



Modelling of electron transport processes in the near surface region of solids

Summary of the PhD thesis

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Introduction

To achieve a higher accuracy in the quantitative surface analytical applications of the electron spectroscopic methods, a deeper understanding of the electron - solid interactions, leading to energy loss of the probing electron, is needed. The most probable electron-solid interaction resulting in energy loss of the electron within the investigated electron energy range (500-5000 eV) is the collective excitation of the free or nearly free electrons of solids, i.e. the plasmon excitation. The nature of these types of excitations in the near surface region of the solid is different from those taking place deeply inside the solid due to the presence of the solid-vacuum boundary and its effect on the electronic structure of the solid. The differences originated from this boundary effect must be taken into account for the accurate modelling of the electron transport processes in the near surface region.

A significant portion of the transport of the medium and low energy electrons backscattered from solid surfaces takes place in the near surface region of the solid. Due to this fact the measurement and theoretical modelling of the energy distribution of the backscattered electrons (REELS spectra) are very important and effective tools for investigating and understanding the electron transport processes in the near surface region. The theoretical models, describing the electron-solid interactions leading to energy loss of the probing electron close to the sample surface, are reviewed including the comparison of the results of my own numerical calculations based on the different theoretical approaches. Following the demonstration of the derivation of the input parameters necessary for the computer simulation of the electron transport in solids, the results of my Monte Carlo simulations based on different approximations of the electron-solid interactions in the surface region, are reviewed.

The theoretical models describing the energy loss process of electrons have two main groups. One of them contains those descriptions where the electron energy loss process is handled as a Markovian process. This means that the past history of the electron does not have any influence on the actual energy loss and the energy loss process is assumed to be a pure stochastic process. The other group of the models takes into account that the changes in the electron structure of the sample caused by the electron at the earlier stage of its trajectory and the properties of the sample determine the nature of the actual energy loss. The energy loss process is handled as a deterministic process in this case. The fact that the electron interacts with the electric field induced in the sample by itself at the earlier stage of its trajectory (i.e. interference effects) is considered in the case of this last group of theories. Consequently, the rate of this interference effect and the error caused by neglecting it are important questions in the case of modelling of electron transport processes in solids.

The information gained from the investigation of the transport processes of backscattered electrons and the new tools developed for these studies result in a more accurate description of the complex energy loss structures appearing in the energy spectra of X-ray excited photoelectrons (XPS) and Auger-electrons (XAES). Consequently, it increases the accuracy of the information on the electron structure properties of the sample extracted from the experiment. The information, obtained from the modelling and simulations of the electron transport processes, provide opportunities to develop more simple procedures as well yielding the same results as the more complex methods in the case of the fulfilment of some assumptions. These simple but still accurate enough procedures are especially important from the point of view of different applications.

Studied problems and applied methods

The near surface transport processes of electrons, backscattered from solid surfaces, are investigated in the first part of my thesis. Following the review and comparison of the theoretical models (Tung-model, Li-model, Yubero-Tougaard model), describing the electron-solid interactions leading to energy loss of the probing electron close to the sample surface, the applications and results of my Monte Carlo simulations based on the different theoretical approximations are presented. The theoretical models and procedures, yielding the normalized distribution of the electrons - suffered only one inelastic collision - from the measured energy loss spectra (REELS), are presented and compared in detail as well. The influences of the elastic scattering and the interference effect (the interaction between the backscattered electron and the electric field induced by itself in the solid, at earlier stages of its trajectory) on the electron transport processes are investigated in detail using stochastic and deterministic approaches of the electron energy loss process caused by collective excitations. The information gained from the investigation of the transport processes of backscattered electrons and the new tools developed for these studies (with small modifications) result in a more accurate description of the complex energy loss structures appearing in the energy spectra of X-ray excited photoelectrons (XPS), as it is presented in the second part of my thesis. Consequently, the combined applications of these methods increase the accuracy of the information on the electron structure properties of the sample gained from the experimental data. The information, obtained from the detailed analysis of the results derived by the Monte Carlo simulation of the photoelectron transport processes, has provided opportunities to develop a simple statistical model as well, applicable to describe the complex background structure appearing in the experimentally measured XPS (and XAES) spectra due to the collective excitations. The presented procedure gives the same results (in the case of the fulfilment of some assumptions) as the more complex methods without applying any Monte Carlo simulation technique, as it is demonstrated.

Applied experimental techniques

The energy loss distributions of electrons backscattered from solid surfaces, i.e. the REELS spectra were measured using the home built ESA 31 electron spectrometer of ATOMKI. A LEG-62 electron gun was used to produce electrons with primary energy of 0.1-5 keV with the option to be accelerated up to 10 keV. The incidence angle of the primary electron beam was 50° and the angle of the analyzed beam was 0° with respect to the surface normal of the sample. The energy resolution of the electron spectrometer at the primary electron energy of 5 keV was 1.5 eV.

The analysed Fe 1s and Ge 2s photoelectron spectra were measured using the Tunable High Energy XPS facility at the BW2 beamline of HASYLAB at DESY (Deutsches Elektronen Synchrotron, Hamburg). The synchrotron provides linearly polarized, monochromatic photons within the 2.2-11 keV energy range. A SCIENTA SES-200 electron spectrometer with a hemispherical energy analyser was applied to detect the excited photoelectrons. The angle of incidence of the photon beam was 45° and the angle of the analyzed electron beam was 0° with respect to the surface normal of the sample. The analyser was used in FAT (Fixed Analyser Transmission) mode with an energy resolution of ~ 0.2 eV. The total instrumental energy broadening was ~ 0.5 eV.

List of models and software applied in the presented calculations

List of software developed by me:

1. A computer code for calculating the differential inverse inelastic mean free path (DIIMFP), the differential surface excitation probability (DSEP), the inelastic mean free path (IMFP) and the total surface excitation probability (SPE) of electrons on the basis of the dielectric theory and the Tung-theory
2. A computer code for calculating the position dependent differential inverse inelastic mean free path, the position-dependent inverse inelastic mean free path and the position-dependent surface excitation probability of electrons using the dielectric theory and the Li-theory (suitable for parallel computer systems)
3. Software for calculating: (i) the effective differential inelastic scattering cross sections of electrons backscattered from solid surfaces and reached the actual value of the maximum depth inside the sample using the Li-theory and the “V-shape” trajectory approximation and (ii) the energy distribution of backscattered electrons suffered a single inelastic excitation applying these effective cross sections and using the same weighting procedure as applied in the Youbero-Tougaard model
4. A computer code for deriving the energy loss distribution of electrons suffered a single inelastic excitation from the measured REELS spectra based on the Tougaard-Chorkendorff algorithm
5. A computer code (including a Fast Fourier Transformation (FFT) algorithm) for deriving the normalised DIIMFP and DSEP distributions from experimental REELS spectra using the W-algorithm proposed by Werner and an additional software for calculating the elements of the coefficient matrices defined in the Fourier space together with the necessary tensor elements
6. A Monte Carlo simulation code for modelling the transport processes of electrons backscattered from solids using the quasi-elastic approximation (path length distribution, elastic and inelastic collision statistics, maximum depth distribution, etc.)
7. A computer code for indirect, fast modelling the energy loss distribution of electrons backscattered from solid surfaces using a FFT algorithm
8. A direct spectrum simulation Monte Carlo code using position-dependent inelastic scattering cross sections of the electrons and the Monte Carlo model developed by me
- 9., A Computer code for calculating the average energy loss of electrons backscattered from solid surfaces through collective excitations (bulk and surface plasmon excitations), using stochastic and deterministic approaches for describing the energy loss process on the basis of the Vicanek-theory in the case of “V-shape” trajectory approximation and in the case of real electron trajectory, including Monte Carlo code (suitable for parallel computer systems)
10. A Monte Carlo code for simulating the transport processes of photo- (and Auger-) electrons excited by X-ray photons (partial depth distribution functions, path length distributions, collision statistics, etc.)
11. A FFT algorithm based spectrum deconvolution code for implementing the partial intensity analysis method
12. A parameter optimisation code for applying the statistical model (developed by me) of the complex energy loss structure appearing in the energy loss distributions of the photo- and Auger electrons, including the FFT procedure

List of other software used in the present work: the differential elastic scattering cross section of electrons was taken from the NIST SRD 64 database; the Yubero-Tougaard XPS software developed by Tougaard and Yubero was applied to calculate the energy loss distribution of photoelectrons suffered a single inelastic excitation, according to the Yubero-Tougaard theory

New scientific results

1. Direct spectrum simulation Monte Carlo procedure based on the position-dependent inelastic scattering cross section of electrons

(a.) A Monte Carlo model has been developed to investigate the near surface electron-solid interactions. This high precision direct spectrum simulation Monte Carlo model accounts for the spatial variation of the surface excitation probability and of the probability distribution of energy loss of electrons moving close to the solid surface both sides of the solid-vacuum interface. [1, 2]

(b.) The required position dependent inelastic electron scattering cross sections were numerically calculated by means of the Li-model based on the dielectric theory, using a parallel computer system. Implementing this Monte Carlo model, a direct spectrum simulation Monte Carlo code has been developed, which allows to take into account the surface excitations during the electron transport at both sides of the surface-vacuum interface, on the basis of a physically correct picture, including the effect of elastic scattering. Energy distributions of electrons - with the primary energy of 0.5-3 keV- backscattered from *Si* and metallic *Cu*, *Fe* samples, have been simulated by using this Monte Carlo procedure. A satisfactory agreement has been found between the simulated and measured spectra, confirming the validity of the presented procedure. [1]

(c.) Since the presented Monte Carlo procedure is able to take into account the contributions from the surface excitations -originated from the vacuum side and from the solid side excitations, respectively- appearing in the spectrum accurately, the rate of these excitations has been investigated. It has been pointed out that the ratio of the contributions from these two types of surface excitations appearing in the spectra are different in the case of electrons with medium and low primary energies. This difference is attributable to the difference between the average depths reached by the electrons inside of the sample and the thickness of the surface excitation zone. [1]

2. Comparison of the Yubero-Tougaard (YT) and the Li theories in the case of Si

(a.) A model and computer code have been developed for calculations of the effective inelastic scattering cross section of the electrons reached the actual value of the maximum depth by using the Li-theory instead of the more complicated YT-theory and the contribution of the electrons suffered a single inelastic excitation is derived from these effective cross sections, using the same weighting procedure as applied in the YT-model. Applying this procedure, the contributions of electrons with primary energies of 800 and 2000 eV , backscattered from a *Si* sample and suffered only a single inelastic scattering, have been calculated and compared with the results of the YT-model, using the same input parameters (i.e. the same model dielectric function) in the case of various scattering geometries. It has been pointed out, that the presented procedure, based on the more simple Li-theory, can provide approximately the same results as the YT-model - using the same assumption on the electron trajectories as applied in the YT-model and the same input parameters for the calculations – although, opposing to the YT-theory, the surface and bulk excitations are completely separated and the interference effect is ignored in the Li-theory. In addition, the results of the theoretical calculations differ from the available experimental data in the case of both procedures discussed above.

(b.) This difference is attributable to the inaccurate description of elastic electron scattering. This assumption has been verified by using my Monte Carlo simulation procedure (accounting accurately for the effect of multiple elastic electron scattering as well) with the same spatially varying inelastic scattering cross section applied in the calculation discussed above. A much better agreement was found in this case comparing the results derived from the Monte Carlo simulated spectra with those derived from the experimentally measured energy distributions of backscattered electrons, than in the case of applying the YT-model, for every primary electron energies (800 and 2000 eV) and geometrical configurations. This means that the error introduced by neglecting the interference effects is considerably smaller, than the error caused by the inaccurate consideration of the effect of elastic electron scattering even at relatively low (800 eV) primary electron energy and in the case of a smooth elastic scattering cross section as a function of the scattering angle (the case of Si) as well. Furthermore, in contrast to the YT-model, the presented Monte Carlo model is able to calculate the whole energy loss distribution of the backscattered electrons.

3. Investigation of average energy loss of electrons backscattered from solid surfaces using stochastic and deterministic approximations of the energy loss processes

(a.) The average energy loss of electrons having 500 eV primary energy, backscattered from a Si surface, is investigated in the next section of the thesis, using different geometrical configurations (normal emission and $\alpha=0^\circ, 5^\circ, 10^\circ, 30^\circ, 50^\circ, 70^\circ$ angles of incidence respect to the surface normal) in the case of the “V-shape” (or straight line) trajectory approximation and in the case of real electron trajectories derived by Monte Carlo simulation, respectively, using deterministic and stochastic approaches for describing the electron energy loss caused by collective excitations during the electron transport. Analyzing the results, it is concluded that the effect of the interference appears to be significant only for the average energy loss by surface excitation which is attributable to the fact that the rate of the oscillations in the average energy loss caused by the interference is comparable with the value of the average energy loss of electrons by surface excitations. Furthermore, the rate of this oscillation is lower in the case of electrons penetrating deeper inside the solid than for those backscattered from shallower regions for the same scattering geometry and electron energy. This is attributable to the fast decay of the charge density oscillations induced by the incoming electron at the initial part of its trajectory. Additionally, the remarkable feature of the oscillations predicted by the “V-shape” trajectory approximation is less pronounced in the case of the real electron trajectory approximation. This difference is attributable to the smaller overlap of the electron trajectories in the real case due to the effect of elastic scattering.

(b.) Analyzing the inelastic collision statistics of the backscattered electrons it is concluded that the neglect of the interference does not cause a significant error, even in the case when the largest error is predicted by the straight trajectory approximation (i.e. normal incidence and emission) and the primary energy of the electrons is low (e. g. 500 eV).

These results confirm my statements made in the previous point regarding the rate of the interference effects.

4. The effect of the polarization of the exciting X-ray beam on the statistics of inelastic collisions of the excited photoelectrons during their transport

A Monte Carlo simulation code has been developed using the quasi-elastic Monte Carlo approach, accounting for the anisotropic angular distribution of the ejected photoelectrons and

accurately modelling the photoelectron transport processes inside the solid. The effect of the polarization of the exciting X-ray beam on the inelastic collision statistics of the excited photoelectrons has been investigated applying this Monte Carlo code. A difference has been pointed out between the statistics of the inelastic collisions suffered by the photoelectrons excited by linearly polarized and unpolarized (or circularly polarized) photon beams during their transport. This difference is attributable to the different angular distributions of the ejected photoelectrons excited by polarized and unpolarized (or circularly polarized) X-rays, respectively.

5. Analysis of the Fe 1s XPS spectrum excited from metallic iron

The energy distribution of Fe 1s electrons excited from Fe metal by X-rays has been modeled using the inelastic collision statistics of the excited photoelectrons calculated by means of the Monte Carlo simulation mentioned above and applying a spectrum-decomposition algorithm based on the partial intensity analysis method. The applied procedure, combining with the energy loss distributions of electrons derived from the experimentally measured REELS spectra using the W-algorithm mentioned previously, provides an opportunity for high precision analysis of the experimentally measured XPS spectra. The contributions of the intrinsic excitations (attributed to the suddenly created core hole) appearing in the measured XPS spectrum have been determined more accurately than the earlier results, applying this combined procedure to eliminate the contributions of the excitation processes occurred during the transport of the photoelectrons (extrinsic excitations). This confirms that the result, published earlier in the literature, overestimates the contribution of both the bulk and the surface intrinsic excitations, as a consequence of the inaccurate energy loss distributions and the inappropriate background estimation procedure used. The present results have been confirmed by the result derived by using the Yubero-Tougaard XPS model calculation procedure as well.

6. The extended Hüfner-model

(a.) A statistical model has been developed that describes the complex background structure - appearing in the experimentally measured XPS (and XAES) spectra due to the collective excitations - without applying any Monte Carlo simulation technique. Additionally, it has been demonstrated that this statistical approach gives the same result (in the case of the fulfilment of the given assumptions) as the more complex and complicated partial intensity analysis method [3].

(b.) A parameter optimization code has been developed using the statistical approach mentioned above applying a Fast Fourier Transform algorithm to accelerate the convolution procedure. The probabilities of plasmon excitations, appearing in the Ge 2s photoelectron energy distributions excited by X-ray photons of different energies (4000 eV, 6000 eV, 8000 eV) have been determined using this statistical approach and parameter optimization code. The applied distributions of the energy lost by the electron in the given single excitation event, have been derived from the experimental Ge REELS spectra using the W-algorithm mentioned previously. These distributions allow to describe the energy loss process of the travelling photoelectrons with a high accuracy. A good agreement has been found comparing the present plasmon excitation probabilities with those derived by using the partial intensity analysis method, confirming the statements above. [3, 4, 5]

Bibliography

[1] M. Novák: *Monte Carlo simulation of energy loss of electrons backscattered from solid surfaces*

Surface Science **602** (2008) 1458

[2] M. Novák, R. J. Berezsky, Z. M. Zhang, Z. J. Ding, J. Tóth, D. Varga, K. Tókési: *Energy loss spectra of iron*

Surface and Interface Analysis **40** (2008) 522

[3] M. Novák, L. Kövér, S. Egri, I. Cserny, J. Tóth, D. Varga and W. Drube: *A simple statistical model for quantitative analysis of plasmon structures in XPS and Auger spectra of free-electron-like materials*

Journal of Electron Spectroscopy and Related Phenomena **163** (2008) 7

[4] M. Novák, S. Egri, L. Kövér, I. Cserny, W. Drube, W. S. M. Werner: *Energy dependence of electron energy loss processes in Ge 2s photoemission*

Surface Science **601** (2007) 2344

[5] L. Kövér, M. Novák, S. Egri, I. Cserny, Z. Berényi, J. Tóth, D. Varga, W. Drube, F. Yubero, S. Tougaard, W. S. M. Werner: *Intrinsic and extrinsic excitations in deep core photoelectron spectra of solid Ge*

Surface and Interface Analysis **38** (2006) 569