

SHORT CONTRIBUTIONS AND POSTERS

SURFACE PHYSICS

SOME PROBLEMS OF QUANTITATIVE AES IN FRACTOGRAPHY

By

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In general the quantitative Auger electron spectroscopic analysis of metal fracture surfaces is based on elemental sensitivity factors of the components, segregated impurities or second phases. In metallurgical AES studies mostly the PHI Auger Handbook is used, the relative sensitivities being determined on atomic clean metal and semiconductor surfaces, or insulating compounds (e.g. MgO, KCl, CdS, GaP). In the literature, many contradictory data are communicated. In the analysis of segregated films, however (C, S, P etc.), the contribution of backscattering from the fractured metal might be important.

Some problems of fracture analysis on steel and tungsten are discussed, considering the backscattering correction, escape depth and excitation cross sections as well.

The use of elemental sensitivity factors in Auger electron spectroscopy is a widely applied practical approximation [1-6]. A reasonable accuracy of surface analysis can be achieved in many cases, under some conditions:

- the energy of Auger peaks (escape depth of Auger electron) is not very different;
- the backscattering excitation can be neglected for elements situated in the neighbourhood in the periodic table;
- Auger emission is produced by atomic transitions (i. e. not KVV or LVV transitions in insulators);
- roughness of the surface can be neglected.

In the analysis of segregated impurities below the monolayer thickness range, considerable discrepancies may occur. Apparently anomalous values or relative sensitivity factors of some segregated (e. g. S) elements have been described in the literature (e. g. [4]).

In the literature of quantitative AES using elemental sensitivity factors, little attention has been paid hitherto to backscattering excitation. After the fundamental works of GALLON and coworkers [7], recently JABLONSKI [8] showed the great importance of the backscattering.

In this paper some problems of quantitative AES of segregated impurities on fracture surfaces are discussed. McMAHON and coworkers published a great number of works on AES studies of steel fracture surfaces (e. g. [9]).

Recently, the author and coworkers reported on AES study of tool steel [10], whereas MENYHÁRD reported on tungsten [11].

In this work analysis is based on the newly published method of MARCHUT and MCMAHON [12], improving their accuracy with considering the effect of backscattering excitation. MARCHUT and MCMAHON derived some simple equations for the case of two component alloys with X_1 and $X_2 = 1 - X_1$ surface composition; associated with I_1 and I_2 Auger peak intensities:

$$\frac{I_1}{I_2} = \frac{P_1}{P_2} \cdot \frac{X_1}{1 - X_1} \frac{1 - k_2}{1 - k_1}, \quad (1)$$

In Eq. (1) P_1 and P_2 are the Auger yields,

$$k_i = \exp\left(-\frac{L}{0,74 L_i}\right);$$

L is the lattice spacing, L_i denotes the escape depth of Auger electrons. The factor 0.74 in k_1 comes from the 42° collecting angle of the CMA.

In a similar way MARCHUT derived a simple expression for the case of a surface impurity (I_i) with coverage Θ on a substrate with Auger emission intensity I_1 :

$$\frac{I_2}{I_1} = \frac{P_2 \Theta}{P_1 \left(\frac{1}{1 - k_1} - \Theta\right)} \quad (2)$$

It will be shown in this paper that P_1 and P_2 can be derived from the elemental sensitivity factors, taking into account the backscattering excitation [r_B] comparing the Auger peak heights of two homogeneous samples:

$$\frac{I_1}{I_2} = \frac{P_1}{P_2} \frac{r_{B1}}{r_{B2}} \frac{1 - k_2}{1 - k_1}. \quad (3)$$

Eq. (3) however corresponds to the Auger spectra presented in the PHI Handbook [1]. The ratio P_1/P_2 can be determined for any pair of elements, provided reliable data are available for the escape depth L_i and the backscattering excitation factors. In our Eqs. (1–3) L_i/L denotes the number of atomic layers crossed by escaping Auger electrons. Our analysis is based on the recently published data of LEHÉRICY [5]. On the other hand, real values of the backscattering factor are rather problematic. Besides of some early experimental data of SMITH [7], GOTO [13], VRAKING [14] below $E_p = 1,5$ keV excitation energy, JABLONSKI's recent calculations gave considerably higher values. Recently, the backscattering spectra of various elements have been measured in our laboratory [15].

The backscattering coefficients — not identical with the Auger excitation backscattering factors — found in our recent work showed similarity

with EVERHART's [16] and MCAFEE's data [17], available unfortunately only below $Z = 32$. For higher Z values, saturation character was observed [16], as found also by SMITH [7] on r_B . For this reason, in some cases r_B values were derived by extrapolating GALLON's experimental data [7]. Some results are summarized in Fig. 1 exhibiting also calculated data of JABLONSKI, for $E_p/E_i = 10$.

It is reasonable to assume that the (Auger excitation) backscattering factor r_B should be proportional to the backscattering coefficient r of the surface. Fitting the experimental r values with JABLONSKI's data, they are conform below $Z = 26$, but above iron, deviation is increasing with Z . JABLONSKI made his calculation up to $Z = 46$ (Pd) only for some elements. Supposing the proportionality, in our analysis, the reduced r_B curve was applied. In Fig. 1 experimental points available [7, 14] are also indicated.

The parameters used in our analysis and results are summarized in Table I. The Auger yield ratios are referred to the 703 eV peak of iron [4] for $E_p = 3$ keV excitation energy. The Auger excitation cross sections σ are taken from VRAKING and MAYER [18], but for 3 keV.

$\sigma(E)$ was calculated according to VRAKING for σ_K and GRYZINSKI [7] for σ_L . In principle, the P_i Auger yield values should be proportional to σ . In a similar

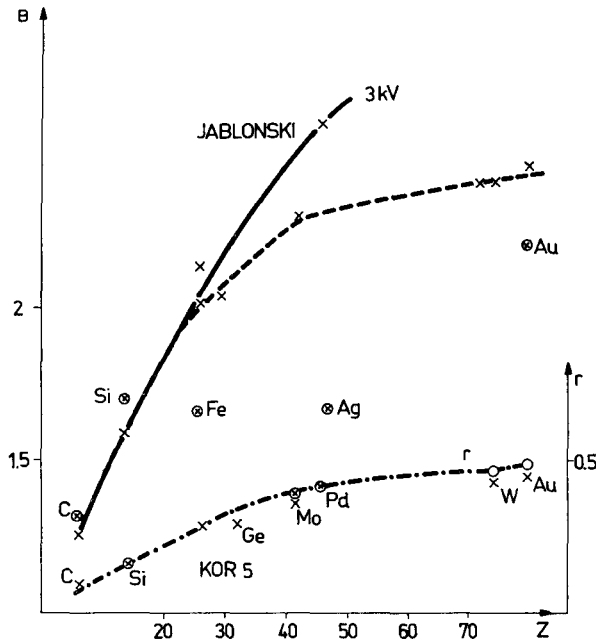


Fig. 1. The r_B Auger excitation backscattering factor and the r backscattering coefficient versus Z — JABLONSKI's data for $E_p = 3$ keV, $E_i = 0.3$ keV. — — — reduced r_B curve. - - - - r , curve of MCAFEE, x points own results. ⊙ points data of SMITH and GALLON

Table I
Numerical values of parameters for AES

Element (compound)	Z	α/α_{Fe} Palmerberg	r_{B1}	L_i/L	$\sigma \times 10^{-19}$ cm ²	P_{Fe}/P_i
C	6	2.08	1.21	3.2	0.43	1.1
Si	14	0.58	1.55	1.8	2.1	0.25
P(GaP)	15/23	0.39	1.75	2	1.9	0.208
S(CdS)	16/32	0.35	1.85	2.3	1.6	0.216
K(KCl)	19	0.28	1.64	3.1		0.19
Fe	26	1	1.61	5	0.3	1
W	74	3.04	2.1	2.85		2.43

way, P_i is proportional approximately to the elemental sensitivity factor, neglecting the effect of backscattering. Let us compare data in Table I with experimental calibration data, published in the literature. For this reason, the Auger signal or coverage has to be compared with them. Introducing the backscattering excitation into Eqs. (2):

$$\frac{I_2}{I_1} = \frac{P_2}{P_1} \frac{r_{B21}}{r_{B1}} \frac{\Theta}{\left(\frac{1}{1-k_1} - \Theta\right)}. \quad (4)$$

r_{B1} denotes the backscattering factor of the substrate, whereas r_{B21} denotes the excitation of segregated impurity by the substrate, taking into account the excitation energies. Knowing parameters P_i and r_{B1} Eq. (4) can be used for evaluating Auger spectra of thin surface layers, segregated on grain boundary fractures.

For two impurities with intensities I_2 and I_3 and coverages Θ_2 and Θ_3

$$\frac{I_3}{I_1} = \frac{P_3}{P_1} \frac{r_{B31}}{r_{B1}} \frac{\Theta_3}{\left(\frac{1}{1-k_1} - \Theta_2 - \Theta_3\right)}. \quad (5)$$

Unfortunately, very few reliable calibration data are available in the literature.

In AES fractography of steel alloys, S, P, and Sb are the most interesting segregating impurities, producing temper embrittlement. For P, Sb and Sn, calibration standards have been studied by MARCHUT [13]. Calculating I_2/I_1 for $\Theta = 0,1$ phosphorus with Eq. (4) gives 0.54, instead of 0.30 found by MARCHUT. The discrepancy can be explained by the inadequacy of $\alpha = 0.55$ elemental sensitivity factor of P, determined on GaP. GaP is a semiconductor crystal of high perfection, possibly providing a higher mean free

path (escape depth) of Auger electrons, as given by the 'immaterial' standard curve. It should be emphasized that in LEHÉRICY's recent paper experimental points are widely scattered around the standard curve. The discrepancy of the α of phosphorus also occurs, comparing its σ excitation cross section with that of Si. The author is not aware of reliable calibration data of S on Fe, but α and σ of S are similar to those of P. Regarding the case of potassium on tungsten, quantitative data are given by THOMAS and HAAS [19]. For $\Theta = 0.5$ Eq. (4) gives 6.1, instead of 2.5 [19]. The ratio of elemental sensitivity factors of K and W makes 27. Even with our corrections in Table I, this ratio is 12.8. The discrepancy can be resolved again by the high escape depth of Auger electrons in KCl, a highly perfect insulator crystal, as found by BATTYE and coworkers [20] on alkali halide crystals. Summarizing the results of this analysis, the evaluation of Auger spectra obtained on fracture surfaces needs extreme care. In case of segregated P or S, or K on W (surface diffusion, as found by MENYHÁRD), the simple use of elemental sensitivity factors is hardly justified.

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