Quantification of TXRF Analysis

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Abstract

A new data evaluation method has been developed for TXRF quantitative analysis based on the fundamental parameter technique. The theoretical calculation considers the geometrical parameters of the detection system and the specimen parameters: size, thickness, angle of the excitation beam to the surface and the optical properties of the specimen holder. The characteristic lines of the specimen holder (Si K\alpha,\beta) were used for quantitative calibration of the specimen composition; therefore neither external nor internal standard specimens were required. A PASCAL code was written in order to solve the general iteration procedure. In order to test the efficiency of the calculation procedure, several experiments were carried out using standard solutions of mixed specimens containing the elements K, Sc, V, Mn, Co and Cu.

Introduction

TXRF analysis is one of the most effectual methods for quantitative analysis of specimens with extremely low mass. A good characterization of trace contamination distribution of different elements on Si wafers can be performed by TXRF with high sensitivity therefore increasing number of application of this technique can be found in the semiconductor industry. Because the primary photons have very low incident angle to the surface of the specimen holder, the penetration depth of the primary photons into the holder is only a few nm; thus the information is coming only from a surface layer of the investigated material with high analytical sensitivity.

In the field of conventional XRF spectrometry, the fundamental parameter method (FPM) offers a reasonable possibility for standardless calibration in order to determine the quantitative specimen composition. This procedure is based on the mathematical relationship between the concentration of the elements in the analyzed specimen and their characteristic intensities. The fundamental parameters are the absorption functions of element, fluorescence yield, relative intensity, absorption jump ratio and the photoabsorption cross section functions. This
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theoretical approach considers the parameters of specimen-detector geometrical arrangement, excitation mode and source parameters and detector efficiency function. The FPM generally requires good specimen homogeneity and approximately flat specimen surface. It can be used in the case of both polychromatic and monoenergetic excitation; however the numerical calculation is much simpler and faster for monoenergetic excitation mode.

The internal standard calibration method [1], [2] is the simplest calibration procedure in the TXRF analysis since no preparation of external standard specimens is needed. However, in some cases the application of the internal standard method is not possible, for example, quantitative determination of impurities on a Si wafer surface since the 'specimen' is originally set on the Si surface before the analysis.

![Schematic geometrical set-up of the TXRF experiments](image)

**Figure 1.** Schematic geometrical set-up of the TXRF experiments

The aim of our project was to present a mathematical description based on the fundamental parameter approach and a practical calculation algorithm of standardless TXRF analysis for particle-type specimen.

**Theory**

Many papers deal with analytical investigation by the TXRF method using theoretical consideration to calibrate the quantitative determination for particle, film and implanted-type specimens [3]-[13]. In order to determine the quantitative composition of a thin particle-type specimen, located on the surface of a specimen holder, an exact mathematical relationship has
to be given between the fluorescence signals and the specimen composition. This model must describe the optical behavior of the specimen holder, including geometry and the excitation. We presumed the following conditions: (i) monoenergetic excitation, (ii) polarized (σ mode) excitation beam, (ii) homogeneous distribution of the specimen elements, (iv) known surface roughness and (v) cylindrical symmetry of the sample. Let us suppose that the specimen consists of \( n - 1 \) detectable elements and the concentrations are \( C_1, \ldots, C_{n-1}, C_n \), where \( C_n \) is the concentration of the residual matrix. This portion of the specimen involves the undetectable light elements in the specimen such as O, N, C etc. On the basis of the FPM technique and following the figure 1, the Kα fluorescence intensity of the detectable elements can be calculated by the following equations:

\[
I_i^{(S)} = I_0(r) \cdot C_i \cdot g_i(E) \int_0^{r_S} \left[ 1 - e^{\frac{G_1 E_i}{d_S}} + R(\phi, E) \cdot e^{\left[ -\frac{2 \mu_{SE} d_S}{\sin(\phi)} \right]} \cdot 1 - e^{\frac{G_2 E_i}{d_S}} \right] G \cdot \varepsilon(E_i) \, dr
\]

where

\[
G_1 = \frac{\mu_{SI}}{\sin(\psi)} + \frac{\mu_{SE}}{\sin(\phi)}
\]

\[
G_2 = \frac{\mu_{SI}}{\sin(\psi)} - \frac{\mu_{SE}}{\sin(\phi)}
\]

\[
\sin(\psi) \approx \frac{d}{\sqrt{d^2 + r^2}}
\]

\[
G \approx \left\{ \begin{array}{ll}
\left( \frac{r_D \cdot (2d - a) - ra \cdot (d - a) \cdot d}{r \cdot (2d - a) - r_D a + 4d^2 \cdot (d - a)^2} \right)^2 & \text{if } r_D \leq r \\
0.5 \cdot \left( 1 - \frac{r_D^2 \cdot \frac{d}{d^2 + d^2}}{\left( \sqrt{r^2 + d^2} \right)^2} \right) & \text{if } r \leq r_D
\end{array} \right.
\]

are the geometrical factors depending on the incident \( \phi \) and the detection angle \( \psi \), \( d_S \) is the specimen thickness, \( g_i(E) \) is the excitation probability: fluorescence yield, ionization probability, relative intensity and absorption jump ratio [5], \( \varepsilon(E_i) \) is the detector efficiency function for the characteristic energy of the \( i \)th specimen element [12], \( I_0(r) \) is the intensity distribution of the primary beam on the specimen surface. The reflectivity function of the specimen holder is given by the Fresnel's formula [19]

\[
R(\phi, E) = \frac{I_0}{I_R} = \frac{\sin(\phi) \cdot (1 - \delta - i \cdot \beta) \cdot \sin(\psi)}{\sin(\phi) + (1 - \delta - i \cdot \beta) \cdot \sin(\psi)}
\]
where $\delta$ and $\beta$ are detailed in ref. [17] and [18]. The compression factor

$$K(\phi, E) = \frac{\sin(\phi)}{z_p(\phi, E) \cdot \mu(E) \cdot \rho_w}$$

describes the change in the density of the energy current at the wafer surface [18]. Similar equation can be written for the intensity dependence of the 'j'th element in the specimen holder where $G_s(r) = \frac{1}{z_p} + \frac{\mu_{wj}}{\sin(\psi)}$ is the geometrical factor and $\phi_{crit}(E) = \sqrt{2 \cdot \delta}$ is the critical angle of the total reflection effect. The expression (4) is the penetration depth which is defined by the deep-dependence of the primary beam intensity

$$y_p(\phi, E) = \frac{12.3981}{\sqrt{4 \pi \cdot F \cdot \delta \cdot \left[ \sqrt{\left( \left( \frac{\phi}{\phi_{crit}} \right)^2 - 1 \right)^2 + \left( \frac{\beta}{\delta} \right)^2} - \left( \left( \frac{\phi}{\phi_{crit}} \right)^2 - 1 \right) \right]}}$$

in the near surface layer of the substrate (see ref. [17],[18]) as it can be seen in function (5).

$$I(y) = I_o(r) \cdot e^{-\mu_S(E) \cdot y \cdot \rho_w \cdot 1 - R(\phi, E) \cdot K(\phi, E)}$$

Some 'undetectable' elements are in the specimen as H, O, C, N etc., but their attenuation coefficient must be calculated for the FPM approach. Of course, the quantity of these elements also are unknown, therefore their absorption function can be approximated about the average atomic number of the specimen [3]. The specimen absorption can be written by the expression (6) where $Z_{res}$ the average atomic number of the residual matrix in the specimen.

$$\mu_S(E) = \sum_{i=1}^{n-1} C_i \cdot \mu_i(E) + \left( 1 - \sum_{i=1}^{n-1} C_i \right) \cdot \mu(Z_{res}, E)$$

Let us suppose, a spherical-shaped specimen is located on surface of a flat Si wafer involving $n$ elements, with concentrations of $C_1, \ldots, C_n$. The unknown variables are the concentrations, specimen thickness $d_S$, specimen diameter $r_S$ and the instrumental factor $I_0$ which takes into account the intensity of the primary beam. Calculating the theoretical fluorescence intensities for every detected element at different incident angles, the optimum
values of the unknown parameters can be determined by searching the minimum value of $\chi^2$ function (7), where $n$ is the number of detected elements in the specimen and $k$ is the number of spectra recorded at different incident angles for the excitation beam.

$$\chi^2 = \sum_{i=1, j=1}^{n, k} \frac{1}{\sigma_i^2} \left( I_{i,j,\text{Meas}}^{(s)} - I_{i,j,\text{Calc}}^{(s)} (C_1, \ldots, C_n, d_s, r_s) \right)^2 = \text{min.} \tag{7}$$

This fitting procedure requires additional independent measurements in order to determine the $I_0(r)$ function. On the basis of the equation (3) this instrumental factor can be calculated using the measured Si Kαβ characteristic intensity which indicates that no standard specimen is needed to solve this analytical problem. The gradient method was used in the numerical minimization procedure to search for the optimal values of the parameters detailed above. A computer code was developed in PASCAL language to calculate this numerical problem and the absolute quantity of the elements in the thin specimens. The input parameters are: characteristic intensities of the analyzed elements at different incident angles, the incident angles, excitation photon energy, geometrical parameters and detection parameters.

The optical property of the specimen holder and the fluorescence intensity depend on the average surface roughness. The Fresnel theory of refraction concerns only an exactly smooth interface surface. The influence of the surface average roughness $\sigma$ on the reflectivity $R(\phi)$ was approximated by the Nevot model [15],

$$n(z) = n_1 + \frac{(n_2 - n_1)}{\sigma \cdot \sqrt{2 \cdot \pi}} \cdot \int_{-\infty}^{z} \exp \left( \frac{-\xi^2}{2\sigma^2} \right) d\xi \quad \text{and} \quad R(\phi) = R_0 \cdot e^{-16\pi^2 \cdot k_{1n} \cdot k_{2n} \cdot \sigma^2} \tag{8}$$

where $k_{1n}, k_{2n}$ are the normal components of the wave vectors on the surface and in the surface of the wafer, $\sigma$ is the average roughness of the Si surface [16] and $n(z)$ describes the dependence of the refractive index on the penetration deep $z$. In recent investigations the average roughness was 0.5-1 nm given by the maker of the Si wafer. Corresponding to ref. [16] the roughness calculation does not cause a significant correction in the reflectivity function as demonstrated by figure 2.

**Experimental procedure**

The measurements were carried out by a RIGAKU 3750 TXRF instrument under vacuum condition. The high voltage of the W rotating anode was 30 keV with 300 mA anode current. The specimen elements were excited by the WLβ1 line ($E=9.672$ keV).
Figure 2. Si Kα intensity at different incident angles and at different average roughness values.

The analytical procedure such as, specimen changing, specimen moving into different x-y positions, setting the incident angle and spectra collection were controlled by a personal computer. The specimen holders were moved by an in-vacuum robotics wafer transport system in and out of the measuring chamber. The material of the specimen holder was pure Si wafers with 0.48 mm thickness and 5” diameter. In order to test the present evaluation method, standard mixed solutions were prepared containing K, Sc, V, Mn, Co, Cu elements with 0.05, 0.1, 0.2, 0.5, 1.0, 10 ppm concentrations. Two sets of these solutions were dropped independently on the surface of different Si wafer with quantities of 10 μl and 1 μl. All of the specimens were excited at angles of 0.05 and 0.1 deg respectively. In order to test the validity of this theoretical approach, the calculated Si Kα intensities were compared directly to the measured values depending on the grazing incident angle, and a reasonably good agreement was found between them as demonstrated in fig. 3 by the angle scanned Si signal.

Detection and beam homogeneity

The detected area on the Si wafer surface, from where the secondary photons were emitted, had an approximate diameter of 18 mm. This was a relatively large area, therefore the beam homogeneity had to be investigated empirically: 1 μl quantity of a standard solution of mixed specimen with a concentration of 1 ppm was dropped on a Si wafer surface. After
drying, diameter of the specimen spot was found to be approximately 1.5-2 mm. The specimen was moved in the horizontal x-y plane into different positions and the fluorescence spectra were collected. Calculating the geometry factor by equation (1), an approximately constant beam distribution was found as can be seen on figure 4, where the Co Kα intensity distribution is plotted along both of the x and y axes with the fitted calculated values.

![Figure 3](image)

**Figure 3.** Calculated and measured Si Kα intensity versus incident angle (σ=0 nm).

The detector efficiency was considered by the following expression [15]:

$$
\varepsilon(E) = \exp \left( - \frac{\mu_{Be} \cdot d_{Be} + \mu_{Au} \cdot d_{Au} + \mu_{Si} \cdot d_{Si,act}}{\sin(\phi)} \right) \cdot \left( 1 - \exp \left( - \frac{\mu_{Si} \cdot d_{Si,in}}{\sin(\phi)} \right) \right)
$$

(11)

where the thickness of the Be window $d_{Be}$, active $d_{Si,act}$ and inactive $d_{Si,in}$ layers of the Si(Li) crystal and the Au layer $d_{Au}$ on the detector surface were known.

**Results**

Comparing the nominal and the calculated quantities of the specimen elements on different Si wafers, a good agreement was found between predicted and nominal values; the average differences were within 10 relative %. As an example, the figures 5.a. and 5.b. contain the calculated mass versus the certified values for Co and Mn.
Figure 4. Dependence of the Co Kα intensity on the x and y positions in the plane of the Si wafer.

Spherical symmetric specimen shape and constant specimen thickness were supposed, however the thickness of the real specimens or the impurities on the wafer's surface were generally not constant. Therefore, the result of this analysis refers only to an average value of the specimen thickness related to the area of the analyzed surface. This problem can be neglected by decreasing the analyzed surface area. This model does not describes the situation if the specimen is located asymmetrically to the detection--wafer axis (see fig. 1); therefore an improvement of this model calculation is required in the near future.

Conclusion

We have presented a new data evaluating method for quantitative determination of trace impurities located on the surface of Si wafers using TXRF analysis. The theoretical calculation based on the fundamental parameter approach using the Si Kα signal for the determination of the instrumental parameter. The comparison of the calculated and the measured composition of the prepared standard specimens confirmed the validity of this calibration method.
Figure 5.a. Comparison of the nominal and the calculated values of Co mass in the dropped (10 µl) standard specimens.

Figure 5.b. Comparison of the nominal and the calculated values of Mn mass in the dropped (10 µl) standard specimens.

References


2. R. Klockenkamper, A. von Bohlen and B. Wiecken,


8. B. Gilles and M. Brunel, Nuclear Instrument and Methods, B44, 331-335 (1990)


