The Modification of TXRF-Method by Use of X-ray Slitless Collimator.

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Abstract

The design and analytical possibilities of the TXRF spectrometer modified by using a slitless collimator for the primary X-ray beam are described. The design of the TXRF spectrometer is simpler in the construction and lower in cost as compared with the standard one but is characterized by acceptable analytical and operational parameters. It supplies detection limits of Fe group elements for the surface analysis near \(10^{10}\) atoms/cm\(^2\) using the excitation by the standard X-ray tube with Mo anode during the time of 600 sec. The peculiarities and properties of the TXRF spectrometer setup with slitless collimator are discussed.

Introduction

The method of X-ray fluorescence at a total-reflection of initial X-ray radiation (TXRF) is today a standard analytical method for surface analysis at super lower trace level detection limits[1]. There are industrial TXRF spectrometers, for example RIGAKU-3700 or PHILIPS-TREX610S&T, which supply the detection limits for the metal impurities on silicon wafers down to \(10^9\) atoms/cm\(^2\). The standard TXRF spectrometer is comprised of an X-ray source, the crystal monochromator or the multilayer Bragg’s reflector, the collimator system, the target table with some degrees of freedom and a Si(Li) solid state detector with a multichannel analyzer. This work describes the design and analytical possibilities of the modified TXRF spectrometer supplied by the slitless X-ray collimator instead of the monochromator, the slit system and the target table. This spectrometer is very simple and may be constructed and used in any X-ray laboratory for the routine surface diagnostics with detection limits for main impurities near \(1\cdot10^{10}\) atoms/cm\(^2\).

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Principles of the slitless collimation.

The slitless collimator of X-ray radiation is formed by two quartz polished plates mated together. Slitless collimator is the conventional name because the X-ray beam is passed through the clearance between the plates but the slit is not observed by a visual perception. The size of the clearance is defined by values of roughness and microsphericity of the plates. The Attenuated Total Reflection of a laser beam on the plate's clearance shows that the width of the microslit "d" is near 30 nm. The X-ray beam propagates through the microslit by way of repeated total reflections between surface flats of the plates. Moreover it is possible that a standing wave arises in the clearance between plate surfaces. In any case, the experimental fact exists that the clearance of two mated glass plates transports the X-ray beam on a distance of nearly 100 mm with almost no decrease in intensity [2].

The Fresnell coefficients for a single X-ray beam reflection can be written as [3]:

\[
\begin{align*}
R_\parallel & = \frac{|E_\parallel|^2}{|E_\parallel|^2} = \frac{(\theta - 2\delta \theta - a)^2 + (b + 2\beta \theta)^2}{(\theta - 2\delta \theta + a)^2 + (b - 2\beta \theta)^2}; \\
R_\perp & = \frac{|E_\perp|^2}{|E_\perp|^2} = \frac{(\theta - a)^2 + b^2}{(\theta + a)^2 + b^2}
\end{align*}
\]  

(1)

Expressions for "a" and "b" have the next forms:

\[
\begin{align*}
a^2 & = \frac{1}{2} \left[ \sqrt{(\theta^2 - 2\delta)^2 + 4\beta^2} + (\theta^2 - 2\delta) \right]; \\
b^2 & = \frac{1}{2} \left[ \sqrt{(\theta^2 - 2\delta)^2 + 4\beta^2} - (\theta^2 - 2\delta) \right]
\end{align*}
\]  

(2)

where \( \theta \) is an incident angle of the beam, \( \delta \) and \( \beta \) are parameters of the complex addition to the matter refraction index \( n \) in the form:

\[
n = 1 - \delta - i\beta
\]  

(3)

The real parameter \( \delta \) is related to with the critical incident angle \( \theta_c \):

\[
\theta_c = \sqrt{2\delta} = \sqrt{\frac{Z \cdot 1004 \cdot Z}{A \cdot E^2}}
\]  

(4)

where \( \theta_c \) is represented in radians, \( \rho \) is a material density (g/cm³), \( E \) is the radiation energy (keV), \( Z \) is the target element atomic number, \( A \) is the atomic weight (\( Z \) and \( A \) are dimensionless values). The imaginary parameter \( \beta \) is related to linear X-ray absorption coefficient of the material:

\[
\tau = \frac{4\pi}{\lambda} \beta
\]  

(5)
where \( \lambda \) is the wavelength of the incident radiation. Figure 1 shows dependence of reflection factors \( R_{||} \) and \( R_\perp \) for single and frequency X-ray beam reflections from a quartz plate (\( \delta_{\text{SiO}_2} = 1.6 \cdot 10^{-6} \), \( \beta_{\text{SiO}_2} = 0.4 \cdot 10^{-8} \)). From this figure we notice that the X-ray beam after multireflection is not characterized by any preferred direction of the polarization. The divergence of the X-ray beam after multireflection is strictly equal to \( \Delta \theta = 2 \theta_0 \). The integral factor of the reflection for the fan-shaping beam after one hundred reflections must fall down to 0.7 approximately. In light of such predictions it is desirable to evaluate the real number of reflections taking place in X-ray beam propagation in the slitless collimator of our TXRF spectrometer.

Figure 1. Dependence of reflection factors \( R_{\parallel} \) and \( R_\perp \) from incident angle for the single reflection (a), ten consecutive reflections (b), one hundred consecutive reflections (c), thousand consecutive reflections (d).

Figure 2 illustrates the model geometry of X-ray beam reflections for some angles in the plate's clearance of the slitless collimator. The depth penetration of X-ray radiation into the material in condition of the total reflection may be represented by expression [3]:

\[
R \approx \frac{1}{1 + \frac{1}{2} \left( \frac{\lambda}{d} \right)^2}
\]
The depth penetration is the function of the X-ray incidence angle. To evacuate the real number of reflections in the clearance the effective $X_e(\theta)$ must be calculated. As the slitless collimator transports X-ray partial beams with reflection angles from the interval $0 \leq \theta < \theta_c$ the effective angle would be choose for the creation of the simplified model described the multireflection process of the X-ray sector-shaped beam. As a such one the half critical angle $\theta_c/2$ may be offered [4]. The effective depth penetration is corresponded to $\theta_c/2$.

The phenomenon of a wave total reflection is characterized by the longitudinal displacement of the beam reflection position about the point of the beam’s incoming place [5]:

$$
\Delta Z = \frac{\lambda}{\pi} \frac{1}{\sqrt{\theta_c^2 - \theta^2 + 2 \beta}}
$$

Maximum displacement corresponds to $\theta=\theta_c$. The displacement module in that case is equal to:

$$
|\Delta Z_{\text{max}}| = \frac{\lambda}{\pi} \frac{1}{\sqrt{2\beta}}
$$

Minimum displacement is arrived at $\theta=0$ and has the value:

$$
\Delta Z_{\text{min}} \approx \frac{\lambda}{\pi \theta}
$$

Effective value $\Delta Z_e$ may be calculated by using the reflection angle $\theta_e=\theta_c/2$. The effective displacement $\Delta Z_{\text{ef}}$ of the total reflection point on the quartz reflector for the MoK$_\alpha$ radiation is equal to 146 Å and the displacement interval stretches from 128 Å to 2500 Å. Knowledge of $\Delta Z_{\text{ef}}$ value and the size of the clearance permits the quantity (N) of beam reflections in the clearance:

$$
N = \frac{L}{\Delta Z_{\text{ef}} + a \cdot \cot(a \theta_c/2)}
$$

where $L$ is a length of the collimator. “a” is the size of the clearance. For real collimator (L=5 cm; a=30 nm) N is approximately equal to 3000. Comparison of the X-ray beam intensity calculated from the multireflection model (Fig. 1) ($I_{\text{mm}}(\theta_c/2)=0.0003I_0$) with real intensity at the output of the slitless collimator [2,4] ($I_{\text{sc}}=0.98I_0$) shows that the model is unsuitable for a
description of the X-ray beam transportation by the slitless collimator. This contradiction assumes that the slitless collimator transports the X-ray beam by creating a standing wave in the clearance – the standing wave channel. This assumption agrees with the fact that the surface roughness of the plates does not influence the intensity of the emergent X-ray beam. The influence of the channel size on the standing wave field character is studied today.

Figure 2. Scheme of reflections for partial X-ray beams entered into the clearance between the quartz plates formed the slitless collimator under $\theta_e$ and $\theta_e/2$ angles. Angles are increased for clarity.

Character of TXRF spectroscopy with slitless collimator.

The use of the sector-shaped primary X-ray beam for an analysis and the presence of the white X-ray radiation ($\lambda > \lambda_{MoK_a}$) are fundamental characteristics of the TXRF spectrometer using the slitless collimator. The spectrometer does not need a monochromator, a slit system and a table for the target's positioning. The slitless collimator is formed by long and short quartz plates. The analyzing target is pressed to the surface of a long quartz plate and forms with it the continuation of the slitless collimator. Across the diagnostic hole ($\Theta-10$ mm) the fluorescence irradiation arrives to a semiconductor photon detector and collects by a multichannel analyzer. The principle design of our TXRF spectrometer with the slitless collimator is shown on Figure 3.
Figure 3. Design of TXRF spectrometer supplied by the slitless collimator for the analysis of trace level contamination concentrations on the surface of targets.

The primary X-ray beam formed by monochromator in standard TXRF spectrometers is characterized by very low divergence $\delta\alpha \sim 0.001^\circ$. But the divergence of X-ray beam after the slitless collimator is equal to double the critical angle of the total reflection. Inasmuch as the X-ray angle density irradiation for X-ray tubes in the angle interval $\delta\alpha \sim 0.1^\circ$ is approximately constant the excitation intensity on a target in a slitless TXRF spectrometer will be higher two orders in compared with a standard one because the density irradiation will be proportional to an angle of the sector-shaped beam.

Science all flow of the sector-shaped excitation beam will be undergo the total reflection on a target the background in the TXRF spectrum for the spectrometer with slitless collimator would not exceed the one for the standard TXRF spectrometer. Hence it is to be expected that detection levels for TXRF spectrometer with a slitless collimator must be two orders lower compared to the standard one all other factors being the same.

The availability of the white radiation in the emergent beam increases the analytical sensitivity of the method. This leads to the appearance of additional complications. Intensities of structural peaks in the study of monocrystals increase [4]. The contribution of the argon
fluorescence line comes into particular prominence. Special curves of the relative fluorescence intensity need to be prepared [6].

Figure 4 shows a TXRF spectrum of a Cu (240 Å)/Si film target. The spectrum was acquired by using our slitless TXRF spectrometer at the X-ray source power regime V=25 keV, I=10 mA during τ=300 sec. There are fluorescence lines: CuKα, CuKβ, FeKα, CaKα, ArKα and SiKα. The peak of ArKα is due to the atmosphere. Silicon fluorescence line is from the substrate. Lines CaKα and FeKα correspond to atoms of impurities presented in the film. The copper film is characterized by a polycrystalline structure and structural peaks do not appear in the TXRF spectrum [6].
Figure 4. TXRF spectrum of Cu (240 Å)/Si film target obtained with X-ray source power condition: U=25 keV, I=10 mA. Molybdenium radiation. Shown every third channel. τ=300 sec. 16 eV/ch.

Quantity concentration analysis and detection limits.

The quantity analysis of contaminant concentrations on surface targets by use of a slitless TXRF spectrometer is carried out by the relative method. Matrix elements may be used as an interval standard. But in this case the excitation volume would be calculated. Our spectrometer is built so that the fluorescence yield is characterized by an area 1 cm². Consequently it is necessary to define the effective depth penetration for the studied material and to calculate the quantity of matrix atoms in the excitation volume from structure considerations [7]. The effective
depth penetration of the molybdenum radiation into a copper structure is 3 nm. Inasmuch as Cu structure is characterized by FCC lattice with the size of an elementary cell been equal to 3.608 Å, the quantity of matrix atoms (\( N_\text{M} \)) in the excited volume is \( N_\text{M}=1.9\cdot10^{16} \) at/cm\(^3\). The quantity of impurity atoms \( N_\text{IM} \) may be calculated by use of a standard expression [5]:

\[
N_\text{IM} = N_\text{M} \left( \frac{S_\text{M} F_\text{M} \varepsilon_\text{M}}{S_\text{IM} F_\text{IM} \varepsilon_\text{IM}} \right)
\]  

(9)

where \( S_\text{M} \) and \( S_\text{IM} \) are pure peak areas under matrix and impurity lines in a TXRF spectrum, \( F_\text{M} \) and \( F_\text{IM} \) are relative atomic fluorescence intensities (experimental data for our slitless TXRF spectrometer [6]), \( \varepsilon_\text{M} \) and \( \varepsilon_\text{IM} \) are detection efficiencies of a detector [8]. For example, we can calculate the numbers of impurity atoms in the surface of the copper film from the TXRF spectrum shown in Figure 4.

The area for the line CuK\(_\alpha\) (without background) is 855000 counts. Similar area for the iron peak is 3600 counts. The relative fluorescence intensities for these elements are 2.96 and 1.78 respectively [6]. The detection efficiencies for these lines are equal one. Substituting these values in expression (9) we obtain:

\[
N_\text{Fe} = 1.9\cdot10^{16} \cdot \frac{3600 \cdot 2.96}{855000 \cdot 1.78} = 1.33\cdot10^{14} \text{ at}
\]

Similar calculation for Ca gives the value \( N_\text{Ca}=6.4\cdot10^{13} \) at. These values must be considered as atoms per cm\(^2\) because the registration square is approximately equal to 1 cm\(^2\).

Estimation of the detection limits for these elements under the chosen experimental condition arouses considerable interest. In order to identify a spectrum area as a peak the following relation should be valid [9]:

\[
S_{\text{m, IM}} > 3\sqrt{S_f}
\]

(10)

To calculate the value \( S_f \) the same energy interval as one of the information peak is required. Substituting this relation in (8) we obtain the expression for the limit detection:

\[
N^{\text{LD}}_\text{IM} = N_\text{M} \frac{3\sqrt{S_{\text{IM}}} \cdot F_\text{M} \cdot \varepsilon_\text{M}}{S_\text{M} \cdot F_\text{IM} \cdot \varepsilon_\text{IM}}
\]

(11)

Under the conditions of the TXRF spectrum shown on Figure 4 we can calculate \( N^{\text{LD}}_\text{Fe}=2.7\cdot10^{12} \) at/cm\(^2\), \( N^{\text{LD}}_\text{Ca}=1.4\cdot10^{12} \) at/cm\(^2\), \( N^{\text{LD}}_\text{Zn}=1.4\cdot10^{11} \) at/cm\(^2\). Zn atoms are absent in the film.
We analyzed the quantity of contamination on the surface of a silicon wafer with [111] orientation using our slitless TXRF spectrometer. (Figure 5). The spectrum was obtained in the suitable orientation ensured the absence of structural peaks \([4,6,10]\). There are present some lines of X-ray fluorescence origin. There are SiK\(_\alpha\), ArK\(_\alpha\), CaK\(_\alpha\), CoK\(_\alpha\), NiK\(_\alpha\), ZnK\(_\alpha\). Taking the SiK\(_\alpha\) line to be the matrix one can obtain the concentration of contamination and the limit of detection for the wafer in power source conditions \(V=25\) keV, \(I=10\) mA at time registration \(\tau=1000\) sec. Surface layer of the Si wafer contains: \(N_{Fe}=4.2\cdot10^{11}\) at/cm\(^2\), \(N_{Ca}=9.1\cdot10^{11}\) at/cm\(^2\), \(N_{Co}=8.1\cdot10^{10}\) at/cm\(^2\), \(N_{Ni}=1.8\cdot10^{11}\) at/cm\(^2\), \(N_{Zn}=6.7\cdot10^{10}\) at/cm\(^2\). Limit detection values for chosen conditions are: \(N_{Fe}^{LD}=1.6\cdot10^{10}\) at/cm\(^2\), \(N_{Ca}^{LD}=7.1\cdot10^{10}\) at/cm\(^2\), \(N_{Co}^{LD}=1.8\cdot10^{10}\) at/cm\(^2\), \(N_{Ni}^{LD}=2.1\cdot10^{10}\) at/cm\(^2\), \(N_{Zn}^{LD}=2.3\cdot10^{11}\) at/cm\(^2\).
Figure 5. TXRF spectrum of the monocrystalline silicon substrate [111] obtained with X-ray source power condition: V=25 keV, I=10 mA. Molybdenium radiation. Shown every third channel. $\tau=1000$ sec. 16 eV/ch.

The data on the detection limits obtained in this work are not ultimately possible for this kind of a spectrometer design. Using X-ray tube in the rate duty (P=2 kW), X-ray detector with best resolution ($\delta E=120$ eV) and making some improvements of the slitless collimator can obtain the lowest detection limits for the Fe group elements up to $1 \times 10^9$ atoms per cm$^2$.

In conclusion, it should be noted that the use of a slitless collimator has some disadvantages. However, it is very efficient for the routine surface diagnostic because of the TXRF analysis in this case may be carried out by unskilled staff, the slitless TXRF spectrometer
is two orders lower in cost as compared with the standard TXRF analytical equipment, and offered by the better analytical parameters.

References.


