the atomic ratios w_k, and the $x_k(E)$ are weighted generation rates. Treating energy E as a discrete parameter, and relabeling the coefficients as y_k, we obtain the representation $\vec{d} = \mathbf{X} \cdot \vec{y}$. A collection of spectra can be combined into the matrix form $\mathbf{D} = \mathbf{X} \cdot \mathbf{Y}$. Singular-value decomposition allows factorization as $\mathbf{D} = \mathbf{R} \cdot \mathbf{C}$, where the columns of $\mathbf{C}$ contain the eigenvectors of $\bar{\mathbf{D}} \cdot \mathbf{D}$. ($\bar{\mathbf{D}}$ is the transpose of $\mathbf{D}$.) The contribution of each factor to the spectra is represented in a column of $\mathbf{R}$; the relative significance of each towards accurate reproduction of the data matrix is proportional to the eigenvalues. Factors or low significance are then eliminated, along with their corresponding loadings, contained in the rows of $\mathbf{C}$. Using spectra obtained from selected standards with known compositions, we find a matrix $\mathbf{Z}$ satisfying $\mathbf{Y} = \mathbf{Z} \cdot \mathbf{C}$. Noting that:

$$n \cdot D_e \cdot T = \sum_k (\mathbf{Z} \cdot \vec{c})_k \qquad (2)$$

the normalization method in [1] can be applied:

$$\vec{w} = \frac{\mathbf{Z} \cdot \vec{c}}{\sum_k (\mathbf{Z} \cdot \vec{c})_k} \qquad (3)$$

The procedure requires knowledge of at least one foil thickness among the spectra included in $\mathbf{D}$ (not necessarily with known composition). The components of $\mathbf{Z}$ are found by minimizing

$$\Delta^2 = \sum_{k,\ell}\left\{\sum_{i,j}\left[\left(w_k^{(\ell)} - \delta_{ik}\right)\cdot c_j^{(\ell)}\right]\cdot Z_{ij}\right\}^2 , \qquad (4)$$

where the index ℓ identifies the standards. The least-squares minimization can be formulated as an eigenvalue problem. Multiple solutions $\mathbf{Z}_m$ to (4) may be found, which are combined linearly to most closely satisfy (2). The resulting matrix $\mathbf{Z}$ can then be applied to related specimens, using the factor loadings $\vec{c} = \mathbf{R}^L \cdot \vec{d}$ computed from their measured spectra as input, then using $\vec{y} = \mathbf{Z} \cdot \vec{c}$. The output then contains the computed thicknesses of all included spectra. This only has quantitative importance if an absorption correction is applied, in which case the algorithm is iterated until convergence. In addition, the weighted generation matrix can be computed, using $\mathbf{X} = \mathbf{R} \cdot \mathbf{Z}^L$, allowing the simulation of spectra for arbitrary, related compositions. Flow chart in figure 1 describes the process in detail.

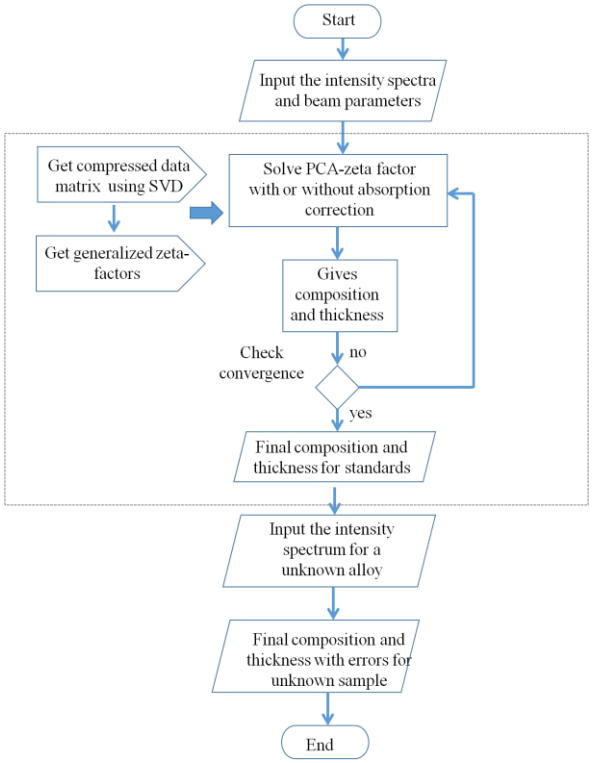

Figure 1. Flow chart describing the computational logic to solve compositions

Various tests were run on III-V multicomponent alloys, using readily available III-V binary endpoint compounds as reference standards. We mainly describe application of the technique to the III-V ternaries $GaP_{1-y}As_y$, $InP_{1-y}As_y$, $Ga_xIn_{1-x}As$, and $Ga_xIn_{1-x}P$ alloy and quaternary $Ga_xIn_{1-x}P_{1-y}As_y$ alloys. But we believe that this technique can be used for any alloy if the required reference standards are available.

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