

## Filled out Correcting in Auger Electron Spectroscopy

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The concept "correcting" in Auger quantification is filled out by the idea "total correction". 2 new groups of corrections – for the analysis regime (presented in this work by the factors "primarily beam energy" and "modulation voltage") and for the apparatus (presented by the quantity "spectrometer' energy resolution") are included more except the matrix. The analyses accuracy' increase (with the increase of the correction steps) is monitored on the base of AlN standard quantification.

The filled out correction provides to compare the accuracy of Auger quantitative methods. The introduced term "autocorrecting" indicates the inner insurance for a condition (a priori worsening the accuracy) from the method itself. One method is more accurate at more complete "autocorrecting". The experiment compares six Auger quantitative methods.

**Keywords:** Auger electron spectroscopy, AES, quantification, correcting, correction

### INTRODUCTION

Usually the AES applications require quantitative results. Unfortunately an accuracy of less than 10% remains a difficult task for AES. During the first significant attempt for quantitative Auger analysis, Palmberg *et al.* [1] define the content of an element *A* from the sample  $c_A$  as proportional to its spectral intensity  $I_A$ :

$$c_A = (I_A/I_0) / \sum_i (I_{Ai}/I_{0i}) \quad (1)$$

where the sum is over all elements of the sample and the relative Auger elemental sensitivity factor (RAESF)  $I_0$  is the spectral intensity from the pure (100%) element. The atomic density  $N$ , electron back-scattering factor  $R$  and attenuation depth  $\lambda$  of the emitting surface act as multipliers in the emission intensity. If the analyzed element is built into the matrix in small amounts, these quantities would be those of the matrix. For a true comparison of the intensity of the sample with that of the standard, the Auger emission from both have to run in the same way, i.e. the composing multipliers  $N$ ,  $R$  and  $\lambda$  have to be equalized. For example for  $R$  ( $R_M$  and  $R_0$  respective to the sample and the standard), the sample's intensity is multiplied with  $R_0/R_M$ . The  $N$ ,  $R$  and  $\lambda$  differences' equalizing for

the sample and the standards is known as matrix correction. It notes the second stage in AES quantification (binary alloys' theory). But it proves that the matrix corrected result is still not right. That is because the quantification errors are not only due to the Auger process, but also to other factors, being different for the sample and the standard.

We consider that the quantitative Auger analysis will be accurate, if all of its aspects (Auger process, data processing, quantification procedure etc.) are equal (or corrected appropriately) for the sample and the standard. The aim of this work is an experimental verification of the above statement. A layer of aluminium nitride AlN<sub>x</sub> is chosen as an object of the analysis. An attempt is done to systemize the main factors, differing for sample/standards. The error is traced after subsequently introduced correcting steps.

Above, can be provides to the methods themselves. We affirm that one quantification method is more accurate, if it equalizes better the analysis' aspects for the sample and the standards. The statement is studied by comparing the results obtained by 6 methods.

### EXPERIMENTAL

*General Setting.* The aluminum content from an AlN<sub>x</sub> standard is evaluated by an quantification procedure, containing the sequentially introduced

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correcting steps. The error in a certain stage is the difference between the calculated content and the real one.

*Standard creation and Auger experiment.* For clear setting of the experiment a binary standard is chosen with high sensitive ingredients having one order concentrations. A layer of  $AlN_x$  is deposited on Si polished wafer at the temperature of 200°C by DC magnetron sputtering of Al target in the presence of  $N_2$ , diluted 6:5 with  $Ar_2$ . Layer depth of 150 nm is suitable for both Auger profiling and Electron Probe Microanalysis (EPMA). EPMA is used for the layer's composition calibration and is performed on ESEM XL30 FEI Co. It gives for the specimen 57.9 at.% Al, 40.6 at.% N and 1.5 at.% oxygen. It is supposed that the oxygen binds part of aluminium (1 at.%) as  $Al_2O_3$ . If the oxygen and Al, bonded to it, are not accounted in the composition, its reduced (binary) content is: 58.4 at.% Al and

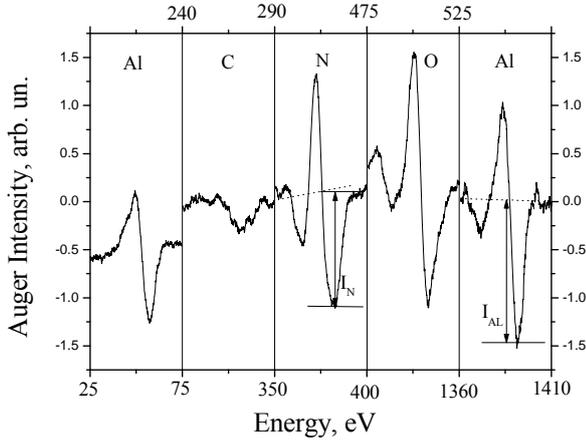


Fig. 1. Auger spectrum of the  $AlN_x$  surface

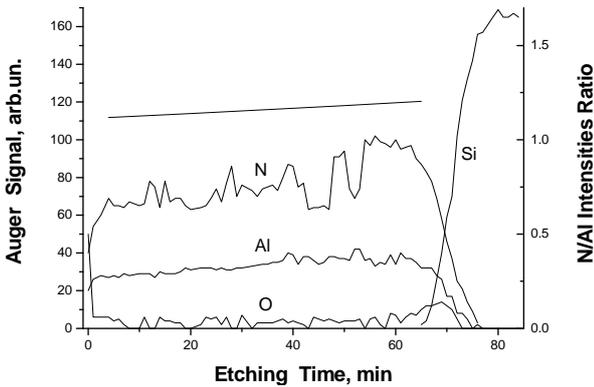


Fig. 2. Auger profile of the  $AlN_x$  specimen

41.6 at.% N. EMPA's result gives the integral composition of the layer. The Auger analyses are performed by microprobe with a beam energy  $E_p$  up

to 10 keV and an energy resolution  $\Delta E/E \sim 0.3\%$ . Our regime is  $E_p = 3$  keV and  $V_{mod} = 4$  V<sub>ptp</sub>. The differential mode peaks for N, O and Al 1398 eV are monitored. The intensity is measured by the peak's negative wing ("ptb"), as shown in Fig. 1.

Auger profiling of the layer (performed by 3 keV  $Ar^+$  ion sputtering) shows the rather good homogeneity in the depth, Fig. 2. That allows Auger data to be averaged for the layer. As above, Al-peak is reduced for the available oxygen (by  $Al_2O_3$  spectrum) and the relative "binary" intensity  $I_{N/Al}$  of the laboratory standard is determined.

*Quantification.* The experimental input quantity is one for binary case. It is the relative intensity of the components  $I_{N/Al}$ ,  $I_{N/Al} = I_N/I_{Al}$ . Now Eq. 1 becomes:

$$X_{Al} = (1 + F \cdot S_{Al/N} I_{N/Al})^{-1} \quad (2)$$

where the aluminium content  $X_{Al}$  is in atomic parts,  $F$  is the correction factor and  $S_{Al/N} = S_{Al}/S_N$ . If the intensity does not contain the corrected quantity  $Y$  as a multiplayer, but it is a function of it,  $f(Y)$ , the correction is introduced by the factor  $F(Y) = f(Y_0)/f(Y_M)$ .

*Comparison of Auger quantification methods.* Four methods are considered in the work, as one of them has 3 varieties. The main difference is the way of determining  $S_{N/Al}$ . Here is a brief characterization of the methods: Ia) RAESF's method is standardless and uses a data bank for RAESFs and Eq. 2 (with  $F = 1$ ); Ib) It can be applied also with own (local) standards, calibrating laboratory's RAESFs. In our Auger experiment the nitrogen sensitivity was determined at taking as a standard silicon nitride for electronic uses ( $Si_{55}N_{45}$ ); Ic) The RAESF's determination from another data is made by using the the work [2]; II) At "one binary standard calibration" method  $S_{Al/N}$  is calculated from the standard content  $X_{Al}^{St}$  and the measured relative Auger intensity  $I_{Al/N}^{St}$  by Eq. 2. Knowing  $S_{Al/N}$ , the Al content of the specimen is calculated by its relative Auger intensity (Eq. 2); III) The "near standard" method [3] uses layer standards of  $Si_3N_4$ ,  $SiO_2$  (compounds of Si which is near in Auger behavior to Al) and  $Al_2O_3$ .  $S_{Al/N}$  is calculated by directly measured intensities of the compounds indicated in the brackets:

$$S_{Al/N} = I_{Si/N}(Si_3N_4) \cdot I_{Al/O}(Al_2O_3) \cdot I_{O/Si}(SiO_2) \quad (3)$$

IV) "One peak's" method uses only the standard's content  $X_{Al}^{ST}$  and intensity  $I_{Al}^{ST}$ :

$$X_{Al} = (I_{Al}/I_{Al}^S) \cdot X_{Al}^{ST} \quad (4)$$

## RESULTS AND DISCUSSION

*Types of corrections.* We determined as important for our analysis not only the classic matrix correction  $F_m$  but 3 more groups of factors: the analytic regime  $F_R$ , the instrument  $F_A$  and the peak shape  $F_{PS}$ . With corrected there factors in the brackets and since the correcting of independent factors is multiplicative, the total correction  $F_{tot}$  is:

$$F_{tot} = FR(E_p, V_{mod}, \dots)FA(\Delta E/E, \dots)F_m(N, R, \lambda)FPS \quad (5)$$

*Corrections introduction.* The regime'  $E_p$ -correction can be done: I. experimentally; II. according to a data bank (the available spectra' atlases should be assigned here); III. theoretically – by the curves of Sato *et al.* [4]. As a RAESF' data bank we use the atlases of PEI [1] (3 keV, 2 V<sub>pp</sub>; 0.6%; TaN), McGuire [5] (5 keV, 4 V<sub>pp</sub>; 0.6%; Si<sub>3</sub>N<sub>4</sub>) and Jeol [6] (10 keV, 5 V<sub>pp</sub>; 0.5%; Si<sub>3</sub>N<sub>4</sub>); the analytical regime,  $\Delta E/E$  and the standard for nitrogen are shown in brackets. Chew and Huang's  $S_{Al/N} = 0.98$  at  $E_p = 10$  keV and  $V_{mod} = 10$  V<sub>pp</sub> [2]. The correcting for  $V_{mod}$  at the same  $\Delta E/E$  also can be done experimentally or by McGuire [5]. But a common correction for  $\Delta E/E$  and  $V_{mod}$  is going on when there is a difference in  $\Delta E/E$ . The universal dependency  $f$  of the signal intensity on  $V_{mod}$  includes the parametric peak half-width  $W$  [7]. For the peak of  $i^{th}$  element:

$$I_i = f(V_{mod}/W_i)/W_i \quad (6)$$

$W_i$  includes the intrinsic half-width  $W_{0i}$  due to  $\Delta E/E$  enlargement. At energy  $E_i$ :

$$W_i^2 = W_{0i}^2 + [(\Delta E/E)E_i]^2 \quad (7)$$

$W_{0i}$  is determined from a spectral window almost filled up by the peak. We set a time-constant 3s, a record rate of 0.017 V/s and  $V_{mod} = 1$  V<sub>pp</sub> and received  $W_{0Al}$  and  $W_{0N}$ . The correction at the transition from one to the other parameters ( $\Delta E/E$ ,  $V_{mod}$ ) is:

$$F(AlN)_{(\Delta E/E; V)1 \rightarrow 2} = \frac{f(V_2/W(Al)_2)}{f(V_2/W(N)_2)} \cdot \frac{W(N)_2}{W(Al)_2} \cdot \frac{f(V_1/W(N)_1)}{f(V_1/W(Al)_1)} \cdot \frac{W(Al)_1}{W(N)_1} \quad (8)$$

We applied the classic matrix correction in the binary alloys theory version with Seah and Dench [8] relationship for the inelastic mean free path of the electroSn and Shimizu relationship [9] for the back-scattering calculation. For our standards (Al

and Si<sub>3</sub>N<sub>4</sub> for N), given in the brackets the material for which the quantity is relevant to:

$$F_m = \left[ \frac{N(Si_3N_4)}{N(Al)} \right]^{1/2} \cdot \frac{R_{Al}(AlN)}{R_N(AlN)} \cdot \frac{R_N(Si_3N_4)}{R_{Al}(Al)} \quad (9)$$

*Comparison of correction results.* The rows of Tables 1 and 2 present the separate correcting steps. Each following correction is done on the base of the results of the previous one. Table 1 shows Al content. Table 2 gives the average quantification error. The first row of data in the tables show the uncorrected results. The correction for the regime starts from  $E_p$  and is shown in the next table row.  $\Delta E/E$  is different for the sample (our analysis) and the 4 sources for RAESF (used as standards for Al and N); and that enforces a common correction with  $V_{mod}$ . Thus, correcting for regime and apparatus completes in the third row. The next row shows the triple classic ( $N, R, \lambda$ ) matrix correction. In our case the influence of the peak form is in the error' limits.

*Correcting comments.* With regard to the accuracy of the quantification, the performance of an additional correction gives a next (better) approximation and should improve the result. That is observed in the Tables 1 and 2 and appears as a confirmation for both the right choice and the exact modeling of the corrected effects. The exception for the Jeoul' data at the first correction have an explanation too: The effects from  $E_p$  and  $\Delta E/E$  are with an opposite sign and not corrected compensate each other partially. The total correction introduced by us has turned out sufficient, i.e. the quantification error is of the same order as that of the intensities' measuring (3.6% for the profile and 1% for our standards). From the above it follows that: I. The basic factors requiring a correcting are determined truthfully; II. It confirms the basic conception that at total correcting (e.g. elimination of all main sources of uncertainties) the result is exact; III. The last is valid for the 4 data banks. The results from the 3<sup>rd</sup> row of 2<sup>nd</sup> table confirm the published error up to 30% in RAESD' method with data bank by Chang [10]. The published 30-50% [11] are probably relative to different apparatuses and the comparison must be with the upper row (46.4, 44.6, 42.9) with a good confirmation. According to this work the quantification improvement is 31% after a regime's plus instrumental correction and another 12% after a matrix one. The matrix effects' correction conforms by literature data 13% at 50% of the binary couples

(or 30% at 85% ) [12, 13]). For the analyzed AlN, some factors (as chemical changes, changes in the surface composition due to preferential ion sputtering, roughness etc.) are not essential. There are quite a few factors, influencing the Auger

analysis [14] and a negligible to an analyzed object factor might turn out crucial to another. An algorithm is given for data transfer from one regime and an apparatus to others.

**Table 1.** Comparison for the correction' steps results (instead of 58.4 at.%)

| Correction               | By RAESF' with a Data Base |                 |                     |                   |
|--------------------------|----------------------------|-----------------|---------------------|-------------------|
|                          | Shew/Huang Data            | PEI (3keV, 2eV) | McGuire (5keV, 4eV) | Jeol (10keV, 5eV) |
| None                     |                            | 80.9            | 71.3                | 60.8              |
| Regime's, E <sub>p</sub> | 88.9                       | (80.9)          | 80.1                | 79.2              |
| Mod. & Instr.            | 61.3                       | 66.5            | 64.5                | 68.0              |
| Matrix                   | 56.7                       | 56.5            | 60.2                | 64.6              |
| Peak' Shape              | ?                          | ?               | ?                   | ?                 |

**Table 2.** Mean error of the quantification:  $(|\Delta c_{Al}|/c_{Al} + |\Delta c_N|/c_N)/2$ .

| Correction               | By RAESF' with a Data Base |                 |                     |                   |
|--------------------------|----------------------------|-----------------|---------------------|-------------------|
|                          | Shew/Huang Data            | PEI (3keV, 2eV) | McGuire (5keV, 4eV) | Jeol (10keV, 5eV) |
| None                     |                            | 46.4            | 28.6                | 4.9               |
| Regime's, E <sub>p</sub> | 62.8                       | (46.4)          | 44.6                | 42.9              |
| Mod. & Instr.            | 6.0                        | 16.7            | 12.2                | 19.8              |
| Matrix                   | 3.5                        | 3.9             | 3.7                 | 12.3              |
| Peak' Shape              | ?                          | ?               | ?                   | ?                 |

**Table 3.** Quantification methods compared after their autocorrecting and the error from the quantification (%):  $(|\Delta c_{Al}|/c_{Al} + |\Delta c_N|/c_N)/2$  mean relative

| Correction       | Methods and their errors                                   |                                |                           |                     |                |           |
|------------------|--|--------------------------------|---------------------------|---------------------|----------------|-----------|
|                  | Standardless   |                                | ... with Standards        |                     |                |           |
|                  | RAESF' with a Data Base                                    | RAESF' from Another one's data | RAESF' with Own Standards | 1Calibration Point' | Near Standard' | One Peak' |
| None             | 46.3 <sup>a</sup><br>26.5 <sup>b</sup><br>4.9 <sup>c</sup> |                                |                           |                     |                |           |
| + Regime's       |  | 62.8 <sup>d</sup>              |                           |                     |                |           |
| + Instrumental   |  |                                | 4.3                       |                     |                | 27.8      |
| + Matrix = Total |  |                                |                           | 4.3                 | 2.9            |           |

*Quantification methods discussion.* Every introduced correcting step removed (or at least decreased) the influence of certain factors worsening the analysis. The set of potential worsening factors is divided for any method in two: active (which elimination requires correction) and such, which are removed by the nature of the method. I.e. the provision of certain condition can be intrinsic (attribute) for certain method. If one method provides a condition, we will say that the condition is "autocorrected" (or that the method is "autocorrected" in respect to this condition). Our base conception is that one quantitative AES method is more accurate when it is more complete autocorrected (placed down in the correction scheme). This really turns into tendency in Table 3.

The latter explains the accuracy of the separate methods, as well as of already expressed expert opinions. For example the methods with standards are more accurate than with RAESF from data banks [11] and the RAESF method is more accurate

by own standards used [15, 16] – it comes to two auto-correcting degrees more.

At a complete autocorrecting, the inaccuracy is of the order as the intensities' error.

The conclusion that one calibrating point method is the most accurate would be wrong. It ignores the matrix effects and its result is true if the analyzed composition is near to the standard (in our case the difference in N concentration for both binary material is ~1%). The "near standard" method is applicable with an element available, near in Auger behaviour to the metal component, which compensates the matrix effects. The "one peak method" Eq. 4 is readily obtained from Eq. 1, if the correcting is ignored and the denominator is 1. But without a normalization the quantification result can turn out to be distorted. Therefore the method is not advisable in the AES practice.

## CONCLUSIONS

The concept of "correcting" is filled out and the

term “total correction” is introduced (The total correction equalizes all the analytical parameters for the sample and the standards).

Two new groups of correction parameters are introduced – for the analysis regime (primary beam energy and modulation voltage) and for the apparatus (spectrometer’ energy resolution). The total correction is modeled by them and the classic matrix ( $N$ ,  $R$ ,  $\lambda$ ) correction for AES quantitative analysis of AlN. In this case it turns out to be enough.

The influence of the different corrections over the analysis accuracy is followed.

The term “autocorrecting” is introduced, which denotes the provision of one condition (by default worsening the accuracy) from the analysis itself. “Autocorrecting” is intrinsic characteristic of every AES quantification method. The last is more accurate at more complete “autocorrecting”. That is verified by 6 quantification methods.

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## РАЗШИРЕНО КОРИГИРАНЕ В ЕЛЕКТРОННАТА ОЖЕ СПЕКТРОСКОПИЯ

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(Резюме)

Понятието “коригиране” в количествената Оже спектроскопия е разширено чрез идеята за “пълна корекция”. Две нови групи корекции – за аналитичния режим и за апаратурата са добавени към матричната ( $N$ ,  $R$ ,  $\lambda$ ) корекция. Нарастването на точността на анализа при последователно въвеждани коригиращи стъпки е проследено чрез количествен анализ на AlN стандарт.

Разширеното коригиране дава възможност да се сравни точността при различни методи за количествен Оже анализ. С въведения термин “автокоригиране” се обозначава осигуряването на едно условие (априорно влошаващо точността) от самия метод. Един метод е по-точен при по-пълно “автокоригиране”. Експерименталната проверка е за 6 метода за количествен Оже анализ.