INVESTIGATIONS OF THIN LAYERS BY TEY, XRF, EPMA AND XPS -
A COMPARISON OF X-RAY ANALYTICAL METHODS

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INTRODUCTION

Irradiation of solid specimens by x-rays causes an electron emission. The electrons are
Auger, photo, Compton and secondary electrons. In the course of their migration through
matter they systematically lose energy by inelastic collisions. Thus, the escape energy of the
electrons is in general smaller than their original kinetic energy. The total electron yield
(TEY) is obtained by an electron detection without energy dispersion. A jumplike increase
(TEY jump) of the electron emission can be observed as the irradiation is performed with
monochromatic x-radiation and the photon energy is varied from an energy below the
absorption edge of one of the chemical elements of the specimen to above the edge energy.

We have investigated the analytical application of the TEY jumps to quantitative analysis and
the determination of layer thicknesses in analogy with the fundamental parameter approach of
quantitative XRF\textsuperscript{1,2}. Furthermore, we continued with

\begin{itemize}
  \item[i] the sampling depth of TEY\textsuperscript{3}
  \item[ii] the evaluation procedure of TEY jumps\textsuperscript{4}
  \item[iii] the influence of low energy secondary electrons\textsuperscript{5}
  \item[iv] the influence of higher order excitation processes on the analytical results\textsuperscript{6}
  \item[v] the determination of layer thicknesses by the substrate method\textsuperscript{6}
  \item[vi] the statistical significance of TEY results\textsuperscript{7}
\end{itemize}

Our present research activities are dedicated to the introduction of a new concept of electron
escape probabilities in matter and the comparison of the features of TEY and the results of
compositions, layer thicknesses and detection limits obtained by TEY to other x-ray analytical
methods. It is the aim of the present paper to introduce the theoretical concept of the layer
method for determination of layer thicknesses by TEY. The results and the detection limits are
compared to XRF, EPMA and XPS.
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THEORY OF THE LAYER METHOD

A flux $x_E$ of monochromatic x-rays (photons/second) of photon energy $E$ impinges on a plane layer and will be attenuated on its path from the surface of the thin layer of element $i$ to depth $t$ by $\exp(-\tau_{E,i})/\rho_i/t$/$\cos \alpha$. $\tau_{E,i}$ is the coefficient of photoelectric absorption of photons of energy $E$ in the chemical element $i$, $\rho_i$ the density and $\alpha$ the angle between incident x-rays and the surface normal. We expect in the differential layer volume with thickness $dt$ in depth $t$ a photoelectric absorption in the shell or subshell $j$ of the element $i$ which is directly proportional to $dt \cdot \tau_{E,j} \cdot \rho_i/t$/$\cos \alpha$. $\tau_{E,j}$ is the coefficient of photoelectric absorption in the shell or subshell $j$ of the element $i$. The process of photoelectric absorption is followed by deexcitation either by the emission of characteristic radiation with probability $\omega_{ij}$ or by the emission of an Auger electron with probability $1-\omega_{ij}$. $\omega_{ij}$ is the fluorescence yield of level $j$ in element $i$. The kinetic energy $E_{\text{kin}}$ of Auger electrons is known. Thus, we have Auger electrons leaving an atom in depth $t$ of the layer in an arbitrary direction with regard to the direction of the incident x-rays. The escape probability $p_{\text{escape}}(i,t,E_{\text{kin}},\Omega,50\text{eV})$ of electrons describes the fraction of electrons released under arbitrary direction in depth $t$ and being detected after leaving the surface of the layer. The detection of low energy secondary electrons can be suppressed by a retarding potential $U_{\text{ret}}=50\text{V}$ in front of the electron detector. Consequently, our escape probability must be valid for electrons leaving the surface with an energy of more than $50\text{eV}$.

$$dn_{ij} = x_E \cdot e^{-\tau_{E,j} \cdot \rho_i / \cos \alpha} \cdot \frac{dt \cdot \tau_{E,j} \cdot \rho_i}{\cos \alpha} \cdot (1-\omega_{ij}) \cdot p_{\text{escape}}(i,t,E_{\text{kin}},\Omega,50\text{eV})$$

$dn_{ij}$ is the contribution of the differential volume in depth $t$ of the layer to the measured electron signal. The measured signal $n_{ij}$ is obtained from $dn_{ij}$ by an integration from $t=0$ to the layer thickness $d$. Therefore, we have to deal with the $t$-dependence of the escape probability. $p_{\text{escape}}$ depends on the material $i$, the depth $t$ where the electron were released, the kinetic energy $E_{\text{kin}}$, the electron acceptance cone $\Omega$, and the retarding potential $U_{\text{ret}}$. 

![Fig.1 Escape probability in dependence on the depth of origin of 5keV electrons in Cr for an electron acceptance cone of ±20° with regard to the surface normal. Data points are from Monte Carlo calculations and the curve is a least squares fit of a superposition of two exponential responses.](image)

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energy $E_{\text{kin}}$ and on the solid angle $\Omega$ of electron detection. Fig. 1 depicts the escape probability of 5keV electrons in Cr for an acceptance cone of electron detection of $\pm 20^\circ$ with regard to the surface normal and an escape energy of at least 50eV. The chosen acceptance angle from 0 to $20^\circ$ is representative for the geometry of our TEY instrument.

For the description of the Monte Carlo results we use

$$P_{\text{escape}} = K_1 \cdot e^{-\frac{t}{\lambda_1}} - K_2 \cdot e^{-\frac{t}{\lambda_2}}$$

The values of the constants for the least squares fit of Fig. 1 are $K_1=0.4274$, $\lambda_1=28.184\text{nm}$, $K_2=0.3410$ and $\lambda_2=14.760\text{nm}$. We learned from a careful analysis of the $K$ and $\lambda$ values of 26 chemical elements from $Z=3$ to 79 and 19 kinetic electron energies from 1 to 30keV that the $K$ values for our electron acceptance cone in the mentioned $Z$ interval can be approximated just by an energy dependent expression

$$K_1 = 0.3656701 + 0.04370954 \cdot \log E_{\text{kin}} - 0.003275835 \cdot (\log E_{\text{kin}})^2$$

$$K_2 = 0.2709986 + 0.04240546 \cdot \log E_{\text{kin}} - 0.003178205 \cdot (\log E_{\text{kin}})^2$$

whereas the $\lambda$ values have to be approximated by a product of an element dependent factor $A_i/\rho_i Z_i$ ($A_i$ atomic weight and $Z_i$ atomic number) with an energy dependent expression $f(E_{\text{kin}})$

$$\lambda_{1,1} = \frac{A_i}{\rho_i Z_i} e^{2.470678+1.166637 \cdot \log E_{\text{kin}}+0.08334102 \cdot (\log E_{\text{kin}})^2}$$

$$\lambda_{1,2} = \frac{A_i}{\rho_i Z_i} e^{1.798438+1.178633 \cdot \log E_{\text{kin}}+0.0802149 \cdot (\log E_{\text{kin}})^2}$$

With the specific parameters of Fig. 1 one obtains from our approximation $K_1=0.4275$, $\lambda_1=28.922\text{nm}$, $K_2=0.3310$ and $\lambda_2=14.933\text{nm}$. Table 1 illustrates a comparison of the escape probabilities from the least squares fit of Fig. 1 and from the $K$ and $\lambda$ values of our approximation. An averaged deviation of 6% of the escape probabilities and an identical position of the maximum of the distribution results.

<table>
<thead>
<tr>
<th>depth (nm)</th>
<th>l.s.f.</th>
<th>appr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.086</td>
<td>0.097</td>
</tr>
<tr>
<td>5</td>
<td>0.115</td>
<td>0.123</td>
</tr>
<tr>
<td>10</td>
<td>0.127</td>
<td>0.133</td>
</tr>
<tr>
<td>15</td>
<td>0.128</td>
<td>0.133</td>
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<tr>
<td>20</td>
<td>0.122</td>
<td>0.127</td>
</tr>
<tr>
<td>25</td>
<td>0.113</td>
<td>0.118</td>
</tr>
<tr>
<td>30</td>
<td>0.103</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Table 1 Comparison of the escape probabilities from the least squares fit of Fig. 1 with our approximation for an escape depth interval from 0 to 30nm

After this detailed treatment of our universal expression for the escape probability the integration of $d\pi_{ij}$ from $t=0$ to $d$ can be performed. Usually $d$, $\rho$ and $\tau$ are given in units of cm, g/cm$^3$ and cm$^2$/g. But, with our functions $f_{1}(E_{\text{kin}})$ and $f_{2}(E_{\text{kin}})$ the values of $\lambda$ are obtained in nm. Therefore, we use $10^{-7} f(E_{\text{kin}})$ in the following equations and $d$ in cm. Similar to XRF, EPMA and XPS TEY allows no determination of the layer thickness $d$ but only of the product $\rho_i d$ which is the mass per unit area $m_{i}/F$ of the layer.

$$n_{ij} = x_{E} \cdot \frac{\tau_{E_{ij}} \cdot \rho_i}{\cos \alpha} \cdot (1 - \omega_y) \cdot \int_{t=0}^{d} e^{-\frac{t}{\lambda_1}} \left( K_1 \cdot e^{-\frac{t}{\lambda_1}} - K_2 \cdot e^{-\frac{t}{\lambda_2}} \right) \cdot dt$$
Photoelectrons from the photoelectric absorption of incident x-rays $x_F$ in the j-shell have kinetic energies $E_{km}=E-E_{j\text{-edge}}$. The TEY jumps are reduced from experimental data by extrapolating the kinetic energy of primary photoelectrons to almost $E_{km}=0$. A numerical evaluation allows us to neglect the contribution from the primary photoelectrons to $n_{ij}$. A numerical treatment of secondary excitations\(^1\), like photoelectrons from the sequence incident radiation $x_E \rightarrow$ photoelectric absorption in the K-shell $\rightarrow$ Kα1-radiation $\rightarrow$ photoelectric absorption in the L1-subshell of the substrate element $\rightarrow$ emission of a substrate photoelectron gave negligible contributions to $n_{ij}$. Thus, our theoretical approach deals for $j=K$ only with KLL and LMM-Auger electrons.

Applying the equation for $n_{ij}$ to thin Cr layers on Fe substrates the indices $i$ and $j$ are valid for Cr and the K-shell. The atomic number is $Z_{\text{Cr}}=24$ and the atomic weight $A_{\text{Cr}}=51.996$g/mole. From Hubbell’s tables\(^2\) follows the fluorescence yield $\phi_{\text{Cr}}=0.286$ and from McMaster’s tables\(^8\) the density $\rho_{\text{Cr}}=7.19g/cm^3$, the energy of the K-edge $E_{\text{CrK}}=5.989$keV and the coefficient of photoelectric absorption just above the K-edge $\tau_{0.5989\text{keV,Cr}}=549.3cm^2/g$. The photoelectric absorption in the K-shell $\tau_{5.989\text{keV,Cr}}$ is calculated with K-edge jump $S_K=8.779$ by

$$
\tau_{5.989\text{keV,Cr}} = \frac{S_K-1}{S_K} = \frac{7.779}{8.779} \cdot 549.3 = 486.7cm^2/g
$$

Siegbahn\(^10\) gives Cr KLL-transitions with energies of 4.557, 4.651, 4.683, 4.687, 4.692, 4.757, 4.778, 4.788 and 4.795keV. We use the mean value of 4.710keV for $E_{\text{5.989keV,Cr}}$. In addition to Cr KLL-Auger electrons Cr LMM-Auger electrons have to be expected too. There exist two mechanisms for the generation of Cr LMM-Auger electrons. The emission of Cr Kα-radiation with probability $\phi_{\text{CrK}}$ causes a single hole in the Cr L-shell and the emission of Cr KLL-Auger electrons with probability $1-\phi_{\text{CrK}}$ causes two holes in the Cr L-shell. De-excitation of these holes is primarily caused by the emission of Cr LMM-Auger electrons ($\phi_{\text{CrL}}=0$). Either two Cr LMM-Auger electrons are emitted with probability $1-\phi_{\text{CrL}}$ or a single Cr LMM-Auger electron is emitted with probability $\phi_{\text{CrL}}$. In order to quantify the emission of LMM-Auger electrons we replace the factor $(1-\phi_{\text{CrL}})$ by $2-(1-\phi_{\text{CrL}}+\phi_{\text{CrK}}=(2-\phi_{\text{CrL}}))$ in the equation for $n_{ij}$. A negligible fluorescence yield leads to the release of 2 LMM-Auger electrons and with a fluorescence yield close to 1 the release of LMM-Auger electrons decreases from 2 to 1. Thus, we replace $1-\phi_{\text{CrL}}$ by $2-\phi_{\text{CrL}}$ for our treatment of Cr LMM-Auger electron emission.

The kinetic energy $E_{\text{kin}}(\text{Cr LMM})$ follows from the edge energies of Cr $L_1$, Cr $L_2$ and Cr $L_3$ with 0.695, 0.584 and 0.575keV and of Cr M1 to Cr M5 with 0.074, 0.043, 0.043, 0.023 and 0.023keV respectively. We approximate the kinetic electron energy of Cr LMM-Auger electrons by the difference of the mean values of L and M-edge energies $E_{\text{kin}}(\text{Cr LMM})=0.618-2 \cdot 0.041=0.536$keV.

The incidence angle in our instrument is $\alpha=78^\circ$ and we assume a flux $x_F$ of 1 photon/s. Consequently, the results of our calculations are given by detected electrons per photon.

$$
n_{\text{CrK}} = 1671.4 \left[ 0.426 \cdot \frac{1-e^{-550207.19d}}{55020} - 0.329 \cdot \frac{1-e^{-1040997.19d}}{104099} \right] + 4012.3 \left[ 0.339 \cdot \frac{1-e^{-7502517.19d}}{750251} - 0.245 \cdot \frac{1-e^{-147873717.19d}}{1478737} \right]
$$

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The first term describes the contribution of Cr KLL-Auger electrons to the measured Cr K-jump and the second term the contribution from Cr LMM-Auger electrons. Fig. 2 illustrates the numerical results for the layer thickness interval from 0 to 100 nm. For layer thicknesses greater than 100 nm the number of electrons per photon is between $8 \times 10^3$ and $9 \times 10^3$, or approximately 1 electron per 100 photons has to be expected. KLL-Auger electrons (dashed curve) are characterized by a greater electron range and a smaller initial slope. The KLL-Auger electrons dominate the response at thicknesses greater than 10 nm. For thicknesses of a few nm the depth dependence of the escape probability corresponding to Fig. 1 causes a smaller initial slope of the KLL response. The much smaller electron range of the low energy LMM-Auger electrons is responsible for a comparably steeper initial slope of the LMM response (dotted curve) and a comparably smaller contribution to the measured Cr K-jump at greater layer thicknesses. A typical feature of TEY-jump responses versus thickness is the remarkable decrease of the slope of the resultant curve (solid curve) where the low energy contribution becomes constant.

![Cr K-jump in electrons per photon versus thickness of the chromium layer in nm (solid curve). Contributions from Cr KLL-Auger electrons are represented by the dashed curve and from Cr LMM-Auger electrons by the dotted curve.](image)

**EXPERIMENTAL**

Our experiments were performed with a ROKAPPA Q-EDP 100 instrument with rotating Cu anode (30 kV, 100 mA) and Ge(111) or Si(111) crystal. A set of 10 Cr layers on Fe substrates was prepared by sputter deposition. In Fig. 3 the measured TEY responses in the photon energy interval from 5.75 to 6.25 keV are shown. The jump at the Cr K-edge increases with greater layer thicknesses. We quantify the jumps by linear least squares fits to the TEY responses below and above the edge and their intersections with the vertical line $E=5.989$ keV (full squares). The distance between the squares is the numerical value of the jump ($n_0$ or $n_{0\text{Cr}}$). Table 2 contains thickness values in nm from the quartz crystal monitor and from the investigations by EPMA, XRF and TEY. Additionally the measured Cr K-TEY jumps in electrons/10$^4$ photons and the normalized Cr K-TEY jumps are included. For layers with
thicknesses greater than approximately 150nm the TEY jump remains constant within the statistical significance. We formed for this reason the mean value of the jumps corresponding to thicknesses of 150, 200, 300 and 500nm and used the mean value of 74.675 electrons/10^4 photons for the normalized Cr K-jumps given in the last column of Table 2. Our theoretical jumps were normalized by the jump corresponding to a thickness of 600nm.

Fig.3 Measured Cr K-TEY responses versus photon energy of 10 Cr layers on Fe substrates
Table 2 Thicknesses of the investigated Cr layers from different methods and values of the TEY jumps in electrons/10⁴ photons and normalized TEY jumps with regard to the jump of bulk Cr.

<table>
<thead>
<tr>
<th>Crystal monitor (nm)</th>
<th>EPMA (nm)</th>
<th>XRF (nm)</th>
<th>TEY (nm)</th>
<th>Cr K-jumps electrons/10⁴ photons</th>
<th>normalized Cr K-jumps</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>17.5</td>
<td>15.7</td>
<td>10±1.3</td>
<td>22.375</td>
<td>0.300</td>
</tr>
<tr>
<td>20</td>
<td>34.1</td>
<td>26.2</td>
<td>20±2.0</td>
<td>35.247</td>
<td>0.472</td>
</tr>
<tr>
<td>40</td>
<td>59.1</td>
<td>45.9</td>
<td>39±4.5</td>
<td>53.709</td>
<td>0.719</td>
</tr>
<tr>
<td>60</td>
<td>85.1</td>
<td>71.7</td>
<td>62±10</td>
<td>65.663</td>
<td>0.879</td>
</tr>
<tr>
<td>80</td>
<td>112.4</td>
<td>90.7</td>
<td>93±17</td>
<td>71.977</td>
<td>0.964</td>
</tr>
<tr>
<td>100</td>
<td>143.7</td>
<td>123.3</td>
<td>-</td>
<td>74.066</td>
<td>0.992</td>
</tr>
<tr>
<td>150</td>
<td>221.7</td>
<td>-</td>
<td>-</td>
<td>74.680</td>
<td>1.000</td>
</tr>
<tr>
<td>200</td>
<td>272.3</td>
<td>235.2</td>
<td>-</td>
<td>72.538</td>
<td>0.971</td>
</tr>
<tr>
<td>300</td>
<td>439.4</td>
<td>380.5</td>
<td>-</td>
<td>74.715</td>
<td>1.001</td>
</tr>
<tr>
<td>500</td>
<td>680.6</td>
<td>605.6</td>
<td>-</td>
<td>76.768</td>
<td>1.028</td>
</tr>
</tbody>
</table>

Fig. 4 Theoretical response of the normalized Cr K-jump versus thickness of the Cr layer and results of our experiments from 10 chromium layers.

The curve in Fig. 4 displays the theoretical normalized Cr K-jump for a thickness interval from 0 to 600nm and the normalized Cr K-jumps of our specimens over their crystal monitor thicknesses. A comparison of the experimental data with the theoretical response recommends the application of TEY to Cr layers up to 80nm.
DETECTION LIMIT

In the TEY responses of Fig. 3 the background is defined by the intersection of the linear least squares fit of 21 data points between 5.75 and 5.95 keV with the vertical line E=5.989 keV. The usual definition of the detection limit asks for a signal \( n_{ij,\text{min}} \) of \( 3 \cdot \sigma_{\text{background}} \). Thus, a signal \( n_{ij,\text{min}}=3 \cdot \sigma_{\text{background}} \) describes the minimum detectable layer thickness. From the statistical scatter of the linear least squares fit through the 21 data points it is possible to calculate \( \sigma \) as follows. The abscissa \( x_i \) is measured with regard to the absorption edge at energy \( E_{K\text{-edge}} \) and is given by \( x_i=E_i-E_{K\text{-edge}} \). In our linear least squares fit the statistical weight of the complete set of data points is assumed to be identical. Thus, the error definition becomes

\[
v_i = y_i - a - b \cdot x_i
\]

with the intersection \( a \) at \( x=0 \) and the slope \( b \) of the linear fit. The chi-square merit function is

\[
\chi^2(a,b) = \sum_{i=1}^{N} v_i^2
\]

and from the minimum conditions of the chi-square merit function

\[
\frac{\partial \chi^2(a,b)}{\partial a} = 0 \quad \text{and} \quad \frac{\partial \chi^2(a,b)}{\partial b} = 0
\]

follow

\[
a = \frac{S_{xx} \cdot S_y - S_x \cdot S_{xy}}{N \cdot S_{xx} - S_x^2} \quad \text{and} \quad b = \frac{N \cdot S_{xy} - S_x \cdot S_y}{N \cdot S_{xx} - S_x^2}
\]

with the abbreviations

\[
S_x = \sum_{i=1}^{N} x_i, \quad S_y = \sum_{i=1}^{N} y_i, \quad S_{xy} = \sum_{i=1}^{N} x_i \cdot y_i, \quad S_{xx} = \sum_{i=1}^{N} x_i^2
\]

\( N \) is the number of data points (in Fig. 3 \( N=21 \)).

Fig. 5 Standard deviation \( \sigma_a \) of the lower point \( a \) of the Cr K-jumps of Fig. 3 versus layer thickness
The standard deviation $\sigma(y_i)$ of the data points from the linear fit is

$$\sigma(y_i) = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (y_i - a - b \cdot x_i)^2}$$

and the standard deviation $\sigma_a$ of the intersection at $a$ is obtained from $\sigma(y_i)$ by

$$\sigma_a = \sigma(y_i) \cdot \sqrt{\frac{S_{xx}}{N \cdot S_{x}^2 - S_{x}^2}}$$

$\sigma_a$ is equal to the interesting standard deviation $\sigma_{\text{background}}$. Our evaluation routine computes the linear fit, the ordinate $a$ of the intersection and the $\sigma_a$-value. In Fig.5 $\sigma_a$ is displayed versus layer thickness. There exists no thickness dependence and we describe $\sigma_a$ by the mean value 0.289. The $3\sigma_{\text{background}}$ interval is 0.866. From the corresponding normalized signal $0.866/74.675=0.0116$ and an initial slope of the theoretical normalized signal of 0.05015/nm a minimum detectable layer thickness $d_{\text{min}}=0.0116/0.05015=0.23$nm is obtained.

An additional investigation was performed on Cr layers on different substrates by an application of the substrate method (Fig.6) and of the layer method (Fig.7). Longer time of data acquisition gave a better statistical significance and a lower detection limit. The results of this experimental investigations are given in monolayers of Cr. A monolayer thickness $ML_{\text{Cr}}$ of Cr is twice the atomic radius $r_{\text{Cr}}$ of Cr ($ML_{\text{Cr}}=2r_{\text{Cr}}=2\cdot0.128=0.256$nm). Thus, the value of 0.4$ML_{\text{Cr}}$ for Fe substrates in Fig.7 is 0.102nm, or less than 50% of the above mentioned detection limit of 0.23nm. The results of Figs.6 and 7 indicate an increase of the detection limit with increasing atomic number $Z$ of the substrate material. This increase can be explained by the $Z$-dependence of the background. Furthermore, it becomes evident from a comparison of Figs.6 and 7 that the detection limits of the layer method are better than of the substrate method.

![Detection Limit of Chromium in Dependence on the Atomic Number Z of the Substrate Element](image)

**Fig. 6** Detection limits of Cr layers on different substrates from the K-jumps of substrate elements.
Figure 7 Detection limits of Cr layers on different substrates from the Cr K-jumps of the layer

A further series of experiments was performed on thin Au layers on Si wafers. Layers with thicknesses of 0.05, 0.5, 3, 20 and 100 nm were prepared by sputter deposition and the thicknesses are from the quartz crystal monitor. All layers were again investigated by XRF (Au Lα), EPMA (Au Lα), XPS (Au 4f) and TEY (Au L3-edge).

Figure 8 Ratio r of the normalized Au L3-jump of the layers and the 3σ-background-interval versus Au layer thickness. The intersection of the linear responses indicates a detection limit of 0.037 nm for TEY.

Figs. 8 to 11 illustrate the evaluation of the measured results with regard to the detection limits of the different methods.
The detection of Au by XPS, even in case of 0.05nm layer caused no problem. But, the determination of the layer thicknesses by the method of variable take-off angle suffered from interdiffusion of Si and Au in the interface\textsuperscript{14,15,16}. The coexistence of Au and Si on the surface of extremely thin Au layers is responsible for a stronger drop of the Au$4f$ signal with decreasing layer thickness. Therefore, we were only able to estimate the detection limit of XPS for Au. A detection limit of 0.001nm or 0.004ML$^{-1}$ seems to be realistic. The values of the detection limits of TEY, XRF, XPS and EPMA for Au are in general better than for Cr.

Finally, our considerations on the detection limit can be extended to the standard deviation $\sigma_d$ -or better $3\sigma_d$- of layer thicknesses determined by TEY. The measured Cr K-jumps of our investigations on Cr layers on Fe substrates have been given in Table 2. From the standard deviations of Table 3 the averaged standard deviations of the reference become $\sigma_{d}\rm{(ref)} = (0.306+0.235+0.237+0.273)/4 = 0.263$ and $\sigma_{e}\rm{(ref)} = (0.979+0.966+0.910+0.937)/4 = 0.948$. 

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**Fig.9** Au L$\alpha$-signal and $3\sigma$$_{\text{background}}$-interval versus Au layer thickness. The intersection of the linear responses indicates a detection limit of 0.67nm for XRF.

**Fig.10** Au$4f$-signal and $3\sigma$-interval versus Au layer thickness. The intersection of the linear responses indicates a detection limit of about 0.001nm for XPS.
Fig.11 Au Lα-signal and 3σ-interval of the background versus Au layer thickness. The intersection of the linear responses indicates a detection limit of 0.32nm for EPMA.

The reference signal is the difference of two values with standard deviations $\sigma_a$(ref) and $\sigma_a$(ref). The standard deviation of the reference signal follows from the law of error propagation

$$\sigma(\text{ref}) = \sqrt{0.263^2 + 0.948^2} = 0.984\text{electrons/10}^4\text{electrons}$$

The 10nm Cr layer has a standard deviation of the measured jump of

$$\sigma(10\text{nm}) = \sqrt{0.283^2 + 0.390^2} = 0.482\text{electrons/10}^4\text{photons}$$

The normalized jump 0.300 is the ratio of the jumps 22.375 and 74.675 (see Table 2) with standard deviations $\sigma(10\text{nm})$ and $\sigma(\text{ref})$ and the standard deviation $\sigma(10\text{nm,ratio})$ of the ratio becomes with the law of error propagation

$$\sigma(10\text{nm,ratio}) = \frac{1}{74.675^2} \cdot \sqrt{74.675^2 \cdot 0.482^2 + 22.375^2 \cdot 0.984^2} = 0.00757$$

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$\sigma_a$ (electrons/10⁴ photons)</th>
<th>$\sigma_u$ (electrons/10⁴ photons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.283</td>
<td>0.390</td>
</tr>
<tr>
<td>20</td>
<td>0.306</td>
<td>0.590</td>
</tr>
<tr>
<td>40</td>
<td>0.202</td>
<td>0.621</td>
</tr>
<tr>
<td>60</td>
<td>0.276</td>
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<tr>
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Table 3 Standard deviations of the lower ($\sigma_a$) and of the upper ($\sigma_u$) intersections(squares) of the linear fits with the vertical lines at E=5.989keV of the measured responses in Fig.3.
Under the assumption of an error interval of $3\sigma(10\text{nm}, \text{ratio})$ for confidence of 99% of the final result the experimental normalized Cr K-jump of the 10nm layer becomes $0.300 \pm 0.023$ and from the slope of the theoretical normalized Cr K-jump versus Cr layer thickness of 0.018/nm at a layer thickness of 10nm the $3\sigma_{t}$ interval of the layer thickness $3\sigma_{t} = 0.023/0.018 = 1.3\text{nm}$ or 13% of the thickness value. Table 2 contains the thicknesses from TEY together with $3\sigma_{t}$-intervals.

CONCLUSIONS

The theoretical background of quantitative TEY allows accurate layer thickness determinations. The values from XRF, EPMA, quartz crystal monitoring and TEY agree within the significance of the different methods. The detection limit of TEY depends on the material of both, the substrate and the layer. Our investigations gave values between 0.05 and 0.5nm. An application of thickness measurements by TEY is recommended for layers from 0.1 to 100nm. TEY fills with its typical thickness range and detection limit the gap between XPS on the side of small layer thicknesses and XRF and EPMA of great layer thicknesses. An essential improvement of detection limits has to be expected from the much higher primary x-ray fluxes of synchrotron sources.

REFERENCES

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A confirmation of our theoretical concept and the absolute values of the escape probabilities follows from the comparison of the theoretical value for bulk Cr of $0.00879$ electrons/photon with our measured result of $74.675/10^4 = 0.00747$ electrons/photon. Another confirmation comes from the absolute values of the escape depths (values of $\lambda_{Cr,1}$ and $\lambda_{Cr,2}$) and the result of layer thickness determinations.