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Reflection electron energy loss spectroscopy of structures based on silicon and transition metals

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Abstract. The investigation of iron silicides FeSi₂, FeSi and Fe₅Si₃ with the methods of reflection electron energy loss spectroscopy and inelastic electron scattering cross-section spectroscopy was carried out. It is shown that the shape and peak energy position of electron energy loss spectra are almost identical to silicides with different composition, while the amplitude of inelastic electron scattering cross-section spectra decreases with increasing of iron content. The decomposition of inelastic electron scattering cross-section spectra of FeSi₂, FeSi and Fe₅Si₃ to Tougaard peaks is used for unresolved energy loss peaks analysis, determination its energies and identification bulk and surface peaks. The amplitude of fitting peak describing bulk plasmon excitation can be used for identification of the iron silicides with different composition.

1. Introduction

Fe-Si system is promising for basic research and applied applications in devices of nanoelectronics, spintronics and photonics [1]. Elemental analysis of ferrosilicon structures is complicated by the formation of the silicides because the chemical shifts in X-ray photoelectron spectra (XPS) practically do not depend on the iron silicide composition [1, 2] and bulk plasmon energy in reflection electron energy loss spectra (REELS), obtained by different authors give conflicting results [3].

In this paper the results of iron silicides investigation with the methods of REELS and inelastic electron scattering cross-section spectroscopy are presented. It is shown that the amplitude of the inelastic electron scattering cross-section spectra is more sensitive to the elemental composition of iron silicides that REELS peaks energies. The decomposition of experimental inelastic electron scattering cross-section spectra to the Tougaard peaks is used for unresolved loss peaks analysis, determination its energies and identification bulk and



surface peaks. The amplitude of fitting peak describing bulk plasmon excitation can be used for identification of the iron silicides with different composition.

2. Experimental

Iron silicides FeSi_2 , FeSi , Fe_5Si_3 produced by melting a mixture of iron and silicon in atomic ratios of 1×2 , 1×1 , 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 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 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 E_0 (zero loss) and the reflected electron energy E , $T = E_0 - E$. 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 (so-called $K\lambda$ -spectra [4]) which are the products of inelastic mean free path λ and inelastic scattering cross-section $K(E_0, T)$ were calculated from the experimental reflection electron energy loss spectra with the software package QUASESTM XS REELS (Quantitative Analysis of Surfaces by Electron Spectroscopy cross section determined by REELS) [6] based to the algorithm suggested in [7]. Inelastic electron scattering cross section spectra indicate the probability of electron energy loss T in a single scattering event. $K\lambda$ -spectra can be used for quantitative determination of element concentrations in two-component composite structures. The ability of quantitative determination of atomic element concentrations in $\text{Fe}_x\text{Si}_{1-x}$ [8, 9], $\text{Mn}_x\text{Si}_{1-x}$ [7] and $\text{Ge}_x\text{Si}_{1-x}$ [10] systems were investigated earlier with the dependence of the maximum value of $K\lambda$ -spectra for the standard samples.

3. Results and discussion

3.1. The comparative analysis of the reflection electron energy loss spectra and the inelastic electron scattering cross-section spectra

Fig. 1 (a) shows REELS for elemental Si, Fe and silicides FeSi_2 , FeSi , Fe_5Si_3 , obtained at the primary electron energy 1200 eV. The main peak energy for Si is 17.1 ± 0.2 eV, for Fe - 22.8 ± 0.4 eV, for FeSi_2 , FeSi , Fe_5Si_3 – respectively, 20.8 ± 0.1 , 21.0 ± 0.1 , 21.5 ± 0.1 eV. These values are close to the energies of bulk plasmons of these materials [3]. These energies defined using the spectra in differential form, since this form is more accurate and allows determining the energy of the unresolved bulk plasmon in spectra of iron. On the spectra of silicon and iron silicides multiple energy loss due to excitation of bulk plasmons are present. At energy loss of 10.7 ± 0.3 eV in the spectrum of silicon the feature corresponding to the excitation of surface plasmon [3] is observed. In the spectrum of iron intense losses at the low-energy region and the one-electron transition M_{23} with energy losses 54.3 ± 0.3 eV [11-14] are observed.

As can be seen from the Fig. 1 (a), REELS spectra of iron silicides FeSi_2 , FeSi , Fe_5Si_3 slightly different in bulk plasmon energy and are almost identical in shape and intensity, which is measured in arbitrary units. The surface plasmon is unresolved in the spectra of iron silicides. Elemental Si and Fe stand out: silicon has a much lower energy of bulk plasmon and iron has a more extended form, due to intense energy loss for surface excitation.

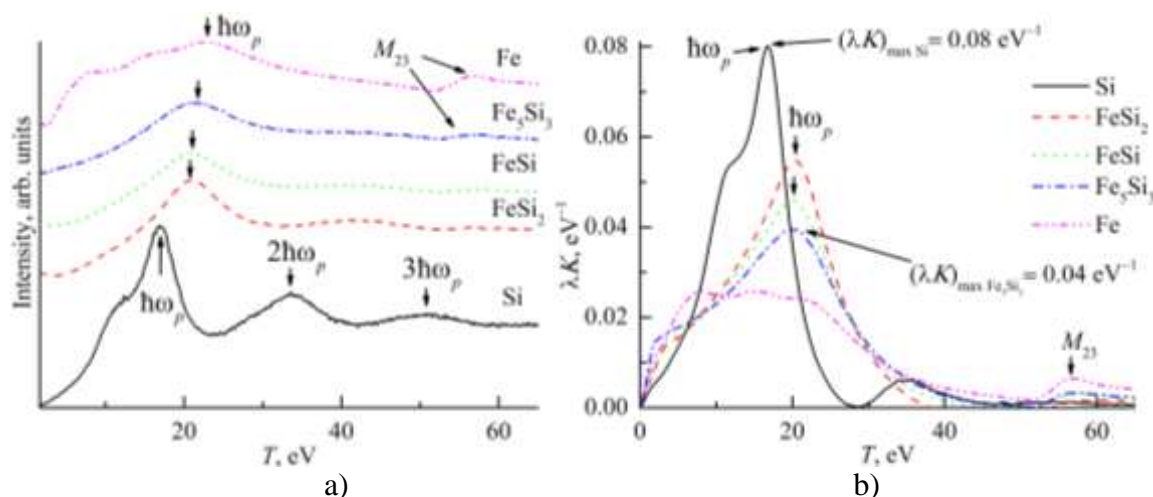


Figure 1. Reflection electron energy loss spectra (a) and inelastic electron scattering cross-section spectra (b)

At Fig. 1 (b) the comparison of the inelastic electron scattering cross-section spectra for silicides FeSi_2 , FeSi , Fe_5Si_3 and elemental Si, Fe, obtained with primary electron energy 1200 eV, is carried out. Differences in $K\lambda$ -spectra of these materials are more significant than in the REELS. First, the spectrum amplitude decreases with increasing of Fe content. Secondly, the spectrum width increases with increasing of Fe content. The main peak energy in REELS is almost independent of primary electron energy and increases monotonically with increasing of primary electron energy in inelastic electron scattering cross-section spectra. With increasing of primary electron energy increases the depth analysis, resulting in decreasing of surface-like excitation intensity and increasing of bulk-like excitation intensity. This intensity redistribution causes a change of whole spectrum shape and peak position. This assumption is confirmed by simulation of $K\lambda$ -spectrum as a superposition of two unresolved peaks [15]. The presence of unresolved surface plasmon in $K\lambda$ -spectra of iron silicides manifests in decreasing of FWHM.

In Table 1 the bulk plasmon energies obtained using experimental REELS and $K\lambda$ -spectra in differential form are shown.

Table 1. The bulk plasmon energies (eV)

	REELS	$K\lambda$ -spectra	Fitting $K\lambda$ -spectra
Silicide	The bulk plasmon energy, eV		
FeSi_2	20.8 ± 0.1	20.6 ± 0.2	21.1 ± 0.0
FeSi	21.0 ± 0.1	20.0 ± 0.6	20.9 ± 0.1
Fe_5Si_3	21.5 ± 0.1	20.0 ± 0.7	20.7 ± 0.0

Thus, firstly, the peaks positions in inelastic electron scattering cross-section spectra depend on the different processes relative contributions and may differ from the true energy loss peaks. In determining the energy peaks in $K\lambda$ -spectra the obtained values can be influenced by surface excitations. Second, the composition of the iron silicides can not be reliably determined from the bulk plasmon energy in REELS and $K\lambda$ -spectra, because silicides of different composition has an overlap of bulk plasmon energy ranges.

3.2. The fine structure of inelastic electron scattering cross-section spectra

The variation of inelastic electron scattering cross section spectrum shape with the primary electron energy is affected by the variation of surface-like and volume-like excitation intensities. In Ref. [9, 10] the method of inelastic electron scattering cross-section spectra fine structure analysis was suggested. The fine structure analysis is based on fitting $K\lambda$ -spectra to the 3 parameters Lorentzian-type formula of Tougaard [11]:

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

B , C , D are fitting parameters and have special values for different elements [11]. The peak intensity depends on parameter B , peak energy depends on parameter C , peak width and, indirectly, peak energy depend on parameter D .

We chose the 3 parameters Lorentzian-type formula of Tougaard because it describes the inelastic electron scattering mechanisms. The $K\lambda$ -spectra fitting to the Tougaard peaks can be used to analyze different mechanisms of inelastic electron scattering such as volume plasmon excitations, surface plasmon excitations and interband transitions.

The results of fitting the FeSi_2 and Fe_5Si_3 $K\lambda$ -spectra that were obtained with primary electron energies 600 and 1900 eV are shown in figures 2 and 3. The decomposition of inelastic electron scattering cross-section spectra for elemental Fe, Si and Mn were carried out in [15, 19, 20, 21]. The decomposition of inelastic electron scattering cross-section spectra for silicides FeSi_2 and FeSi were carried out in [22, 23].

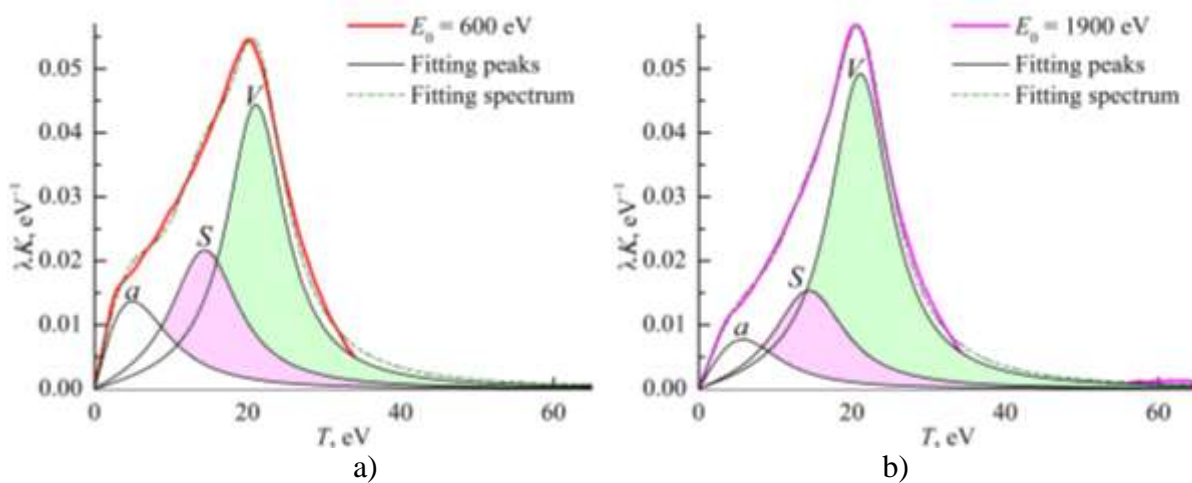


Figure 2. The fine structure of inelastic electron scattering cross-section spectra for FeSi_2 obtained with primary electron energies 300 (a) and 1900 (b) eV

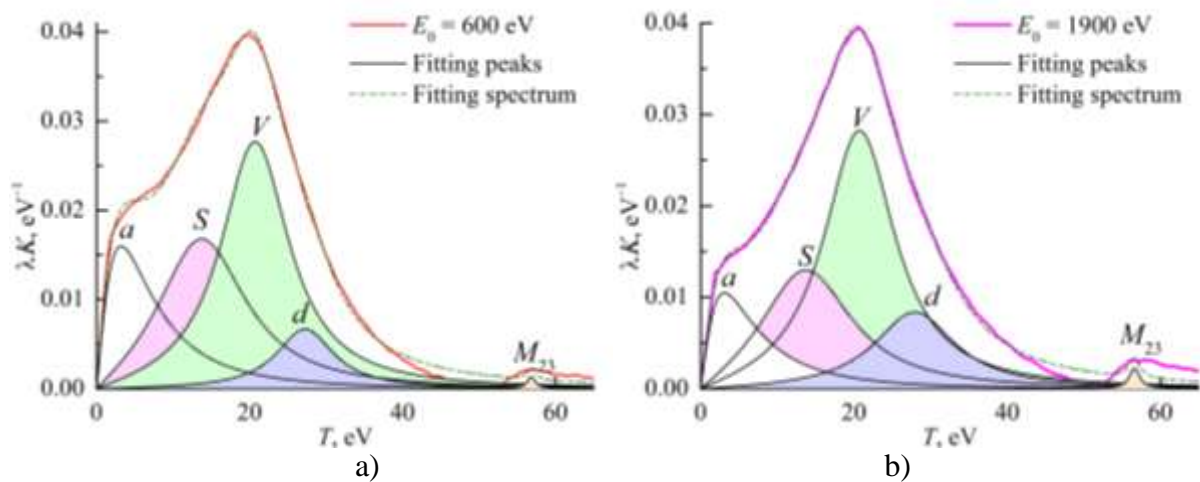


Figure 3. The fine structure of inelastic electron scattering cross-section spectra for Fe_5Si_3 obtained with primary electron energies 300 (a) and 1900 (b) eV.

Peak *V* corresponds to volume plasmon. This peak has gradually increasing primary energy dependence of amplitude which indicate its volume origin (Fig. 5). The peak *S* corresponds to surface plasmon. This peak has opposite to peak *V* gradually decreasing primary energy dependence of amplitude. Surface plasmon is unresolved in experimental spectra for silicides and first its energy sets smaller by a factor of $\sqrt{2}$ to bulk plasmon energy (classical plasmon model [24]) then surface plasmon energy and parameters of other peaks were varied for the best least squared fit to the experimental spectra. This peak was unresolved in REELS and $K\lambda$ -spectra for silicides but the method of fine structure analysis allows determining its energy, intensity and origin. The M_{23} peak related to the electron transition from the level M_{23} and its energy loss is close to the literary data for elemental Fe. Peaks *a* and *d* appearingly related to the interband transitions.

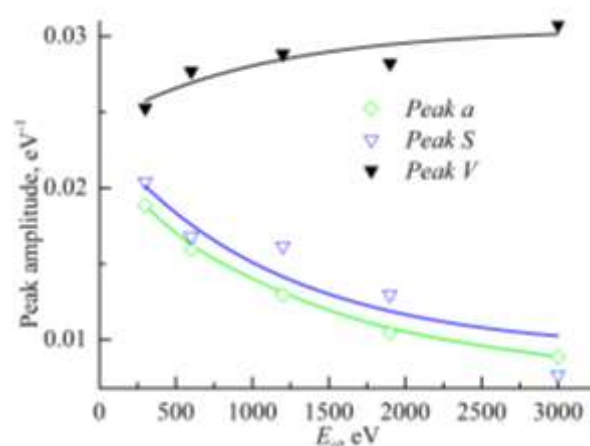


Figure 4. The primary energy dependences of the fitting peaks amplitude

The fine structure analysis method allows determining the peaks energies more accurately than using experimental spectra. Firstly, this method balancing out an effect of summation of different losses intensities to the energies of spectrum maximums. Secondly, the analysis of

unresolved peaks becomes possible. Third, the definition of fitting peak energy is technically more authentic than for the experimental one.

Fig. 5 shows the primary energy dependence of the peak amplitude describing the energy loss due to excitation of the bulk plasmon A_V . For all the investigated materials peak V amplitude is varied enough to be able to uniquely identify Si, Fe, FeSi₂, FeSi, Fe₅Si₃ using this parameter.

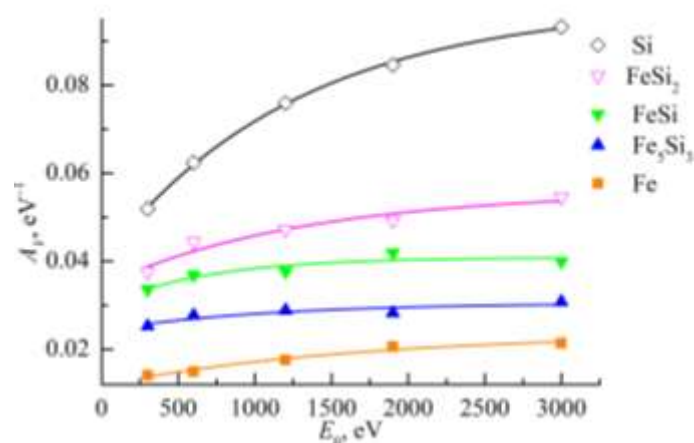


Figure 5. The primary energy dependences of the fitting peak V amplitude for different materials

If the energy peaks positions in experimental REELS and $K\lambda$ -spectra can not be used to distinguish silicides with different composition, the fitting peak V amplitude is can be used to identify silicides with different composition.

4. Conclusions

The reflection electron energy loss spectra and the inelastic electron scattering cross-section spectra for silicides FeSi₂, FeSi, Fe₅Si₃ and elemental Si, Fe were investigated. It is shown that the composition of the iron silicides can not be reliably determined using the peak energies in REELS and $K\lambda$ -spectra. If REELS of silicides with different composition are substantially identical in shape and main peak energy, the amplitude of $K\lambda$ -spectra noticeably decreases with increasing of Fe content.

Decomposition of FeSi₂, FeSi, Fe₅Si₃ $K\lambda$ -spectra to Tougaard peaks allowed to identify the unresolved loss peaks, determine its energies, intensities and origin. It is shown that the peak amplitude describing the energy loss due to excitation of the bulk plasmon can be used to identify silicides with different composition.

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