

## Surface Excitation Correction for Elastic Peak Electron Spectroscopy (EPES)

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Elastic peak electron spectroscopy (EPES) is the quantitative spectroscopy of quasi-elastically backscattered electrons, detected by an electron spectrometer, and affected by its parameters (angles, energy resolution, etc). The integrated elastic peak intensity is determined by electron transport parameters: the differential elastic and inelastic scattering cross sections, the inelastic mean free path (IMFP), and the surface excitation parameter (SEP) for detected electrons. EPES experiments are evaluated by Monte Carlo simulation. EPES is the best experimental tool for determining the IMFP. Surface excitations (characterized by the SEP parameter), such as surface plasmons, decrease the intensity of the elastic peak, and AES and XPS peaks. The IMFP determined experimentally with neglect of surface excitation is different from that calculated for the bulk material by Tanuma et al. The goal of this paper is the improvement of experimental IMFP by SEP correction. This was achieved by comparing the integrated experimental elastic peak ratios of sample and reference for sample pairs of standard metals (Ag, Cu, Ni, Au) and Si. The procedure is a further development of Tanuma's algorithm. Chen's model for the SEP and material parameters, the NIST SRD64 (version 3.1 2003) database and EPESWIN software are applied. Experimental SEP corrected IMFPs are presented for Si, Ni and Ag. They show better agreement with calculated IMFPs from TPP-2M data, than those calculated with 1996 version of SRD 64 for Si and the standard metals Ag, Ni, Cu. In favorable cases > 50% improvement was found. Other effects might be important, such as experimental uncertainties and, especially the input parameters in the MC simulation

### INTRODUCTION

Elastic peak electron spectroscopy (EPES) [1] is the quantitative spectroscopy of quasi-elastically backscattered electrons detected by an electron spectrometer. Recently a review paper of the author was published [1] that summarizes the experimental measurements (peak position, FWHM) and physical parameters of the elastic peak intensity  $I_e(E)$ . The relevant parameters are: the intensity ( $Z$  atomic no), angular conditions ( $\theta_i$  incidence,  $\theta_d$  detection, with respect to the surface normal), and the recoil effect [1,2]. The elastic peak corresponds to the electron elastic electron-reflection coefficient of the sample within the angular conditions of detection. It is determined by electron transport processes [3] and parameters: the

elastic (NIST SRD64) and inelastic scattering cross-sections, the inelastic mean free path  $\lambda_i$  (IMFP) of electrons [4] and the surface excitation parameter  $P_{se}$ . (SEP) [5]. Surface excitations decrease the intensity of the elastic peak, of the Auger and XPS peaks by  $\exp(-P_{se})$ .

EPES is an auxiliary method of surface analysis with AES, XPS and REELS. The giant elastic peak is advantageous with respect to the low signals of other methods. It is suitable for identification of elements. The recoil effect (fundamental works of Boersch, Seah and Goto are summarized in [1]) produces splitting of the elastic peak in compounds. Recently the hydrogen elastic peak was directly observed on polyethylene [2].

Few experimental results are available on

absolute values (%) of the elastic peak. K. Goto published fundamental data obtained with his CMA system [6,7]; they are summarized in [1] together with RFA and AREPES (angular) experimental data. The hardest problem is measurement of the spectrometer transmission [1]. This is eliminated by comparing the integrated elastic-peak intensities of the sample  $I_{es}(E)/I_{er}(E)$  and a reference sample (e.g. Ag, Cu, Ni). The elastic peaks are processed by background subtraction [8] as well.

The IMFP is a fundamental bulk material parameter used for quantitative surface analysis. EPES is the most practical method for its experimental determination, recommended by authors in [4]. It is based on the comparison of the experimental ratio  $R_e = I_{es}/I_{er}$  and the ratio of the calculated values  $R_c = I_{cs}/I_{cr}$ , using Monte Carlo (MC) simulation [4]. The IMFP (TPP-2M) data of Tanuma [9] et. al. are applied. In the previous works [4], surface excitations were fully neglected.  $I_{er} = C(E, R_e, \theta)$  supplies the uncorrected IMFP  $I_{er}$  for the sample). Comparing however  $R_e$  and  $R_c$  data, in practice, they are different. Assuming, that the difference is due (at least partly) to the different SEP parameters of sample and reference, the SEP correction was elaborated [10]. In the latter, the NIST RSD 64 database (version 1996) was applied.

The present paper deals with the experimental estimation of  $P_{ses}(E)$ , the surface excitation parameter [5] of the samples. The goal of the work is the elaboration of a simple method for SEP correction of the IMFP, and of AES and XPS peaks.

The IMFPs for Si, Ni, Ag, Cu and Au were corrected for surface excitation.

### EXPERIMENTAL, MATERIALS.

The experimental method and materials have been described in [12]. Electron spectrometers ESA 31 (developed by ATOMKI) [13] and DESA 100 (Staib Ltd) were used. EPES experiments were carried out at  $E = 0.2, 0.5, 1, 1.5$  and  $2$  keV.

The materials are: polySi (fine microcrystalline) Si used in micro-electronics. The preparation of Ag, Ni, Cu and Au samples was electrolytic deposition on highly polished brass

(SR60 60% Cu and 40%Zn) [12]. The rotated sample surfaces were cleaned by  $Ar^+$  ion bombardment and checked by in situ XPS (ESA) and AES (DESA).

The averaged data of 4-5 experiments were evaluated applying the EPESWIN software [14] of Jablonski and NIST SRD 64 (version 3.1, 2003) electron elastic- scattering cross-section database [11].

### THE PROCEDURE FOR DETERMINING THE SEP PARAMETER AND CORRECTION OF THE IMFP

A new procedure was developed in [10]. It is based on the difference between  $R_e$  (experiment) and  $R_c$  (MC) results for sample and reference. It is a further development of Tanuma's algorithm [15] applied for the ratio of sample and reference.  $f_c = R_e/R_c$ . The following data were used in our procedure for sample pairs of Si, Ag, Ni, Cu and Au. Surface excitation is a Poissonian process [15].

The TPP-2M IMFPs  $I_{er}$  for the reference samples are applied [9].

$P_{ser}$  data of Chen [16] are applied for the ref. sample (except Ni, no data have been published).

The MC algorithm for calculating  $R_c$  applied EPESWIN software [14] and the NIST SRD 64 (version 3.1, 2003) [11].

Determination of SEP when unavailable (e.g. Ni) or their possible improvement was achieved.

Our algorithm uses eqns (1)-(5).

$$\frac{I_{se}(E)}{I_{re}(E)} = \frac{I_{sc}(E) \exp(-P_{ses})}{I_{rc}(E) \exp(-P_{ser})} \quad (1)$$

$P_{ser}$  and  $P_{ses}(E)$  are given by Chen's formula [15]

$$P_{se}(E) = \frac{a_{ch}}{\sqrt{E}} \left( \frac{1}{\cos \alpha_i} + \frac{1}{\cos \alpha_d} \right) \quad (2)$$

where  $a_{ch}$  is a material parameter

$R_e$  should be corrected by factor  $f_s(E)$

$$f_s(E) = \frac{\exp(-P_{ser})}{\exp(-P_{ses})} \quad f_c = \frac{R_e}{R_c} \quad (3)$$

$$f_s(E) \frac{R_{se}(E)}{R_{re}(E)} = \frac{R_{sc}(E)}{R_{rc}(E)} \quad (4)$$

Eqn. (4) is valid for the ideal case i.e. the difference in  $R_e$  and  $R_c$  is due to surface excitation.

Applying a linear approach, the SEP corrected  $\lambda_c$  is

$$\lambda_u = C(R_e, \lambda_r, E), \quad \lambda_c = f_s * \lambda_u \quad (5)$$

where  $C(R_e, \lambda_r, E)$  represents the calibration curve from EPESWIN.

$a_{chNi}$  was deduced by the best approach of the TPP-2M. It was determined by a trial and error procedure for achieving minimum value of  $\Delta_c$  averaged for all the sample pairs. Its value resulted in  $a_{chNi} = 3.61$ .  $\Delta_u$  and  $\Delta_c$  resp are defined by equation (6) [4]

They characterize the rms deviations from  $\lambda_T$  (Tanuma), averaging data for the 5 energies. The efficiency of SEP correction can be characterized by  $(\Delta_u - \Delta_c) / \Delta_u$ . The quality factor is the rms deviation of the product  $\Delta_{fsc}$  from 1, based on the average for  $n = 5$  experimental data.

The procedure was applied on  $R_e$  and  $R_c$  ratios for sample pairs Si with standard metal reference Si/Ag, Si/Ni etc and Ni/Ag etc, Ag/Ni etc, Cu/Si etc, Au/Si etc all the sample pairs. The SEP correction can be made only for  $P_{ses}(E)$  different from  $P_{ser}(E)$ .

$$\Delta \lambda_u = \frac{1}{n} \sqrt{\sum_{i=1}^n \left( \frac{\lambda_u(E_i) - \lambda_T^i(E_i)}{\lambda_T^i(E_i)} \right)^2} \quad (6)$$

$$\Delta \lambda_c = \frac{1}{n} \sqrt{\sum_{i=1}^n \left( \frac{\lambda_c(E_i) - \lambda_T^i(E_i)}{\lambda_T^i(E_i)} \right)^2}$$

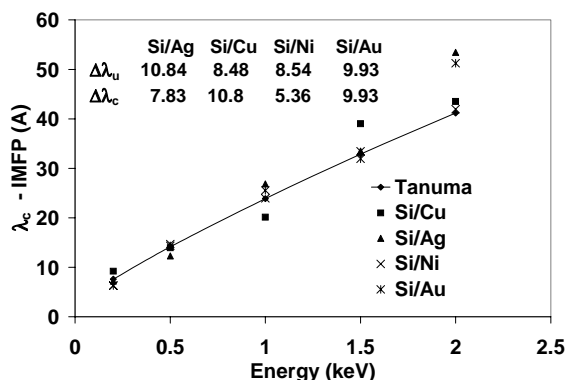


Fig.1. Comparison of the corrected IMFPs  $\lambda_c$  of Si with the calculated TPP-2M data  $\lambda_T$ , for Ag, Cu, Ni and Au reference samples. In the Fig.  $\lambda_u\%$  and  $\lambda_c\%$  data are also indicated.

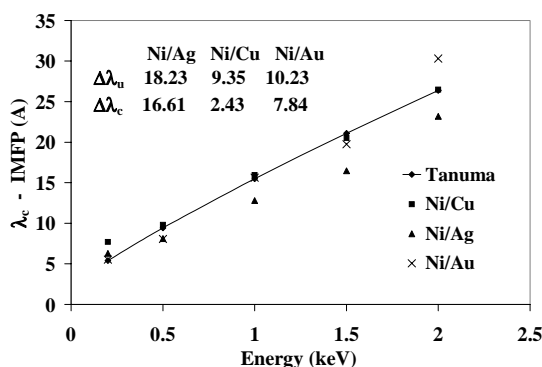


Fig. 2. Comparison of the corrected IMFPs  $\lambda_c$  of Ni with the calculated TPP-2M data  $\lambda_T$ , for Ag, Cu and Au reference samples. In the Fig.  $\lambda_u\%$  and  $\lambda_c\%$  data are also indicated.

### EXPERIMENTAL RESULTS

Experimental results obtained with the ESA 31 are summarized in Table 1. for Si with the various reference samples. Operating parameters are:  $\theta_i = 50^\circ$ ,  $\theta_d = 0^\circ \pm \Delta\theta$  (angular window of detection: 2-5° decreasing with E) and  $\Delta E_S = 100-200$  meV energy resolution. Following data are presented:  $R_e, f_c, u / T, fsc$ .

Except for some anomalous cases (believed due to an experimental problem),  $f_c(E)$  data are close to the  $u(E) / T(E)$  ratios. This justifies the linear approach of eqn (5) and the approximately linear calibration curves for  $u(E)$  obtained by MC simulations [4, 12]. In most cases  $f_c$  shows random (R) fluctuations, due to experimental uncertainties.

For Ni  $f_c > 1$  or for Au  $< 1$ . They are systematic.  $f_s f_c$  is presented for each energy.

The quality factors rms ( $\Delta f_s f_c$ %) are displayed in last column containing also the remarks.

In Fig. 1 the SEP corrected IMFPs of Si are presented for four reference samples. The rms% values for  $\Delta \mu$  (uncorrected) and  $\Delta c$  (corrected) IMFPs are also displayed in Fig.1. Fig. 2 represents similar results for Ni. In most cases improvement was found, but never 100% correction, i.e., the difference is partly due to surface excitation, partly to other factors. Comparing the  $\Delta \mu$  and  $\Delta c$  data in Fig. 1. considerable improvement was observed for Si/Ni and some improvement for Si/Ag. The anomaly for Si/Cu can be explained by  $Ar^+$  ion implantation (1-2%), increasing the  $I_{eSi}(E)$  and decreasing  $I_{eCu}(E)$ . The data  $a_{chSi}$  and  $a_{chCu}$  are close. As for Si/Au no correction was found.  $a_{chSi} = 2.5$  and  $a_{chAu} = 3.06$  are also close. The other reason might be the strong angular variation of the differential elastic scattering cross-sections of Au, producing big changes for a slight error in alignment within the very small angular window for 2 keV.

The situation is better for Ni resulting in efficient correction of Ni/Cu and slight correction for Ni/Ag and Ni/Au. For some pairs of elements, somewhat better improvement was achieved by modifying  $a_{chAg}$  and  $a_{chAu}$ . Similar results were found with the DESA 100 spectrometers.

The SEP correction and the  $f_s$  factors were calculated also using Werner's material parameters [3]. Except for some cases, better correction was found with Chen's parameters. Chen's model is different from Werner's [3].

Our procedure [10] proved to be suitable for conducting polymers [2].

## DISCUSSION, CONCLUSIONS

A simple new procedure was elaborated for experimental estimation of the surface-excitation parameter, based on Tanuma's [15] and Chen's [16] models. The reasonable agreement was found between SEP corrected experimental and calculated

elastic- peak intensity ratios and between  $c$  corrected IMFPs and  $T$  calculated data. These results confirm the adequacy of the procedure and the validity of Chen's material parameters for surface excitation. The value of the Chen parameter  $a_{chNi} = 3.61$  was determined experimentally.

The application of NIST SRD 64 (version 3.1 2003) database and EPESWIN (2004) software resulted in better agreement with TPP-2M IMFPs than use of previous versions of this database [10].

In most cases SEP correction reduced the difference between the uncorrected and calculated (TPP-2M) IMFPs. Larger uncertainties occurred for low E (0.2 keV) and 2 keV. Full correction was not achieved. Thus surface excitation can explain only partly the differences between  $\mu$  and  $T$ . The  $P_{se}(E)$  data of Chen (and our new value for Ni) should be applied for correction of Auger and XPS peak intensities applying the relationship  $I(EAES)^{exp} = I(EAES)^{phys} * \exp(-P_{se}(EAES))$ . The case is different from EPES, when SEP is produced by incident and escaping electrons.

The remaining differences between calculated and measured IMFPs can be assigned to several factors such as:

Experimental uncertainties, stability of the spectrometer etc. (random error)

Sample position, alignment for non perfectly plane-parallel sample (systematic error due to the low angular window for 2 keV)

The state of the sample surface (contamination from residual gases), damage ( $Ar^+$  cleaning, roughening), particularly for low E.

Implantation of  $Ar^+$  ions (1-2%), increases  $I_{eS}$  of Si and decreases it for higher Z elements (Cu, Ag, Au)

Validity of the models and of the input parameters for MC simulation (elastic scattering cross-section database, IMFP, SEP parameters).

Our simple procedure is a practical approach. A more exact solution was given for REELS of W by Werner et al [17] and for Ag by Ding et al [18], without communicating  $P_{ses}$  data needed for SEP correction in EPES, AES and XPS

Table 1. Experimental data and MC simulation data for sample pairs  
Notations - R : random, S : systematic, Discrepancy : D

Sample pairs	E(keV)=	0.2	0.5	1	1.5	2	Remark
Si/Ag	R <sub>c</sub> :	0.5959	0.915	0.4218	0.2105	0.154	
	f <sub>c</sub> :	0.9865	1.002	0.87881	0.8289	0.8935	<b>R, f<sub>c</sub>&lt;1</b>
	λ <sub>w</sub> /λ <sub>T</sub>	0.9625	0.9468	0.8708	0.8402	0.9009	<b>S</b>
F <sub>s</sub> f <sub>c</sub> and	Δf <sub>s</sub> f <sub>c</sub> %	1.0155	1.0202	0.9908	0.8377	0.902	<b>6.11</b>
Si/Cu	R <sub>c</sub> :	1.413	0.567	0.2994	0.2607	0.2076	
	f <sub>c</sub> :	1.061	1.0562	1.0417	1.1294	0.9897	<b>R~1</b>
	λ <sub>w</sub> /λ <sub>T</sub>	1.195	0.9808	1.0825	1.182	1.045	<b>R</b>
F <sub>s</sub> f <sub>c</sub> and	Δf <sub>s</sub> f <sub>c</sub> %	1.070	1.0625	1.0459	1.1331	0.9927	<b>6.38</b>
Si/Ni	R <sub>c</sub> :	1.288	0.666	0.311	0.254	0.232	
	f <sub>c</sub> :	1.0605	1.2586	1.150	1.105	1.132	<b>R, f<sub>c</sub>&gt;1</b>
	λ <sub>w</sub> /λ <sub>T</sub>	1.106	1.182	1.0825	1.0943	1.0771	<b>R</b>
f <sub>s</sub> f <sub>c</sub> and	Δf <sub>s</sub> f <sub>c</sub> %	0.8659	1.1086	1.0512	1.0270	1.0625	<b>7.67</b>
Si/Au	R <sub>c</sub> :	2.174	0.3356	0.208	0.256	0.271	
	f <sub>c</sub> :	0.8396	0.8052	0.6767	0.8988	1.122	<b>R, D</b>
	λ <sub>w</sub> /λ <sub>T</sub>	0.9184	0.855	0.9645	0.9637	0.9685	<b>R, f<sub>c</sub>&lt;1</b>
f <sub>s</sub> f <sub>c</sub> and	Δf <sub>s</sub> f <sub>c</sub> %	0.7859	0.755	0.6554	0.8662	1.0867	<b>17.0</b>

The notations in the Table 1. (R, S, D) characterize the terms *fc* (random or systematic) and *w/T*. The similarity of these terms for each E value is remarkable. In the last column the rms% deviations of Δf<sub>s</sub>f<sub>c</sub> averaged for the five energies are indicated.

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