Factor analysis of inelastic electron scattering cross section spectra of Si, Fe and iron silicides FeSi$_2$, Fe$_5$Si$_3$

A Yu Igumenov$^1$, A S Parshin$^1$, Yu L Mikhlin$^2$, T A Andryushchenko$^1$ and V O Kanzychakova$^3$

$^1$ Reshetnev Siberian State University of Science and Technology, 31 Krasnoyarsky Rabochy Av., Krasnoyarsk, 660037, Russia
$^2$ Institute of Chemistry and Chemical Technologies of the Siberian Branch of the Russian Academy of Sciences, 660036, Krasnoyarsk, Russia
$^3$ OOO «RN-KrasnoyarskNIPIneft», 660022, Krasnoyarsk, Russia

E-mail: igumenovau@mail.ru

Abstract. The inelastic electron scattering cross-section spectra of Si, Fe and iron silicides FeSi$_2$, Fe$_5$Si$_3$ were calculated from the experimental reflected electron energy loss spectra as the product of the average inelastic mean free path and the differential cross section of the inelastic electron scattering. The inelastic electron scattering cross-section spectra were studied using factor analysis. This method allowed us to quantitatively separate the surface and volume contributions to the spectra, and determine the energy of the bulk plasmon more accurately than it is possible using traditional methods.

1. Introduction

The creation of nanoelectronics, nanophotonics and spintronics devices based on silicon and transition metals should be provided with a number of requirements for the structure synthesis methods, and for the analysis methods. Electron spectroscopy methods such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and reflection electron energy loss spectroscopy (REELS) are widely used for the study of these structures. The research of Fe-Si system is perspective from fundamental and applied points of view [1]. However, the elemental analysis of iron silicides by XPS and REELS is difficult, because the energies of photoelectron and plasmon peaks for silicides of different compositions are close to each other [2].

The inelastic electron scattering cross section spectra (so-called $K_{\lambda}$-spectra [3]) are the products of inelastic mean free path $\lambda$ and inelastic scattering cross-section $K(E_0, T)$, where $T$ is energy loss, calculated as the difference between the primary electron beam energy $E_0$ (zero loss) and the reflected electron energy $E$, $T = E_0 - E$. The advantage of inelastic electron scattering cross section spectra is that, unlike the REELS, the $K_{\lambda}$-spectra exclude multiple excitations losses, and the intensities are determined in absolute units. These spectra are also more sensitive to changes in the of the primary electron energy and the emission angle [4–6]. Inelastic electron scattering cross section spectroscopy allows determining the elemental composition with much greater accuracy than the traditional REELS [6].

In this paper, we used factor analysis (FA) to study the inelastic electron scattering cross section spectra of Si, Fe and silicides FeSi$_2$, Fe$_5$Si$_3$. This method allowed us to solve the actual problem of decomposition spectra to different origin contributions, quantify it and determine the volume plasmon energies more accurately than the traditional methods. The study of electron energy loss processes by...
decomposition spectra to the different origin contributions is one of the most important problems of electron spectroscopy, which can be used to assess the effect of surface excitations on the REELS, XPS and AES [1-15]. Earlier, we studied Si, Fe, and FeSi₂, Fe₃Si₃ silicides in [16-21] using the author’s method of spectra decomposition to loss peaks.

2. Experimental Part

We investigated commercial single crystal Si(100) substrates. The Fe samples were fabricated by high-vacuum thermal evaporation. Iron silicides FeSi₂, Fe₃Si₃ produced by melting a mixture of iron and silicon in atomic ratios of 1×2, 5×3 under high vacuum conditions using the vacuum deposition installation UVN-2M-1. The mixture was maintained at the melting temperature for 15 min, after which the annealed alloy was crushed and again melted for 15 min. The 1 mm thick washers were cut of bulk samples. Before the spectroscopic investigations the washers were polished.

The spectroscopic experiments were carried out using a photoelectron spectrometer SPECS (German production) equipped with the spherical energy analyzer PHOIBOS MCD9, double anode X-ray tube as an X-ray source, and a Microfocus EK-12-M electron gun (STAIB Instruments) for excitation of the REEL spectra. The probing and reflected electrons angles were respectively α₀ = 59°, α₀ = 0°. The surface contaminations, protecting layers and oxide layers were removed applying Ar⁺ ion etching (accelerating voltage of 2.5 kV, ion current of 15 μA) with an ion source PU-IQE-12/38 (SPECS) in the analytical chamber of the spectrometer before the REELS measurements; the completeness of the procedure was controlled via the relevant photoelectron and Auger spectra. REEL spectra were acquired in the interval of 150 eV below the elastic peak with an energy step of 0.1 eV. Energy loss T was calculated as the difference between the primary electron beam energy E₀ (zero loss) and the reflected electron energy E, T = E₀ - E. The primary electron beam energies were 300, 600, 1200, 1900, 3000 eV, and the full width at half-maximum (FWHM) of the primary electron beam was less than 1 eV.

The inelastic electron scattering cross section spectra were calculated from the experimental reflection electron energy loss spectra with the software package QUASES™ XS REELS (Quantitative Analysis of Surfaces by Electron Spectroscopy cross section determined by REELS) [22] based to the algorithm suggested in [23]. Inelastic electron scattering cross section spectra indicate the probability of electron energy loss T in a single scattering event. The values of the maxima of these spectra determine the probabilities of single energy loss for surface or volume excitations. Due to the absolute intensity values of the energy loss, the inelastic electron scattering cross section spectra, compared with the traditional reflected electron energy loss spectra, allow to compare and analyze the spectra of different materials not only by peak energies, but also by its intensities.

Factor analysis is a statistical method widely used in electron spectroscopy [10]. Factor analysis is using to study the spectra representing a linear combination of components with concentration varying during some process. This method is relevant for AES, where the simple decomposition of spectral lines into components is impossible, because in the Auger spectra, in addition to the chemical shift, the shape of the lines also changes [11–13]. In electronic Auger spectroscopy, FA is used for the processes of layer-by-layer etching of thin films [12], to study the processes of adsorption [13, 14].

In [15], the XPS method was used to study chemical changes induced in a natural pyrite crystal (Fe₅S₈) under the influence of a He⁺ beam. It is shown that the application of conventional analysis together with FA can be a powerful technique to identify elements, when changes in binding energy and broadening occur simultaneously. Through a combination of conventional analysis of the XPS spectra and FA, the full signal Fe 2p XPS was analyzed.

As remarked in [15], the important advantage that FA, in contrast with conventional analysis, uses the whole set of spectra, along the full ion bombardment process (while conventional fits each spectrum at a time), and it does not require neither preconditions nor predefined lineshapes to start with. FA does not require the previous knowledge of the shape and position of XPS yields, allowing us to obtain both these results just by using only the experimental yields. On the other hand, this is the reason of the noisy aspect and poorer definition of these lineshapes compared to conventional results.

The inelastic electron scattering cross section spectra obtained at different primary electron energies or different probing and reflected electron angles are data series. The relative contributions of
surface and volume losses vary systematically depending on experimental conditions. In [5], factor
analysis is used as a method for decomposing the inelastic electron scattering cross section
spectra into two contributions (volume and surface) in the study of Si and SiO₂.

Factor analysis is performed as follows. The matrix with intensity values of energy loss at different
energies of the primary electrons (columns) is prepared. At the first stage, the main factors
(components) are selected, which together give a spectrum close to the original one. After, from the
obtained matrix two columns with the highest intensities are distinguished - the main abstract factors
(main components). Then the data is transformed by multiplying with the rotation matrix R (target
rotation):

\[
R = \begin{bmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{bmatrix}
\]

Target rotation transforms abstract factors into physically significant ones by achieving a
predetermined criterion of peak shape. In [5] the Lorentz form of the peak corresponding to the
excitation of a volume plasmon (so called volume-loss component or volume factor) was adopted, and
by changing the angle \( \varphi \), the shape of the component is reached close to the Lorentz peak, which has a
maximum at the energy of the volume plasmon. Then additional rotation was achieved the most
correct form of the surface-loss component (surface factor). Next, the source spectrum is reconstructed
as a linear combination of two factors.

In this work, in contrast to [5], the shape of the peaks was chosen not close to the shape of the
standard Lorentz peaks, but to the shape of the Tougaard peaks [24]:

\[
\lambda K = \frac{BT}{(C-T^2)^2 + DT^2}
\]

\( B, C, D \) are fitting parameters and have special values for different elements [21]. The peak intensity
depends on parameter \( B \), peak energy depends on parameter \( C \) but does not correspond to it explicitly,
peak width and, indirectly, peak energy depend on parameter \( D \). Tougaard functions (universal classes
of inelastic electron scattering cross section) are used to describe inelastic electron scattering cross
section spectra.

The Tougaard three-parameter function has been modified:

\[
\lambda K = \frac{BT}{\left(T_p \left(-T_p + \sqrt{4T_p^2 + D}\right) - T_p^2\right) + DT^2}
\]

where the parameter \( T_p \) corresponds to the position of the peak maximum in absolute units.

3. Results and discussion

Figures 1–8 show the \( Kz \)-spectra of Si, Fe and silicides FeSi₂, Fe₅Si₃ for \( E_0 = 300 \) eV and \( E_0 = 3000 \)
eV. The main peak energy is 16.6 ± 0.3 eV for Si, 22.4 ± 0.4 eV for Fe, 20.6 ± 0.2 and 20.0 ± 0.7 eV
for FeSi₂ and Fe₅Si₃ respectively. These values are close to the energies of the volume plasmons of
these materials in the REELS spectra [25]. The energies are determined from spectra in a differential
form, since this approach allows one to determine the energies more accurately. In the spectra of
silicon at energy loss 10.8 ± 0.1 eV, a shoulder due to the presence of a surface plasmon is observed
[25]. In the spectra of Fe peak at energy of 15.4 ± 0.4 eV corresponds to the surface plasmon, peak at
energy of 6.1 ± 0.2 eV corresponds to the interband transition [25].

These spectra are approximated by a linear combination of surface electronic excitation (surface
factor) and volume -loss components (volume factor). When real factors were obtained, the angle was
selected in such a way that the volume factor was well approximated by the Tougaard peak, similarly
for the surface factor, but its shape remained irregular, indicating the presence of several unresolved
peaks of different origin.
Table 1 presents the energy positions of the factor maxima. The obtained values of the energies of the volume and surface factor are close to the experimental data for the energy of the volume and surface plasmon. The energies of the bulk plasmon for iron silicides in experimental REELS are often the same. As can be seen from table 1, the energies of the volume factor (corresponding to the volume plasmon) for FeSi$_2$ and Fe$_5$Si$_3$ have values that differ by 0.3 eV. This method gives a high accuracy in determining the energy of the bulk plasmon using the criterion of similarity of the volume factor shape and the Tougaard peak.

| Sample    | Surface factor | Volume factor |
|-----------|----------------|---------------|
| Si        | 10.8           | 16.8          |
| FeSi$_2$  | 14.9           | 20.9          |
| Fe$_5$Si$_3$ | 13.7         | 21.2          |
| Fe        | 6.8            | 23.2          |

The ratio of the volume factor energy loss to the surface factor energy loss is close to $\sqrt{2}$, which is well-known from the classical plasmon theory for free electron gas [26]. As shown in [18], for Fe in the low-energy region, the interband transition at energy loss 6.87 eV has the highest intensity, which corresponds to the surface factor energy obtained in this work.

![Figure 1](image1.png)  
**Figure 1.** Si spectra at $E_0 = 300$ eV.

![Figure 2](image2.png)  
**Figure 2.** Si spectra at $E_0 = 3000$ eV.

![Figure 3](image3.png)  
**Figure 3.** Fe spectra at $E_0 = 300$ eV.

![Figure 4](image4.png)  
**Figure 4.** Fe spectra at $E_0 = 3000$ eV.
Figure 5. FeSi$_2$ spectra at $E_0 = 300$ eV.

Figure 6. FeSi$_2$ spectra at $E_0 = 3000$ eV.

Figure 7. Fe$_5$Si$_3$ spectra at $E_0 = 300$ eV.

Figure 8. Fe$_5$Si$_3$ spectra at $E_0 = 3000$ eV.

The primary energy dependences of the factor amplitude are shown on the figures 7 and 8. Volume factor has gradually increasing primary energy dependence of amplitude which indicate its volume origin. Surface factor has gradually decreasing primary energy dependence of amplitude. Surface-loss component was unresolved in $K\alpha$-spectra for FeSi$_2$ and Fe$_5$Si$_3$ but FA allows determining its energy, intensity and origin.

Figure 9. Primary electron energy dependence of volume factor amplitudes.

Figure 10. Primary electron energy dependence of surface factor amplitudes.
The factor analysis, along with the method of $K\lambda$-spectra decomposition to loss components described by Tougaard functions [16-21], can be used to quantify changes in the contributions of various origin to the inelastic electron scattering cross section spectra.

4. Conclusions

The applicability of factor analysis to the separation of volume and surface contributions in the inelastic electron scattering cross section spectra of Si, Fe and silicides FeSi$_2$, Fe$_2$Si$_3$ is substantiated.

The separation and quantitative estimation of the surface and volume origin contributions in the inelastic electron scattering cross section spectra of Si, Fe and silicides FeSi$_2$, Fe$_2$Si$_3$ was carried out using factor analysis. The dependences of the amplitudes of the components on the energy of the primary electrons reflect its surface and volume origin.

References

[1] Galkin N G, Polyarnyi V O and Gouralnik A S 2004 Thin Solid Films 464-465 pp 199-203
[2] Ohtsu N, Oku M, Satoh K and Wagatsuma K 2013 Appl. Surf. Sci. 264 pp 219-224
[3] Tougaard S and Chorkendorff I 1987 Physical Review B 35 pp 6570-6577
[4] Jin H, Yoshikawa H, Iwai H, Tanuma S and Tougaard S 2009 Journal of Surface Analysis 15 p 321-324
[5] Jin H, Shinotsuka H, Yoshikawa H, Iwai H, Tanuma S and Tougaard S 2010 Journal of applied physics 107 pp 083709
[6] Jin H, Shinotsuka H, Yoshikawa H, Iwai H, Arai M, Tanuma S and Tougaard S 2013 Surface and Interface Analysis 45 pp 985-992
[7] Gergely G 2002 Prog. Surf. Sci. 71 pp 31-88
[8] Orosz G T, Gergely G, Gurban S, Menyhard M, Toth J, Varga D and Tougaard S 2003 Vacuum 71 pp 147–152
[9] Tougaard S 1988 Surface And Interface Analysis 11 pp 453-472
[10] Andryushechkin B.V., El'cov K.N., Klimov A.N. 2003 Eksperimental'nya tekhnika, metody i metodika raboty s galogenami na poverhnosti metallov (Moscow, Nauka)
[11] Malinowski E R and Howery D G 1980 Factor Analysis in Chemistry (New York, Wiley)
[12] Gaarenstroom S W 1982 Journal of Vacuum Science and Technology 20 pp 458–461
[13] Steffen J and Hofmann S 1988 Surface Science 202 pp. L607–L611
[14] Hofmann S and Steffen J 1989 Surface And Interface Analysis 14 pp 59–65
[15] Ruano S, Gustavo D and Pomiro F 2018 Surface Science 667 pp 138-147
[16] Parshin A S, Igumenov A Yu, Mikhlin Yu L, Pchelyakov O P and Zhigalov V S 2016 Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika 59 10 pp 82-86
[17] Parshin A S, Igumenov A Yu, Mikhlin Yu L, Pchelyakov O P and Zhigalov V S 2017 IOP Conference Series: Materials Science and Engineering 255 pp 012019 1-7
[18] Parshin A S, Igumenov A Yu, Mikhlin Yu L, Pchelyakov O P and Zhigalov V S 2016 Physics of the Solid State 58 pp 908-914
[19] Parshin A S, Igumenov A Yu, Mikhlin Yu L, Pchelyakov O P and Zhigalov V S 2016 Technical Physic 61 (9) pp 1418-1422
[20] Parshin A S, Igumenov A Yu, Mikhlin Yu L, Pchelyakov O P, Nikiforov A I and Timofeev V A 2015 Semiconductors 49 4 pp 423-427
[21] Parshin A S, Igumenov A Yu, Mikhlin Yu L, Pchelyakov O P, Nikiforov A I and Timofeev V A 2014 Vestn. Sib. Gos. Aerokosm. Univ. 4 (56) pp 230-235
[22] Tougaard S QUASES – Software packages to characterize surface nano-structures by analysis of electron spectra, available at: http://www.quases.com/
[23] Tougaard S and Chorkendorff I 1987 Physical Review B 35 pp 6570-6577
[24] Tougaard S 1997 Surface And Interface Analysis 25 pp 137-154
[25] Lifshits V G and Lunyakov Yu V 2004 Electron Energy Loss Spectra of Surface Phases on Silicon (Vladivostok: Dal'nauka)
[26] Raether H 1988 Surface Plasmons on Smooth and Rough Surfaces and on Gratings (Berlin, Springer-Verlag)