QUANTITATIVE SURFACE ANALYSIS BY X-RAY INDUCED ELECTRON EMISSION

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ABSTRACT

The theoretical approach of TEY (total electron yield) for quantitative surface analysis is demonstrated for binary Au-Cu alloys and the evaluation of thin layer measurements on the example of thin AlGaAs layers on GaAs substrates. Further considerations deal with detection limits of the method. An interesting feature of TEY is the possibility to quantify buried thin layers. The detection limits are less than monolayer thicknesses. Another essential feature of TEY is the much higher electron yield of low Z elements when compared to the yield of characteristic x-ray photons.

INTRODUCTION

Irradiating solids with x-rays causes an electron emission from the irradiated surface, owing primarily to photoelectric absorption. These electrons can be detected under vacuum and are photo-, Auger, Compton and secondary electrons. Due to inelastic collisions most of these electrons have lost some of their original kinetic energy along their path from the atom of origin to the surface of the specimen. The total electron yield (TEY) is measured by nondispersive detection of all emitted electrons. In the photon energy range from 0.5 to 30 keV the probability of Compton scattering of incident x-radiation is much smaller when compared to the probability of photoelectric absorption. Therefore, in our theoretical approach the contribution from Compton electrons is neglected. For TEY measurements an x-ray source with tunable monochromator is obligatory. Information on the qualitative composition is obtained by tuning the photon energy in steps of 10 to 100 eV from below to above of one of the absorption edges of a certain element. In case of presence of this element in the specimen a jump-like increase of the TEY signal (TEY jump) can be detected (Fig. 1).

Fig. 1 Measured Cr K TEY signal (electrons per second) versus photon energy (keV). Measurements have been performed on Cr layer with thickness of 500 nm on Fe substrate. The distance between the intersections (black squares) of the linear least squares fits through the measured responses below and above the Cr K edge with the vertical line at the Cr K edge position (5.989 keV) is used for quantification of the jump.

For electrically nonconductive samples the electron emission is responsible for positive charging of the specimen surface. Consequently, the emitted electron spectrum moves with regard to ground potential towards lower kinetic energies and some of the low energy secondary electrons are no longer able to enter the grounded entrance of the electron detector. Owing to their high flux density, secondary electrons contribute remarkably to measured TEY jumps. Fig. 2 illustrates the influence of charging on measured TEY jumps.
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There are different possibilities to overcome the charging problem: i. Installation of an electron flood gun or another electron source to compensate the loss of electrons, ii. setting the electron detector entrance to a positive bias in order to attract all secondary electrons from the charged specimen, iii. setting the electron detector entrance to a negative bias with regard to ground potential in order to suppress the emission and the detection of secondary electrons from either charged or uncharged specimens. For quantitative TEY we suppress the detection of secondary electrons. Thus, we have to deal with electrons from photoelectric absorption of incident x-rays (primary photoelectrons), electrons from relaxation of atoms after photoionization (primary Auger electrons), electrons from photoelectric absorption of fluorescent x-radiations in the specimen (secondary photoelectrons), electrons from relaxation of atoms after secondary excitation (secondary Auger electrons) and the detection of characteristic x-radiation by the electron detector. The magnitude of the jumps depends on the photon flux, the composition of the specimen, the photoelectric absorption coefficients, the absorption edge jumps, the fluorescence yields and the number and the probability of relaxation processes giving rise to an emission of secondary Auger and photoelectrons and of characteristic x-radiation. The correlation between the jumps and the concentration of the chemical elements is used for quantitative analysis (Fig. 3).

A further essential quantity of TEY is the escape probability $p_{\text{escape}}$ of electrons in matter. $p_{\text{escape}}$ depends primarily on the matrix and the kinetic electron energy. Measurements performed on thin films are an excellent tool to become familiar with the sampling depth $\lambda$ of TEY. The correlation between $p_{\text{escape}}$ and $\lambda$ will later be treated in detail. Thus, thicknesses of thin films can be quantified by TEY measurements. Assuming an exponential correlation
between jump and thickness $t$ (Fig. 4), one obtains from a least squares fit of the measured TEY jumps versus Cr layer thickness $t$ an empirical sampling depth $\lambda = 27$ nm.

![Fig. 4 Exponential least squares fit through measured Cr K jumps of thin Cr layers on Fe substrates.](image)

**THEORY**

In order to explain the concept of TEY we deal with contributions to measured Cu K and Au L3 jumps and with quantitative analysis of binary Au-Cu alloys. For this purpose we start with photoelectric absorption of incoming x-rays in given shells or subshells of the atoms. The next step is dedicated to probabilities of generation of either Auger or photoelectrons due to relaxation of the photoionized atom followed by escape probabilities of these electrons. Finally, the analytical approach is developed.

**PHOTOELECTRIC ABSORPTION COEFFICIENTS**

For our computations we used photoelectric absorption coefficients $\tau$ of the different shells and subshells of Cu and Au published by Scofield$^1$ and described them in the usual way by least squares fits of the numerical values from the tables in dependence on the photon energy $E$ (keV).

$$\tau = \text{conv} \cdot \exp(B_0 + B_1 \ln E + B_2 (\ln E)^2 + B_3 (\ln E)^3)$$

$\text{conv}$ is the conversion constant from barns/atom to cm$^2$/g ($\text{conv}_{\text{Cu}} = 0.00948$, $\text{conv}_{\text{Au}} = 0.00305$).

**PRIMARY AUGER ELECTRONS**

Our measurements of the increase of TEY in the proximity of the K absorption edge of Cu and the L3 edge of Au have been performed by tuning the photon energy in steps of 20 eV from 200 eV below to 200 eV above the edges. The energies of Cu 1s photoelectrons from the Cu K edge scan and of Au 2p3/2 photoelectrons from the Au L3 edge scan become at maximum 200 eV. This relatively low electron energy is responsible for an extremely small escape probability. Therefore, the contribution of these two kinds of primary photoelectrons to the corresponding TEY signals can be neglected. Relaxation of K ionized Cu atoms causes either an emission of Cu KLL and Cu LMM Auger electrons with averaged energies $E_{\text{CuKLL}} = 7.0$ keV and $E_{\text{CuLMM}} = 0.9$ keV or an emission of characteristic Cu K radiations with an averaged photon energy of 8.17 keV combined with Cu LMM Auger electrons. The Auger electrons form the major contribution to the measured increase of TEY at the Cu K edge.
Essential quantities for quantitative description of electron emission probabilities are

- \( \omega_K \)  K shell fluorescence yield\(^2,3\)
- \( \omega_L \)  L shell fluorescence yield\(^2,3\)
- \( p_{ij} \)  probability of radiative electron transition from shell j to shell i\(^4\)
- \( p_j \)  (j=1,2,3) transition probability of KLL Auger electrons\(^5\)
- \( f_{KL} \)  Coster-Kronig transition probability\(^3\)

Numerical values for Cu are

\[
\begin{align*}
\omega_K &= 0.4538 \\
\omega_L &= 0.00939 \quad (\omega_L = \omega_{L1} = \omega_{L2} = \omega_{L3}) \\
p_{KL2} &= 0.584 \quad p_{KL3} = 0.297 \quad p_{KM3} = 0.119 \\
p_1 &= 0.22 \quad p_2 = 0.51 - \omega_K p_{KL2} = 0.38 \quad p_3 = 0.66 - \omega_K p_{KL3} = 0.39 \\
f_{1,3} &= 0.30 \quad f_{1,3} = 0.54 \quad f_{2,3} = 0.028
\end{align*}
\]

The probability \( p_{CuKLL} \) for generation of Cu KLL Auger electrons is given by

\[
p_{CuKLL} = 1 - \omega_K = 0.55
\]

Cu LMM Auger electrons are obtained on the radiative path by the probabilities

\[
\begin{align*}
\omega_K p_{KL2}(1 - \omega_{L2} f_{2,3}) &= 0.13 \quad \text{L2MM} \\
\omega_K p_{KL3}(1 - \omega_{L3}) &= 0.26 \quad \text{L3MM} \\
\omega_K p_{KL} f_{2,3}(1 - \omega_{L3}) &= 0.004 \quad \text{L3MM}
\end{align*}
\]

and on the nonradiative path by the probabilities

\[
\begin{align*}
(1 - \omega_K)p_1(1 - \omega_{L1} f_{1,2} f_{1,3}) &= 0.02 \quad \text{L1MM} \\
(1 - \omega_K)p_{1,2}(1 - \omega_{L2} f_{2,3}) &= 0.03 \quad \text{L2MM} \\
(1 - \omega_K)p_{f_{1,2} f_{2,3}}(1 - \omega_{L3}) &= 0.001 \quad \text{L3MM} \\
(1 - \omega_K)p_{f_{1,3}}(1 - \omega_{L2}) &= 0.06 \quad \text{L3MM} \\
(1 - \omega_K)p_2(1 - \omega_{L2} f_{2,3}) &= 0.20 \quad \text{L2MM} \\
(1 - \omega_K)p_{2,3}(1 - \omega_{L3}) &= 0.01 \quad \text{L3MM} \\
(1 - \omega_K)p_3(1 - \omega_{L3}) &= 0.21 \quad \text{L3MM}
\end{align*}
\]

On the nonradiative path one electron from the L shell is necessary to fill the K vacancy and a second electron leaves the L shell as Cu KLL Auger electron. Thus, two electrons have been removed from the L shell and nearly 100% of the L vacancies relax under emission of LMM Auger electrons (\( \omega_L \approx 0 \)). For this reason, the total probability for generation of Cu LMM Auger electrons after emission of one Cu KLL Auger electron is twice the sum of the seven probabilities of the nonradiative path (2 \cdot 0.531 = 1.062) and the sum of the ten Cu LMM Auger electron probabilities becomes 0.394 + 1.062 = 1.456. An easier explanation of the resultant Cu LMM Auger electron probability can be given from the consideration that the probability is \( \omega_K \) on the radiative path for a single vacancy in the L shell and 2(1-\( \omega_K \)) on the nonradiative path for a pair of vacancies in the L shell. The sum of both probabilities is the resultant probability

\[
2(1 - \omega_K) + \omega_K = 2 - \omega_K = 2 - 0.55 = 1.45
\]

for an emission of LMM Auger electrons after K shell ionization. The numerical values of the probabilities of 1.456 and 1.45 are nearly identical. For a better understanding of the meaning of probabilities greater than 1, two extreme values of \( \omega_K \) may be discussed. In case of \( \omega_K = 0 \) no characteristic K radiation will be emitted and two vacancies in the L shell are formed after emission of the KLL Auger electron. The probability for the emission of LMM Auger electrons becomes \( p_{LMM} = 2 - 0 = 2 \). In case of \( \omega_K = 1 \) no KLL Auger electrons will be emitted and after emission of characteristic K radiation a single vacancy remains in the L-shell (\( p_{LMM} = 2 - 1 = 1 \)). The value \( p_{LMM} = 1.45 \) means that following photoelectric absorption in the Cu K shell, an averaged number of 1.45 LMM Auger electrons will be emitted. Finally, as \( \omega_L \)
deviates from zero, the resultant probability for LMM Auger electron production is described by
\[ P_{LMM} = (2 - \omega_L)(1 - \omega_M). \]
For Au the fluorescence yields of L3 and M are
\[ \omega_{L3} = 0.331, \]
\[ \omega_M = 0.0245 \]
and the transition probabilities of Lβ₂, Lα₁, and Lα₂ are
\[ P_{L3N5} = 0.15, \]
\[ P_{L3M5} = 0.77, \]
\[ P_{L3M4} = 0.08. \]
The probability for Au L3MM and Au MNN Auger electron emission after Au L3 photoelectric absorption is given by
\[ P_{AuL3MM} = 1 - \omega_{L3}, \]
\[ P_{AuMNN} = (2 - \omega_{L3})(1 - \omega_M). \]
The averaged kinetic energies of Au L3MM and of Au MNN Auger electrons are 6.4 keV and 2 keV, respectively.

**SECONDARY PHOTO- AND AUGER ELECTRONS**

Besides the primary generation of Auger electrons in the course of relaxation the process of photoelectric absorption of either characteristic Cu K- or Au L radiation in the specimen is another essential source of electrons. The kinetic energies of the photoelectrons follow from Einstein’s equation
\[ E_{\text{kin}} = h\nu - E_B \]
with photon energy \( h\nu \) and binding energy \( E_B \) of the electrons. Photoelectron energies are defined by two subscripts. The first one gives information on \( h\nu \) and the second one on \( E_B \). Therefore, \( E_{CuK_{\alpha 1}, CuL_{\alpha 1}} \) describes the kinetic energy of photoelectrons after photoelectric absorption of Cu K\( \alpha_1 \) radiation in the Cu L\( \alpha_1 \) level. This is one of the possibilities of the generation of secondary photoelectrons in the binary matrix. The photon energy of Cu K\( \alpha_1 \) is 8.048 keV and the binding energy of the Cu 2s electrons in Cu L\( \alpha_1 \) is identical to the L\( \alpha_1 \) edge energy of 1.096 keV giving rise to kinetic energy \( E_{CuK_{\alpha 1}, CuL_{\alpha 1}} \) of the photoelectron of 6.952 keV. In order to reduce the great number of possible combinations of radiations and atomic levels we replace in our computations the five M and the seven N levels of Au, the three L and the five M levels of Cu by averaged binding energies:
\[ E_{B,AuM} = 2.76 \text{ keV}, E_{B,AuN} = 0.4 \text{ keV}, E_{B,CuL} = 0.99 \text{ keV} \text{ and } E_{B,CuM} = 0.05 \text{ keV. The Au L3 and the Cu K edges remain unchanged: } E_{R,AuL3} = 11.919 \text{ keV} \text{ and } E_{R,CuK} = 8.979 \text{ keV. The number of radiations is reduced to the strongest characteristic radiations after K ionization of Cu (Cu K\( \alpha_1 \), Cu K\( \alpha_2 \) and Cu K\( \beta_1 \)) and L3 ionization of Au (Au L\( \alpha_1 \), Au L\( \alpha_2 \) and Au L\( \beta_2 \)) and is described by the weighted averaged value of photon energies: } h\nu_{CuK} = 8.17 \text{ keV} \text{ and } h\nu_{AuL3} = 9.71 \text{ keV. Secondary Cu LMM Auger electrons are expelled after photoelectric absorption of one of the characteristic radiations Cu K or Au L3 in Cu L and secondary Au MNN Auger electrons after photoelectric absorption in Au M and secondary Cu KLL Auger electrons after photoelectric absorption of characteristic Au L3 radiation in Cu K.}

**ESCAPE PROBABILITY OF ELECTRONS**

The photoelectric absorptions occur in various depths of the specimen. Some of the generated photo- and Auger electrons reach the surface after elastic and inelastic collisions. These electrons can be detected. Whereas the energy of the electrons at their origin is described by discrete values, we observe after their escape from the surface, a continuous energy distribution with a superposition of the original line spectrum of kinetic electron energies. The continuum is caused by inelastic collisions and the subsequent loss of kinetic energy. The electron range decreases with decreasing kinetic energy and therefore only a relatively small amount of the electrons from greater depths is able to reach the surface and to
escape from there. The following considerations deal with the escape probability of electrons in dependence on chemical element, depth where the electrons have been generated, kinetic energy of the electrons and acceptance cone of electron detection. The depth dependent emission characteristics of electrons have been investigated by means of Monte Carlo model calculations. Our model closely follows the model described in detail by Shimizu and Ding Ze-jun. The distribution of scattering angles, or differential elastic scattering cross section was calculated with the relativistic partial wave expansion method after Yates, employing a Thomas-Fermi-Dirac potential specified by the parameters given by Bonham and Strand. For the present purpose, the differential inelastic inverse mean free path provides all necessary information concerning the inelastic electron solid interaction. This quantity was calculated with Penn's formalism employing a quadratic plasmon dispersion relation and using the required optical data compiled in the Handbook of Optical Constants of Solids. The Monte Carlo calculations were performed on 25 chemical elements, 44 electron energies from 0.15 keV to 30 keV and electron acceptance angles with regard to the surface normal in steps of 10° from 10° to 90°. The dependence of escape probability versus generation depth of Cr for the case of isotropic emission, an electron energy of 5 keV and a cone of electron acceptance of 20° is displayed in Fig. 5. An escape energy of at least 50 eV has been chosen. A quite striking feature is seen: the depth dependence deviates from exponential attenuation. This is a well known effect in the quasi elastic case and has been successfully explained by increasing isotropization of the escaping particle flux density as the generation depth is increased. Since elastic scattering is more intensive in the slowing down regime, we may conclude that the same mechanism is responsible for the non-exponential emission characteristics observed here. Erbil and coworkers already suggested a deviation from Beer-Lambert type absorption law for TEY on the basis of a geometric argument. Therefore, we describe the Monte Carlo results by a sum of two exponential responses \( P_{\text{escape}} = A_1 \exp(-t/\lambda_1) - A_2 \exp(-t/\lambda_2) \). The integrated escape probability for depths from 0 to \( \infty \) is given by \( P_{\text{escape}} = A_1 \lambda_1 - A_2 \lambda_2 \) and the sampling depth \( \lambda \) is defined by the depth interval from 0 to \( \lambda \) where the integrated escape probability becomes \( P_{\text{escape}} = (1-1/e) \).

The electron energy of 5 keV of Fig. 5 corresponds to Cr KLL Auger electron energy and the acceptance angle of 20° and the bias of -50 V have been chosen in agreement with the experimental conditions of the results given in Fig. 4. The evaluation of the experiments gave a sampling depth of 27 nm and the Monte Carlo approach \( \lambda = 40.9 \) nm (\( \lambda_1 = 28.9 \) nm, \( \lambda_2 = 14.9 \) nm). An evaluation of the Cr responses in dependence on kinetic electron energies gives sampling depths of 1.78 nm, 40.9 nm and 825 nm for 0.5, 5 and 30 keV, respectively. The influence of the matrix on sampling depths at constant kinetic electron energy of 5 keV may
be illustrated by the variation of $A$ from 19.1 nm for Au to 40.9 nm for Cr and to 295.5 nm for Na. It is evident that Au with the greatest number of electrons per cm$^3$ has the smallest sampling depth and Na with the smallest number of electrons per cm$^3$ the greatest sampling depth. Therefore, we introduce a reduced sampling depth $A' = A \cdot \rho Z/A$ with density $\rho$ in g/cm$^3$, atomic weight $A$ and atomic number $Z$. The products of $A_{Na}$, $A_{C}$, and $A_{Au}$ with the corresponding values of $\rho Z/A$ represent reduced sampling depths $A'$ with the following numerical values: 137.1, 135.7 and 148.5. As this consideration is applied to the total number of investigated elements for an electron energy of 5 keV, an acceptance cone angle of 20° and a bias of -50 V a mean value $\langle A'_{5keV} \rangle = 140$ with standard deviation $\sigma = 14$ is obtained. Corresponding values for 0.5 keV are $\langle A'_{0.5keV} \rangle = 7.78$, $\sigma = 3.08$ and for 30 keV $\langle A'_{30keV} \rangle = 2595$, $\sigma = 540$. Similar results are obtained for $\lambda_1$ and $\lambda_2$. Thus, we replace the quantities $\lambda_1$, $\lambda_2$ and $A$ by $\langle \lambda_1^{* E-kin} \rangle$, $\langle \lambda_2^{* E-kin} \rangle$ and $\langle A^{* E-kin} \rangle$ and describe their energy dependences of $\log(\langle \lambda_1^{* E-kin} \rangle)$, $\log(\langle \lambda_2^{* E-kin} \rangle)$ and $\log(\langle A^{* E-kin} \rangle)$ by cubic polynomials of $\log(E_{kin})$. Amplitudes $A_1$ and $A_2$ do not depend on the matrix, they are characterized by a weak energy dependence and a strong acceptance cone angle dependence. Therefore, we describe $A_1$ and $A_2$ for constant acceptance cone angle by cubic polynomials of $\log(E_{kin})$. The following numerical expressions are valid for bias -50 V, elements $Z \geq 10$, acceptance cone of electron detection from -20° to +20° normal to the specimen surface and kinetic electron energies 0.5 keV $\leq E_{kin} \leq 30$ keV:

$$
\langle \lambda_1^{* E-kin} \rangle = 10^{-7} \cdot \exp(2.5245 + 1.119 \cdot \log E_{kin} + 0.1304 \cdot \log^2 E_{kin} - 0.0086 \cdot \log^3 E_{kin})
$$

$$
\langle \lambda_2^{* E-kin} \rangle = 10^{-7} \cdot \exp(1.7558 + 1.519 \cdot \log E_{kin} + 0.1255 \cdot \log^2 E_{kin} - 0.0100 \cdot \log^3 E_{kin})
$$

$$
A_1 = 0.3224 + 0.0427 \cdot \log E_{kin} + 0.0029 \cdot \log^2 E_{kin} - 0.0020 \cdot \log^3 E_{kin}
$$

$$
A_2 = 0.2322 + 0.0403 \cdot \log E_{kin} + 0.0049 \cdot \log^2 E_{kin} - 0.0022 \cdot \log^3 E_{kin}
$$

The advantage of the general description becomes evident for an arbitrary matrix. After computation of the amplitudes and the values of $A'$ for given electron energy one obtains the values of $\lambda_1$ and of $\lambda_2$ (cm) by multiplication of the reduced quantities with $(A/Z)/\rho$. In the standard analytical approaches $1/(\lambda_1 \cdot \rho) = (Z/A)/(\lambda_1^{* E-kin})$ and $1/(\lambda_2 \cdot \rho) = (Z/A)/(\lambda_2^{* E-kin})$ are the attenuation coefficients (cm/g) for the electron flux, in analogy to photoelectric absorption coefficients $\tau$ for x-rays. In case of a multielement matrix a description of $Z/A$ by

$$
\frac{Z}{A} = \sum_{i=1}^{n} c_i \cdot \frac{Z_i}{A_i}
$$

is recommended. $n$ is the number of chemical elements with compositions $c_i$ in atomic fractions, atomic weight $A_i$, and atomic number $Z_i$. Consequently, the knowledge of the density of the matrix is not necessary.

**ANALYTICAL APPROACH**

The standard derivation of signal equations in quantitative x-ray fluorescence analysis uses a concept where a parallel beam of monochromatic x-rays impinges on the plane specimen under an angle $\alpha$ with regard to the surface normal. The incident radiation is characterized by a total flux $x(E)$ of photons per second with photon energy $E$. The number $dz$ of photoelectric absorptions in atomic level $j$ of element $i$ in depth interval $t$ to $t + dt$ is given by

$$
dz = x(E) \cdot e^{-t \cos \alpha / \rho \cdot \mu_{\alpha, \infty}} \cdot \frac{dt}{\cos \alpha} \cdot \rho \cdot c_i \cdot \tau_{E_{kin}, ij}
$$

In case of TEY the second term of the signal equation describes the probability $p_{ix}$ for generation of electron species $x$ from element $i$ of kinetic energy $E_{kin}$ and the escape probability $p_{escape}$ of this electron. $E_{kin}$, the acceptance angle and the bias are included in the
specific data of the escape probability and the detector efficiency is assumed to be 1. Thus, \( d_n \) becomes

\[
d_n = dz \cdot p_i \cdot \left[ A_1 \cdot \exp \left( -\frac{t}{\langle \lambda_{1, E-\text{kin}} \rangle} \frac{\rho_e \cdot Z}{A} \right) - A_2 \cdot \exp \left( -\frac{t}{\langle \lambda_{2, E-\text{kin}} \rangle} \frac{\rho_e \cdot Z}{A} \right) \right]
\]

and integration from \( t = 0 \) to \( \infty \) gives the contribution \( n_{i,x} \) from electron species \( i,x \)

\[
n_{i,x} = \frac{1}{\cos \alpha} \cdot c_i \cdot x(E) \cdot \tau_{E,i,j} \cdot p_i \cdot \left[ \frac{A_1}{\cos \alpha \cdot \langle \lambda_{1, E-\text{kin}} \rangle} + \frac{1}{\cos \alpha \cdot \langle \lambda_{2, E-\text{kin}} \rangle} \right] - \frac{A_2}{\cos \alpha \cdot \langle \lambda_{1, E-\text{kin}} \rangle}
\]

In addition to these primary contributions secondary Auger and photoelectrons have also to be considered. The derivation of the equations follows the same concept: incident x-rays - primary excited characteristic x-rays - photoelectric absorption of this radiation in one of the elements of the matrix - generation of photo- and Auger electrons and escape of the electrons to the specimen surface. The following equation is valid for the excitation of Au MNN Auger electrons by characteristic Cu K x-rays.

\[
n_{\text{AuMNN}} (\text{CuK} \rightarrow \text{AuMNN}) = \frac{1}{2} \frac{1}{\cos \alpha} \cdot c_{\text{Cu}} \cdot x(E) \cdot \tau_{E, \text{CuK}} \cdot \omega_{\text{CuK}} \cdot c_{\text{Au}} \cdot \tau_{\text{CuK}, \text{AuMNN}} \cdot (1 - \omega_{\text{AuMNN}})
\]

Primary excited x-rays can also be detected by the electron detector. The detector efficiency of our channeltron detector for x-ray photons of energy \( E \) (keV) is given by

\[
\eta_E = \frac{1}{100} \cdot \exp \left[ \ln 20 + \frac{\ln 20 - 0.16}{\ln 0.1 - \ln 10000} \cdot \ln E \right]
\]

and the numerical value for characteristic Cu K x-rays is \( \eta_{\text{CuK}} = 0.03 \). Other characteristic data of our instrument are the solid angle of x-ray detection \( \Omega = 1/44 \) and the angles \( \alpha \) and \( \beta \) of 78° and 0°, respectively. The measured TEY signal \( n_i \) is given by the sum of the different contributions.

**QUANTITATIVE ANALYSES OF BINARY AU-CU ALLOYS**

Four photon energy intervals have been investigated:
1. from 200 eV beneath the Cu K edge to the Cu K edge
2. from the Cu K edge to 200 eV above the Cu K edge
3. from 200 eV beneath the Au L3 edge to the Au L3 edge
4. from the Au L3 edge to 200 eV above the Au L3 edge

**Interval 1**
Primary excited Cu L, Cu M, Au M and Au N photoelectrons and Cu LMM and Au MNN Auger electrons (6 electron species).
Interval 2
In addition to the 6 electron species from interval 1 primary excited Cu KLL and subsequent Cu LMM Auger electrons and by characteristic Cu K x-rays secondary excited Cu L, Cu M, Au M and Au N photoelectrons and Cu LMM and Au MNN Auger electrons and characteristic Cu K x-rays (15 electron species plus x-rays)

Interval 3
Primary excited Au M, Au N, Cu K, Cu L and Cu M photoelectrons and Au MNN, Cu KLL and Cu LMM Auger electrons (8 electron species).

Interval 4
In addition to the 8 electron species from interval 3 primary excited Au L3MM and subsequent Au MNN Auger electrons and by characteristic Au L3 x-rays secondary excited Au M, Au N, Cu K, Cu L and Cu M photoelectrons and Au MNN, Cu KLL and Cu LMM Auger electrons and characteristic Au L3 x-rays (18 electron species plus x-rays).

Figs. 6 and 7 illustrate the components of measured TEY jumps, asking for computation of the background as well as the jump above the edge. The background breakdown above the edge is due to the increased matrix absorption in this interval of photon energies.

![Fig. 6](image1.png)
![Fig. 7](image2.png)

Fig. 6 (left) background (6 electron species from interval 1 and first 6 species from interval 2), (right) signal from interval 2 without the electron species from background.

Fig. 7 Computer simulation of the measured Cu K TEY signal of binary Au-Cu alloy with 50 wt% Au (sum of the responses of Fig. 6 (left and right). For the experiments the convolution of the finite width of the energy distribution of incident monochromatic x-rays with the theoretical response causes a smearing of the edge-like structure (see Fig. 1).

We computed the responses of the TEY signals for Cu K and Au L3 edges and formed the ratios of the jumps and their corresponding pure element jumps. Fig. 3 shows the normalized jumps from experiment and theory for both elements. As an unknown binary Au-Cu alloy has to be analyzed, the Cu K- and Au L3 TEY spectra of the pure elements and the unknown
specimen have to be measured. The analytical approach delivers for Cu and for Au values of the compositions \( c_{Au,TEY} \) and \( c_{Cu,TEY} \) and the final result is obtained from

\[
c_{Au} = \frac{c_{Au,TEY}}{c_{Au,TEY} + c_{Cu,TEY}} \cdot 100 \quad \text{and} \quad c_{Cu} = 100 - c_{Au}
\]

<table>
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<td>100</td>
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</table>

Table 1 Results of the above given procedure (Au concentration in wt%) 

DETERMINATION OF LAYER THICKNESSES BY TEY

Another typical application of the theoretical approach of TEY is demonstrated by the example of GaAs substrates covered with \( Al_xGa_{1-x}As \) layers. Thus, substrate and layer contain Ga and As. Figs. 8 and 9 give the measured Ga K jumps together with the computed responses versus thickness of layers with \( x = 0.2 \) and 0.4. „theor“ describes the sum of 58 contributions from „xray-s“ (substrate Ga K x-rays), „xray-l“ (layer Ga K x-rays), „lay-s“ (secondary excited TEY signal from layer), „sub-s“ (secondary excited TEY signal from substrate), „sub-p“ (primary excited TEY signal from substrate) and „lay-p“ (primary excited TEY signal from layer).

Fig. 8 Measured and computed relative Ga K jumps of \( Al_{0.2}Ga_{0.8}As \) layers on GaAs substrates
EXPERIMENTAL DETAILS and DETECTION LIMIT

We have already described the theoretical concept for the determination of compositions of bulk specimens and thicknesses of thin layers by TEY. An essential feature of quantitative TEY is the statistical significance of the measured TEY jumps. The following considerations are dedicated to the significance of analytical results and the detection limit of TEY for extremely thin layers and consequently, to the minimum detectable mass by TEY. For this purpose we have to quantify the statistical significance of the measured TEY jumps. This statistical concept is developed by an explanation of the procedure how TEY measurements are performed and evaluated. We investigated thin Al$_{0.4}$Ga$_{0.6}$As layers on bulk GaAs substrates and thin Cr layers on bulk Fe substrates and measured the Ga K- and the Cr K jumps. We mounted the specimens in the specimen chamber (10$^{-6}$ mbar) of the x-ray station on a grounded specimen holder allowing a total of six specimens. X-radiation of a rotating Cu anode system (30 kV, 100 mA) was monochromatized by either a Ge (111) or a Si (111) crystal. The electron emission of the specimen was detected by a channeltron detector. Besides the electron emission, we measured the x-ray flux by a gas proportional counter, following the sequence: x-ray spectrum - TEY-spectrum of the specimen - x-ray spectrum. The first step of the evaluation of measured responses of TEY signals in dependence on the photon energy is the elimination of the influence of the x-ray flux. We calculate x-ray fluxes after correction of the measured data for deadtime losses and detector sensitivity in dependence on the photon energy and form the ratio of the TEY and the x-ray flux spectra. Whereas the measured spectra are given in units of electrons per second and photons per second, the reduced TEY spectra give electrons per photon. An example of the data reduction is given in Fig. 10. The response on top is the flux of monochromatic x-rays in the photon energy range from 10.1 keV to 12.2 keV. The W L lines are from surface contamination of the Cu target of the x-ray tube due to evaporation from the tungsten filament. The measured TEY response of pure GaAs contains the Ga K edge at 10.367 keV and the As K edge at 11.868 keV. The reduced TEY response is the ratio of TEY and x-ray flux. This reduced experimental result (thick line) is compared to our theoretical response.
Fig. 10 Measured flux of monochromatized x-rays for photon energies from below the Ga K edge to above the As K edge, measured TEY response of pure GaAs, reduced TEY response and comparison of the reduced TEY response to the theoretical response
An essential feature of the reduced responses has to be mentioned: The responses are influenced by counting statistics.

Defining the lower level of detection or detection limit \( DL \) by

\[
DL = 3 \cdot \sqrt{n_b} = 3 \cdot \sigma_s
\]

with the background signal \( n_b \) and the standard deviation \( \sigma_s \) of the TEY signal corresponding to the lower intersection in the reduced TEY responses we obtain the minimum detectable height of the TEY jump which can be distinguished from the TEY response without the chemical element of interest. An evaluation of our experimental results gave for Cr layers a minimum detectable thickness \( t_{min} = 0.075 \) nm. This is a submonolayer and with the density of Cr of 6.93 g/cm\(^3\), an observed surface area of 0.12 cm\(^2\), a minimum detectable mass (lower level of detection LLD) of 6.2 ng is obtained. Comparing this detection limit of TEY to XRF and EPMA the minimum detectable Cr layer thickness is 1 nm. This means that the detection limit of TEY is more than one order of magnitude better. XPS offers a detection limit of less than 0.01 nm which is one order of magnitude better than TEY. But, TEY offers another interesting feature. When covering the thin Cr layer with an Al layer of 20 nm and repeating the experiments, the minimum detectable Cr layer thickness becomes 0.3 nm. This is approximately a monolayer of Cr and this monolayer is buried under 20 nm Al. Such a Cr layer thickness is not within the detection range of x-ray fluorescence analysis or electron probe microanalysis. In x-ray photoelectron spectrometry and in Auger electron spectrometry the Al overlayer of 20 nm causes a complete suppression of the characteristic spectra of Cr. Thus, the buried Cr layer can be quantified only by TEY.

**COMPARISON BETWEEN TEY AND XRF**

Photoelectric K absorption of monochromatic x-ray photons with an energy close above the K absorption edge of a given element causes K ionization and from relaxation an emission of characteristic K x-rays or KLL Auger electrons. For a defined beam geometry of incident and fluorescence radiations it is possible to compute the number of characteristic K x-ray photons per incident photon in dependence on the atomic number of the elements and to compare this result with the number of electrons per incident photon. The number of electrons is computed for an identical geometry of incident radiation, take-off angle of electrons and solid angle of electron detection. A comparison of both results under neglection
of the energy dependent detector efficiency is given in Fig. 11. An essential feature of TEY is the higher yield in the low Z region of elements.

From these results it can be concluded that
i TEY is a method for quantitative surface analysis (composition, layer thickness),
ii TEY allows a detection and quantification of submonolayers,
ii TEY seems to be the only nonconsumptive method for quantification of buried submonolayers,
iv TEY has, when compared to x-ray fluorescence analysis a better elemental sensitivity in the low Z region of chemical elements.

Further details on this new method for quantitative surface analysis are given in literature\textsuperscript{10-33}.

A final remark on a paper on „Appearance Potential X-Ray Fluorescence Analysis“ by Kirkland and coworkers\textsuperscript{34} should be given. They use instead of electron signals the characteristic x-ray signals and come to the following conclusion: Appearance Potential X-Ray Fluorescence Analysis seems like a technique which may have some value as an alternative to the more conventional x-ray methods. The relative simplicity of the experimental equipment, coupled with the possibility of performing moderate resolution EXAFS measurements to obtain local atomic structure information in addition to the elemental composition, should demonstrate an advantage for those situations where x-ray techniques contribute to the complete characterization of materials. And, if the experimental configuration permits the detection of photoelectrons, the technique can provide some surface information as well.

REFERENCES


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