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DEPTH PROFILING BY MEANS OF TOTAL ELECTRON YIELD MEASUREMENTS

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Total electron yield (TEY) is frequently used for EXAFS measurements. A theoretical correlation of the jump-like increase of TEY in the vicinity of an absorption edge to the composition c and the thickness t of a multicomponent layer allows a quantification of c and t in analogy to XRF. We performed experiments and calculations on thin layers of $Al_xGa_{1-x}As$ on GaAs substrates and confirmed the validity of the theoretical approach in the range $0.2 < x < 0.6$ and 20 nm $< t <$ 120 nm. Thus, TEY is an excellent candidate for quantitative surface analysis in the nanometer range.

1. Introduction

Electron emission from solid samples caused by photoabsorption of X-rays can be used for quantitative analysis and depth profiling. The electrons are ejected by Auger, photoelectric and secondary processes. For nondispersive electron detection, the total electron yield (TEY) is measured. When tuning the photon energy from below to above the absorption edge of one of the elements in the specimen, one observes a pronounced jump-like increase of TEY due to photoabsorption in the corresponding atomic level and the following de-excitation of the atom.

A systematic treatment of possible de-excitation processes after photoionization allows for a quantitative description of the energy distribution of electrons leaving the ionized atom. Additionally, the escape probability of electrons of different kinetic energies from the atom of origin to the specimen surface has to be considered. The escape probability defines the sampling depth of this new surface analytical method. The sampling depth depends on electron energy and specimen composition. The numerical values cover a range from a few nm for kinetic energies of electrons of a few hundred eV up to several μm at energies of about 20 keV.

The correlation between the jump-like increase of TEY and the concentration of the element in the specimen can be treated by a comparison to the fundamental parameter approach of quantitative X-ray fluorescence analysis [1-4]. We show a verification of this concept by the determination of composition and thickness of nanometer layers of $Al_xGa_{1-x}As$ on GaAs substrates.

2. De-excitation, secondary excitation and electron range

The following considerations deal with the correlation between composition x, thickness t of thin $Al_xGa_{1-x}As$ layers on GaAs substrate and measured Ga K–edge and Al K–edge jumps.

2.1. De-excitation

Possible processes of de-excitation of Ga atoms after K–shell ionization are

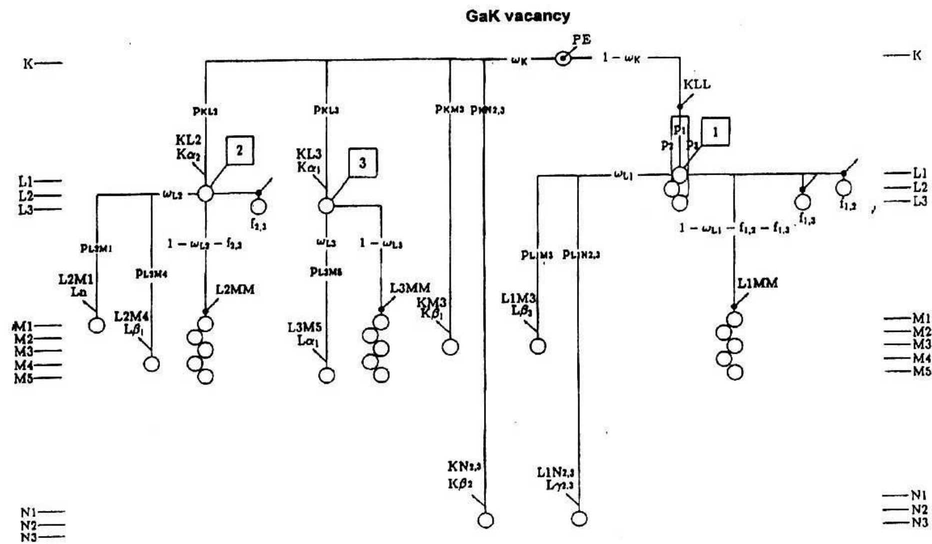

Fig. 1. *Scheme of de-excitation of* K*–ionized* Ga *atoms.*

depicted in Fig. 1. On the left side of the figure is the radiative path with characteristic Kα and Kβ radiation followed by either L– or M–vacancies. Some of these vacancies are filled by radiative transitions and some of them by emission of Auger electrons. The nonradiative path on the right side of the figure gives rise to the emission of KXY Auger electrons. This emission results in a pair of vacancies in the L–, M– or N–shells. Both vacancies are filled also by radiative or nonradiative transitions. The probabilities for Auger transitions $(1 - \omega)$ are quantified by the fluorescence yields ω. Kinetic energies of Auger electrons are obtained from the binding energies of the involved core levels.

2.2. Secondary excitation

Secondary excitation can arise from photoabsorption of characteristic Ga K–radiations. In the case of $Al_xGa_{1-x}As$, photoabsorption of Ga K radiations in K–, L– and M–orbitals in Al, on L–, M– and N–orbitals in Ga and in L–, M– and N–orbitals in As is possible. As a first consequence of secondary excitation processes, photo electrons are observed. Their kinetic energy is given by the Einstein equation. After hole formation in one of the mentioned atomic levels, the question for possible de-excitation processes arises again. This can be treated in a similar way as the de-excitation of the Ga K-vacancy. Consequently, a systematic treatment of the contributions to the measured TEY signals requires inclusion of a great number of secondary excitation processes.

TABLE 1.
Electron contributions to the measured Ga K–jumps from primary and secondary excitations (PE – photo electron, AE – Auger electron).

Radiation	Electron species	Kinetic energy (keV)
Primary	Ga KXY (AE)	8.00
	Ga LXY (AE)	1.02
Secondary (Ga K)	Ga LXY (AE)	1.02
	Ga L (PE)	8.20
	Ga M (PE)	9.30
	Ga N (PE)	9.40
	As L (PE)	7.95
	As LXY (AE)	1.17
	As M (PE)	9.24
	As N (PE)	9.36
	Al K (PE)	7.80
	Al KXY (AE)	1.35
	Al L (PE)	9.36
	Al M (PE)	9.36

Table 1 gives the electron species which were considered in our Ga K–jump calculations.

Table 2 gives the Ga K–jump contributions from secondary excitations of the combination of $Al_xGa_{1-x}As$ layers on GaAs substrates. Each of them can be realized by 4 possible electron species (given in brackets). Thus, a total of 40 secondary excitations has to be computed.

TABLE 2.
Possible secondary excitation processes.

Substrate Ga K	layer	(Ga LXY, Ga L, Ga M, Ga N)
		(As LXY, As L, As M, As N)
		(Al KXY, Al K, Al L, Al M)
	substrate	(Ga LXY, Ga L, Ga M, Ga N)
		(As LXY, As L, As M, As N)
Layer Ga K	layer	(Ga LXY, Ga L, Ga M, Ga N)
		(As LXY, As L, As M, As N)
		(Al KXY, Al K, Al L, Al M)
	substrate	(Ga LXY, Ga L, Ga M, Ga N)
		(As LXY, As L, As M, As)

Finally, Table 3 illustrates the amount of different contributions to the measured Ga K–jumps in arbitratry units.

TABLE 3.
Contributions to the measured Ga K*–jump. The numerical values have been calculated for an angle of 12° between incident X-rays and specimen surface, a composition* $x = 0.3$ *and a thickness of the* $Al_xGa_{1-x}As$ *layer of 100* nm.

Primary excitation	
Ga KXY(substr.)	5271
Ga LXY(substr.)	0
Ga KXY(layer)	5303
Ga LXY(layer)	1057
Secondary excitation	
substrate–substrate	655
layer–layer	37
substrate–layer	759
layer–substrate	27

2.3. Electron range

An essential quantity in TEY is the electron range λ (escape length, sampling depth). We measured the electron ranges for a large number of electron energies and chemical elements. The result of this investigation for the system AlGaAs is described by the following equations:

$$\lambda = 10^{-7}\frac{1}{\rho}\exp\left[3.74 + 1.66\log E_{kin} - 0.02(\log E_{kin})^2\right] \quad \text{cm}, \tag{1}$$

where E_{kin} is the kinetic energy of electron (keV).

The density ρ of $Al_xGa_{1-x}As$ as a function of x is given by

$$\rho = 0.0371[26.982x + 69.723(1-x) + 74.922] \quad \mathrm{g/cm^3}. \tag{2}$$

3. Nanometer layers of $Al_xGa_{1-x}As$ on GaAs substrates

The equations for the description of TEY jumps are derived from the equations for quantitative X-ray fluorescence analysis, replacing the characteristic fluorescence radiation by the corresponding characteristics of the different electron species.

(i) Instead of the photoabsorption coefficient τ for fluorescent radiation in the specimen, we use $1/\lambda\rho$ in the attenuation terms.

(ii) The emission angle β between the specimen surface and detected fluorescence radiation is replaced by 90°.

(iii) The probability for the occurrence of photoelectrons after photoabsorption is 1 and for Auger electrons $1-\omega$.

(iv) The transition probability p for the occurrence of a given fluorescence radiation is no longer of importance. Thus, p is replaced by 1.

The following equations may serve as examples for the contributions from primary excited Ga KXY Auger electrons from the layer and the substrate to measured TEY jumps.

$$n_{prim,\mathrm{GaKXY},lay} = \frac{c_{\mathrm{Ga},lay}(1-\omega_{\mathrm{GaK}})X_E\tau_{E,\mathrm{GaK}}}{(\tau_{E,lay}/\sin\alpha) + (1/(\lambda\rho)_{\mathrm{GaKXY},lay})} \times \left[1 - e^{-\left(\frac{\tau_{E,lay}}{\sin\alpha} + \frac{1}{(\lambda\rho)_{\mathrm{GaKXY,lay}}}\right)\rho_{lay}t}\right] \tag{3}$$

$$n_{prim,\mathrm{GaKXY},sub} = \frac{c_{\mathrm{Ga},sub}(1-\omega_{\mathrm{GaK}})X_E\tau_{E,\mathrm{GaK}}}{(\tau_{E,sub}/\sin\alpha) + (1/(\lambda\rho)_{\mathrm{GaKXY},sub})} \times \left[e^{-\left(\frac{\tau_{E,lay}}{\sin\alpha} + \frac{1}{(\lambda\rho)_{\mathrm{GaKXY,lay}}}\right)\rho_{lay}t}\right]. \tag{4}$$

The meaning of the symbols is:

– $n_{prim,\mathrm{GaKXY},lay}$ – primary excited Ga KXY Auger electrons from the layer (s^{-1}).

– $n_{prim,\mathrm{GaKXY},sub}$ – primary excited Ga KXY Auger electrons from the substrate

(s^{-1}).
– $c_{\mathrm{Ga},lay}$, $c_{\mathrm{Ga},sub}$ – Ga concentration (weightfractions) in the layer and in the substrate.
– ω_{GaK} – fluorescence yield of the Ga K–shell.
– X_E – flux of the incident parallel beam of monochromatic X-rays of energy $E = E_{\mathrm{GaK}} + 0.1$, $(X_E$ in s^{-1}, E in keV).
– E_{GaK} K–edge energy of Ga (keV).
– $\tau_{E,\mathrm{GaK}}$ – mass photoabsorption coefficient of X-rays for photons of energy E in the Ga K–shell (cm^2/g).
– $\tau_{E,lay}$, $\tau_{E,sub}$ – total photo absorption coefficient of X-rays of photon energy E in the layer and in the substrate.
– α – angle between the specimen surface and direction of incident X-rays.
– $\lambda\rho$ – see Eqs. (1) and (2). The subscripts Ga KXY,lay and Ga KXY,sub are for Auger electrons of energy E_{GAKXY}, and lay and sub are an indication for the different compositions of layer and substrate
– ρ_{lay} density of the layer.

4. *Experimental*

The experiments were performed on a Q–EDP 100 instrument (Rokappa) in TEY mode. A rotating anode with Cu target serves as the source of radiation.

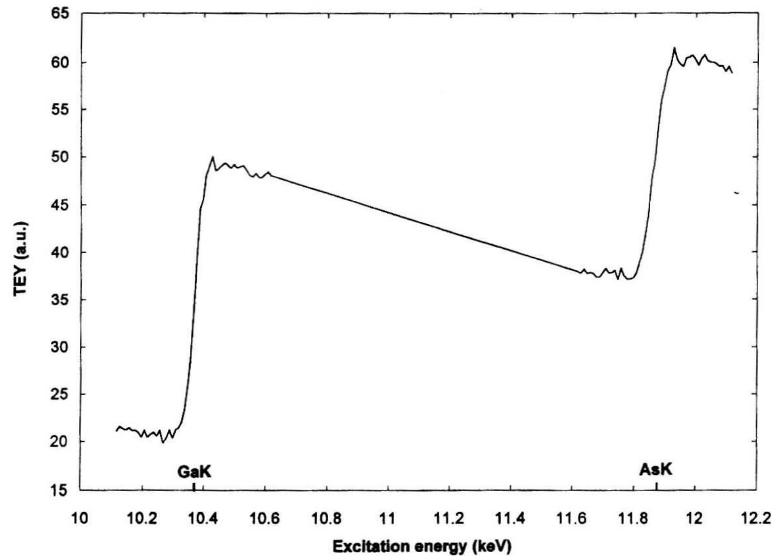

Fig. 2 Measured Ga K *and* As K *jumps of 120* nm $\mathrm{Al_{0.2}Ga_{0.8}As}$ *on* GaAs.

The X-rays enter a helium purged monochromator chamber through an entrance

slit system. We used Si(111), KAP and Mica as monochromator crystals. The specimens were mounted in an evacuated specimen chamber. Between the monochromator chamber and the specimen chamber, a second slit system was arranged. Both slit systems defined the irradiated specimen area and the spectral width of the monochromatic X-ray flux. The total electron yield was measured by a channeltron. Between the specimen and the channeltron entrance we mounted a grid. It was biased with regard to the ground potential and helped to suppress low energy secondary electrons from detection. In Fig. 2 the measured TEY response of pure GaAs in the vicinity of the Ga K– and the As K–edges is shown. Figure 3a gives the response of the reduced Al K–jump in dependence on the film thickness with composition x as parameter. Reduced jumps means that measured or calculated jumps are divided by the value for pure Al. The extremely small values of λ for electrons corresponding to the Al K–jump are responsible for the horizontal response at comparably small layer thicknesses. The responses of Fig. 3a allow to determine the composition x of layers of thicknesses larger than 30 nm without knowledge of the layer thickness t.

Introducing x into the curves of the Ga K–jumps of Fig. 3b gives the unknown layer thickness t. We knew x and t from specimen preparation and therefore calculated the responses for $x = 0.2$, 0.4 and 0.6. The agreement between the measured data and computed curves confirms our theoretical approach.

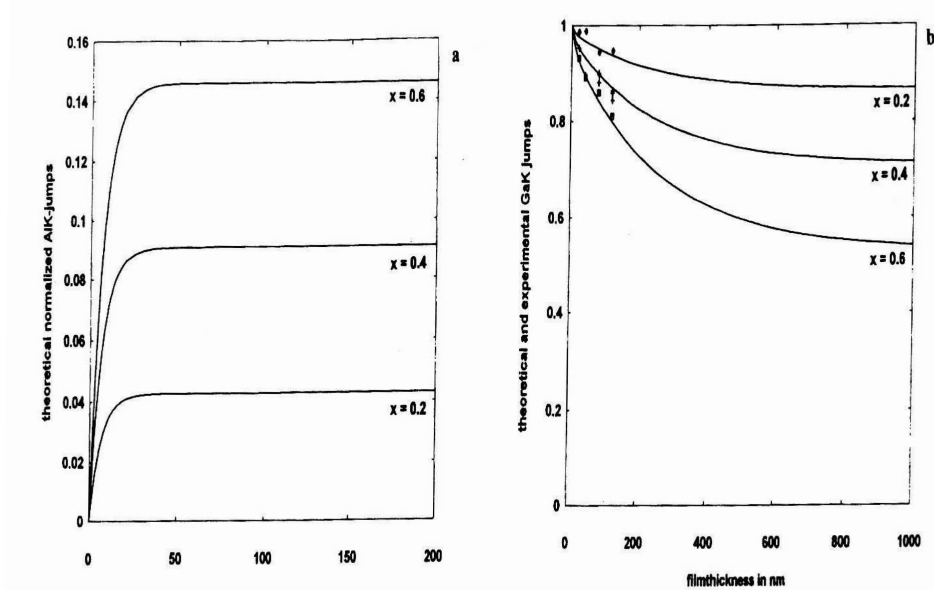

Fig. 3a. Reduced Al K*–jump of thin* $Al_xGa_{1-x}As$ *layers on* GaAs *substrates depending on the layer thickness t with parameter x.*

Fig. 3b. Reduced Ga K*–jump of thin* $Al_xGa_{1-x}As$ *layers on* GaAs *substrates. Curves are from calculations and symbols from experiments (right).*

5. *Conclusion*

In a paper on simulation of X-ray excited electron emission in the vicinity of K-shell electron binding energies, Yur'ev and coworkers [5] describe a quantitative determination of the composition of bulk $Al_xGa_{1-x}As$ specimens by TEY measurements, performed at different angles of incidence of X-rays with respect to the surface normal. They tried to extend their theoretical concept to thin layers and came to the conclusion that for thin films even qualitative agreement with the experimental angular dependence is not obtained.

Our approach does not require a large number of measurementsof the GaK and the As K-edge jumps under different incidence angles. For comparison, we measure the K-edge jumps only under a single incidence angle. Thus, we are able to save nearly 90% of the time for data accumulation. A further essential feature of our concept is the agreement between theory and experiment. Besides, with our theoretical concept we calculated the angular dependence of the thin layer specimen of Yur'ev and coworkers and obtained a perfect agreement with their experimental results. This is an additional confirmation of our theoretical description of TEY-jumps.

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DUBINSKO PROFILIRANJE SLOJA MJERENJEM UKUPNOG ELEKTRONSKOG PRINOSA

Mjerenje ukupnog elektronskog prinosa često se upotrebljava u EXAFS mjerenjima. Ovisnost skokovitog porasta ukupnog elektronskog prinosa u blizini apsorpcijskog ruba o sastavu i debljini sloja s više elemenata omogućuje njihovo odredivanje kao u XRF mjerenjima. Načinjena su mjerenja i računi za tanke slojeve $Al_xGa_{1-x}As$ na GaAs podlozi i potvrđena je valjanost teorijskog pristupa za debljine od 0.2 do 0.6 nm i za debljine 20 do 120 nm. Stoga je ova metoda prikladna za kvantitativne analize u nanometarskom području.