Electron Probe Microanalyses in Auger Electron Spectroscopy

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Abstract – **The electron probe micro analysis (EPMA) is examined as calibrating method for quantitative Auger electron spectroscopy (AES). It is used in AES profile analysis for finding the averaged Auger elemental sensitivity factors, leading to the quantification of the profile.**

EPMA can be also used for evaluating some parameters of the layer (thickness, weight content of component, etc.) if there is other available data for it. The performed Auger analyses of volumetric or layered samples with known composition prove the applicability of the method.

Keywords – **Auger electron spectroscopy, AES, electron probe micro analysis, EPMA, quantification**

I. INTRODUCTION

Micro- and nano-electronics are the main fields of application of Auger analyses. The reason is the unique possibility for element analysis of the surface, expanded with depth profiling. Usually the analysis is required to be quantitative, which is easy and always feasible if being "semi quantitative" is enough while it is traditionally hard – if accuracy is pursued.

The binary alloys' Auger quantification theory [1] states the content (the relative fraction), c_A, of the element A from the sample should be changed proportionally to its spectral intensity I_A:

$$c_A = (I_A / I_{0A}) / \sum_i (I_i / F_{Ai} I_{0i}) \qquad (1)$$

The introduced relative Auger elemental sensitivity factor (RAESF) I_0 is the spectral intensity from the pure (100%) element (so called elemental standard), normalized according to that of an arbitrarily fixed element. The correction factor F aims to equalize differences in the intensities for the sample and the standards, which are not connected proportionally to the concentration. (If a correction is not introduced, F=1). In classic matrix corrections those are due to the different atomic density, N, electron back-scattering factor, R and attenuation depth, λ (differences due to other reasons are also liable to correction).

We should note that ion sputtering is almost always used during the layer analysis. The occurring selective removal of the lighter and less bound component decreases its content in the outermost atom layer [2]. It is important for our presentation that in this case the real concentrations can be found by additional correcting. I.e. the sputtering is taken into account by additional multiplayer in the correction F.

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There are different methods for practical application of (1). The most accurate are the using standard specimens. In literature the electron probe micro analysis (EPMA) is indicated as standardizing analytical method. It has ~5% inaccuracy [3] – better than the desired for AES. But the considerable difference between Auger and EPMA information depth (some monolayers versus some microns) requires special care: EPMA result shows the integral composition of the analyzed layer. Meanwhile we didn't find anything concrete on the matter. Therefore – despite the risk to speak for something referred as obvious – we will share our experience from the last 15 years.

In the current article we will discuss the use of the electron micro analysis (EMPA) for calibrating the quantitative Auger layer-analyses. We will also adduce a few concrete applications.

II. EXPERIMENTAL

The Auger microprobe used has an energy resolution $\Delta E/E$ ~ 0.3 % and a beam energy E_p up to 10 keV. The analytic regime was E_p 3 keV and a modulation voltage V_{mod} 4 V_{pp}. The spectra are monitored in differential mode.

Electron Probe Micro Analyses (EPMA) were performed on ESEM XL30 FEI Co, allowing the light elements detection, at the beam voltage of 3.0 kV.

III. RESULTS AND COMMENTS

Let's assume we have performed Auger profiling of the analyzed layer through ion sputtering, obtaining the result as graphic "Auger intensity *vs* etching time".

A. *EPMA calibration at homogeneous massive sample or layer*

Despite this case is analytically trivial, we dwell on it due to its importance. If the sample is rendered standard (homogeneous and with known content) the EMPA result can be directly used for calibrating the Auger analysis. Otherwise if an unknown layer is analyzed and the Auger profiling shows its homogeneity, the EMPA result can be related to the layer (without performing Auger quantification). (In such case the layer shouldn't contain the same elements as the substratum). Example for this type of analysis is shown on Figure 1.

B. *EPMA calibration in sample with concentration gradient*

At constant sputtering rate in depth of the layer, the relation between the measured by EMPA content of the i-th element in the whole layer X_i (in atomic parts) and the determined by AES local concentration in the layer is:

$$X_i = k\int c_i(x)dx \qquad (2)$$

where k is numeric multiplayer.

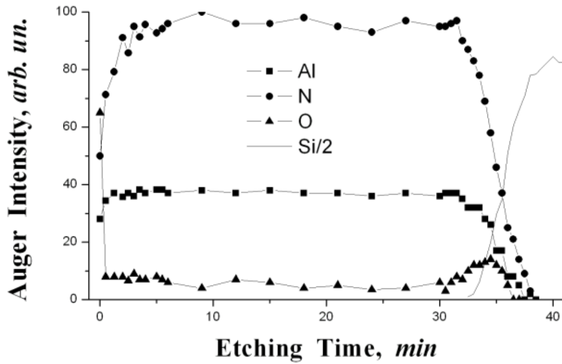

Figure 1. Auger profile of the AlN_x layer. EPMA measurement gives $x = 0.70$ and $c_O = 2.65$ at.%.

If the sum in the denominator of (1) is constant over the layer (mainly, if there are no unrelated to the concentration changes in the intensities), [2] is:

$$X_i = (kI_{oj}'^{-1}\Sigma^{-1}) \int I_i(x)dx = kI_{oj}'^{-1}\Sigma^{-1}.S_i \qquad (3)$$

where I_{oj}' is the corrected elemental sensitivity factor (including the correction for a selective etching), averaged for the layer. S_i is the integral from the intensity i along the layer (the area under the i-th curve, Figure 2). Dividing the expressions (3) for the i-th and j-th element, we get

$$I_{oi}'/I_{oj}' = (S_i/S_j)(X_j/X_i) \qquad (4)$$

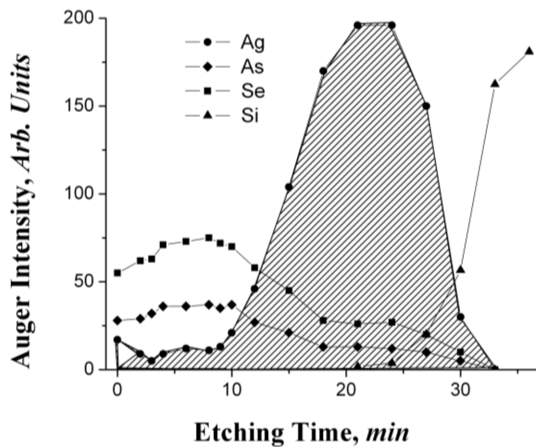

Figure 2. Auger profile of a sample (As_2Se_3 + Ag). The hatched area is for the silver.

(4) gives a linear system of (N-1) equations for the N unknowns I_{oi}', which solution is trivial (to an accuracy of a multiplier) – for example, assuming I_{ok}' = 1. Having RAESF, by (1) we can convert the y-axis of the profile into concentrations, Figure 3.

Evaluation of the inaccuracy of the method is done by the following experiment. Well known compositions – in the current case (As_2S_3 + Ag), (As_2Se_3 + Ag) and ([As, S, Se] + Ag) - are deposed on the silicon wafer by vacuum evaporation. A process of temperature annealing is conducted, leading to diffusion of the Ag in the layers (without evaporation of components). The first two samples are used as base and from their Auger profiles by EMPA calibration the RAESF for As, S, Se and Ag are found. With these RAESF the third profile is quantified. Integrating along the layer, the full content of its elements is found. The comparison with the real one (determined by EPMA) is shown in Table 1.

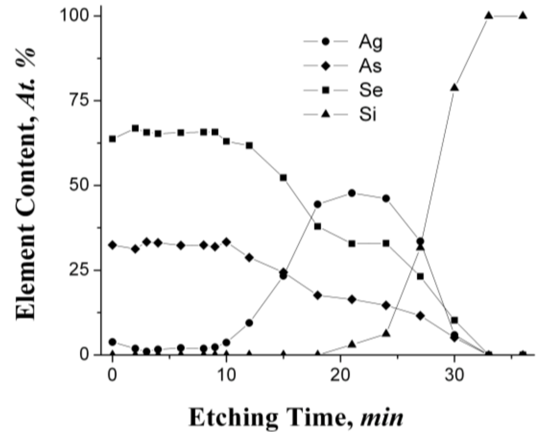

Figure 3. Quantification of the sample from Figure 2.

TABLE 1. ELEMENT CONCENTRATIONS (AT. %) AND THEIR ERRORS.

Ag	As	Se	S	Analysis
25.92	18.58	19.78	35.71	EPMA
26.0	19.2	20.2	34.6	AES
0.08	0.62	0.42	-1.11	Δc
0.3	3.3	2.1	-3.1	Δc/c, %

C. Determination of integral layer parameters using both EPMA and AES

The approach from chapter *III.B.* can be applied for calculating integral parameters of the layers too (i.e. parameters, obtained from integrating concentration-dependent quantities in depth of the layer). This is done as described above; of course additional data for the layer elements/compounds are required. Typical problem is finding the full mass of an element of the layer. We underline, that the state of the component in the layer has to be known, which will define reliable model for the calculations. The most simplistic case is an alloy from the layer components. If the components have weight parts W_i and densities ρ_i, the layer density ρ_l is $\Sigma^{-1}(W_i/\rho_i)$, which allows determination of the mass of the element in the layer if the layer thickness is known. This is demonstrated in Figure 4 and 5 for layer systems (Ag, Cu, As_2S_3, Cr) from a study for ion-selective membranes. In Table 2 the basic steps for checking the accuracy of the method are shown. Here, the first sample is used as a standard for EPMA calibration of RAESF of the elements. Via the determined RAESF the second sample (with known layers) is quantified. The sought integral quantity in the case is the layer thickness, which would contain the full amount of an element from the layer. This quantity is compared with the thickness of the initially deposed elemental layer.

D. Discussion

In the first place stands the issue, to what extend the assumptions, made for deducing (4) are valid. The first – constant sputtering speed along the layer – is assumed correct mostly for easing the presentation. The change in the sputtering speed as a result from the change in the content is a known problem for the ion sputtering (known in Auger profiling as “calibration of the depth scale”).

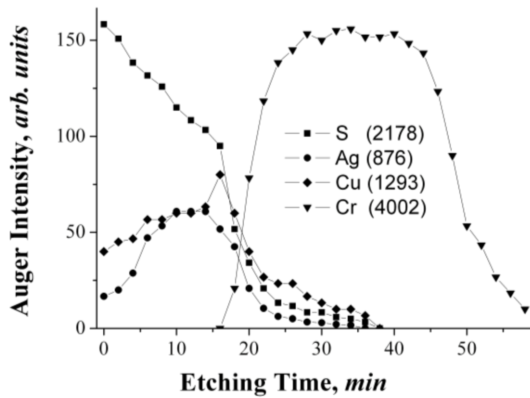

Figure 4. Auger profile of the standard (As_2S_3, Cu, Ag, Cr).

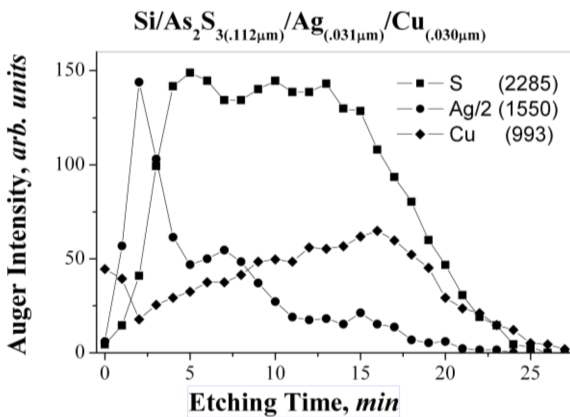

Figure 5. Auger profile of the specimen (Cu, Ag, As_2S_3)/Si. (Silicon intensity is not represented).

The situation is more serious for the factored out the integral sum in (3). This is an approximation and the introduced inaccuracy is smaller, the smaller is the area, related to the analyzed system towards that of the concentration figure (triangle, square, etc.) for the participating elements. In the case the close compositions and their smooth "transfusion" should ensure the lack of both unconnected to the concentration changes in the intensities (there are no metallurgical junctions), and small concentration-dependent corrections, connected to the matrix (close concentrations). This is the situation for several important for the practice cases. For example, in case of ternary or quaternary quasi-binary $A^{III}B^{V}$ solid solutions (Auger analyzed), the concentration of one (or two) of the elements is constant while it is remaining in limited ranges for the rest.

The essence of the suggested method for RAESF determination is finding average ones for the range, which the system is analyzed in. I.e. the found RAESF are local and valid for the concrete analysis (the concentration zone of the system). For some elements from the composition they should be increased (slightly) while for others decreased (slightly), leaving the analysis in the range of acceptable inaccuracy, Figure 6. (The determination of the value of the averaged RAESF is done by calibration with the EMPA data.)

TABLE 2. BASIC STEPS FOR CHECKING THE ACCURACY OF THE METHOD (PROFILE AES + EPMA) AT A DETERMINING THE THICKNESS OF EVAPORATED LAYERS.

Ag	Cu	As_2S_3	Cr	Notice
S	t a n	d a r	d	
0.070	0.105	0.289	0.536	*at.*% (EPMA)
584	431	1452	2668	Area, *arb. units*
8392	4106	5021	4976	Area (100%)
1.000	0.489	0.598	0.593	RAESF
S	p e c	i m e	n	
1550	992.5	2285	-	Area, *arb. units*
1550	2028	3819		Area/RAESF
21.0	27.4	51.6		*at.*% (AES)
32.3	29.5	111.2		d, *nm* *
31	30	112		d experiment, *nm*
4	-2	-1		Δd/d, %

* The measured total layer depth is 173 *nm*.

The question, why the described procedure should be used for obtaining the integral parameters of the layer, instead of directly using the (integral) EMPA data, might arise. The reason is the higher accuracy. Auger profile gives the depth composition in detail, permitting the usage of parameters for the exact compositions (for example, density for Al and Al_2O_3 in different areas of the profile (instead of the averaged for the AlO_x). Also it has EMPA-detectors, which do not register the light elements, not allowing the exact determination of the composition in this case.

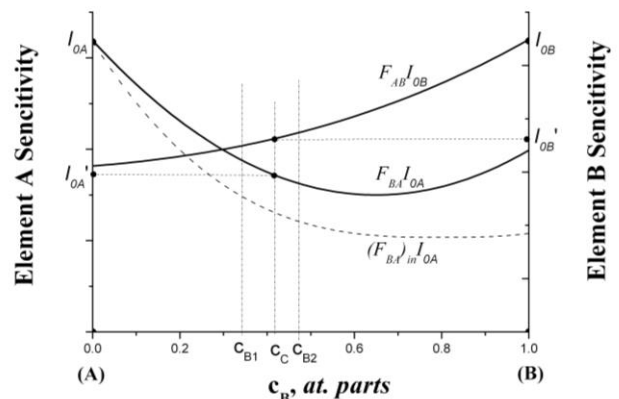

Figure 6. Binary composition of the elements A and B (The concentration figure is a leg). The true sensitivities (after "total correction" F_{ij}) are plotted with solid curves (The dash curve depicts the result of an incomplete correcting). The EPMA result at c_c averages the sensitivity in the profiling range (c_{B1}, c_{B2}).

Evaluation of the inaccuracy of the discussed methods – as usually for the Auger problems – is done by quantitative analysis of standards. Two standards are prepared. In the case, well-known compositions are vacuum evaporated

(metal layers with known thickness). A process of temperature annealing is conducted (without component evaporation). Via the suggested method RAESF are found from one of the standards, through which are determined the integral quantities from the second standard (for example masses of the evaporated metals). The obtained results are compared with the known. During such tests we get match within 10%. Therefore we assume that the incorrectness of the discussed methods is 10%. (Actually it can be lower, since some decrease in the thickness of the evaporated layer occurs during its annealing to a metal; for example for aluminum we have determined the decrease to be 5-10%).

To use the procedure, the occurring processes have to be known in order to use adequate model for describing the integral quantity. (For example, the used above formula for alloys might not be valid if any chemical reactions in the layer have occurred; at temperature processes it is mandatory that there is no evaporation of elements/components from the layer etc.).

Our discussion has been for determining masses, but it is also possible to determine other integral quantities for the layer. Additionally, depending on the experiment or the concrete necessity, the input/output data can be presented according to the need. For example, the evaporated component can be submitted as mass or thickness of the evaporated layer. Overall, in mass measuring, the relation between the mass m, density ρ and the layer geometry (thickness d, area S) – applied to the output and final layers – makes it possible to look for any of the quantities involved:

$$m = \rho d S \tag{5}$$

We have used the suggested quantification method for about 15 years, but it is the first time we publish its reasoning. We have applied it in 4 works for ion-selective membranes (most Auger orientated is [4]); 4 works for deposition and studying AlN (most Auger orientated is [5]); 5 works for humidity and ethanol sensors (most Auger orientated is [6]); 5 works for applications in micro-electronics and others (most Auger orientated is [7]).

IV. Conclusion

1. In the current article we discuss the use of the electron probe micro analysis (EPMA) for calibration in quantitative Auger layer analyses.

2. We suggest a method in which averaged Auger elemental sensitivity factors are determined by EMPA data and Auger profiles. Its essence is calibration through the EMPA data of the integral content of an element in the layer (proportional to the result from the numeric integration of the respectful Auger intensity along the profile).

3. The method is base for determination of the concentration-dependent integral parameters of the layer.

4. The applicability and accuracy of the methods is demonstrated through profile Auger experiments. In one of them the full content of the elements in the layer is determined, while in the other – the thicknesses of the deposed layers (related with their mass).

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