REFLECTION ELECTRON ENERGY LOSS SPECTROSCOPY OF IRON MONOSILICIDE

A. S. Parshin,[1] A. Yu. Igumenov,[1] Yu. L. Mikhlin,[2]
O. P. Pchelyakov,[1,3] and V. S. Zhigalov[1,4]

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X-ray photoelectron spectra, reflection electron energy loss spectra, and inelastic electron scattering cross section spectra of iron monosilicide FeSi *are investigated. It is shown that the spectra of inelastic electron scattering cross section have advantages over the reflection electron energy loss spectra in studying the processes of electron energy losses. An analysis of the fine structure of the inelastic electron scattering cross section spectra allows previously unresolved peaks to be identified and their energy, intensity, and nature to be determined. The difference between energies of fitting loss peaks in the spectra of inelastic electron scattering cross section of* FeSi *and pure* Fe *are more substantial than the chemical shifts in X-ray photoelectron spectra, which indicates the possibility of application of the fine structure of the spectra of inelastic electron scattering cross section for elemental analysis.*

Keywords: iron silicides, iron monosilicide, inelastic electron scattering cross section spectroscopy, reflection electron energy loss spectroscopy, x-ray photoelectron spectroscopy.

INTRODUCTION

Narrow-gap semiconductor iron monosilicide FeSi is promising for the creation of light sources or detectors in the near-infrared region [1]. In [2, 3] interest in the fundamental magnetic, thermal, and electrical FeSi properties as well as in a study of the special features of metal-dielectric transition was indicated. From the fundamental viewpoint, silicide FeSi is of interest as insufficiently investigated almost magnetic semiconductor with unique magnetic, thermal, and electric properties [2] as well as for studying the special features of the metal-dielectric transition in a system with hard fermions [3]. A study of iron silicides of different compositions and of iron monosilicide, in particular, by the methods of electron spectroscopy, gave unambiguous [4, 5] and sometimes contradictory results [6].

The elemental analysis of the Fe/Si system is most often performed by the methods of electron spectroscopy, including the Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and reflection electron energy loss spectroscopy (REELS) [4–9]. Consideration of silicide formation is needed for quantitative elemental analysis of layered ferrosilicon structures [9]. The composition of iron silicides is determined by the above-mentioned methods from energies of photoelectron, characteristic, and Auger peaks whose difference is several fractions of electron volt for silicides of various compositions that hinders the elemental analysis of the Fe/Si system [4, 6]. The main parameter of the REEL spectra used to analyze the examined materials is the energy of the characteristic peaks, primarily of a bulk plasmon. This energy for silicides of various compositions depends on the iron content and increases

with iron concentration [6]. According to the literature data, the bulk plasmon energy in the REEL spectra of iron monosilicide varies in the region 20.9–21.5 eV [6, 8, 11].

The Tougaard–Chorkendorf algorithm [10] allows the inelastic electron scattering cross section spectra to be calculated from the REEL spectra. These spectra represent the dependences of the product of the electron inelastic mean free path λ and of the differential inelastic electron scattering cross section $K(E_0, T)$ (the so-called $K\lambda$-spectra [10]) on the energy losses T equal to the difference between primary (E_0) and reflection (E) electron energies: $T = E_0 - E$. In accordance with this algorithm, the spectra of inelastic electron scattering cross section contain only single-scattering energy losses whose intensity is determined in absolute units. This allows not only the energies of the characteristic peaks, but also their intensities to be compared for different materials [7–9, 11, 12]. In [8, 9, 11, 12] advantages of $K\lambda$-spectra over the REEL spectra were indicated. In [7–9] the Fe/Si system was comprehensively investigated by the methods of REELS and inelastic electron scattering cross section spectroscopy. In the present work, results of investigation of iron monosilicide by the methods of XPS, REELS, and $K\lambda$-spectroscopy are presented. An analysis of the fine structure of the $K\lambda$-spectra based on their approximation by the Lorentzian-like Tougaard functions allows the intensities of individual loss peaks, including unresolved ones, to be determined quantitatively and peaks of bulk and surface nature to be separated.

1. EXPERIMENTAL TECHNIQUE

A FeSi specimen was prepared by melting the silicon and iron mixture in the 1:1 atomic ratio in vacuum not worse than 10^{-4} Pa using a UVN-2M-1 installation for vacuum deposition. A washer with a thickness of about 1 mm was cut from the obtained alloy, and after polishing, spectroscopic investigations were performed.

The photoelectron and integral reflection electron energy loss spectra were measured using an ultra-high vacuum photoelectron spectrometer (SPECS GmbH, Germany). The spectrometer was equipped with a spherical energy analyzer PHOIBOS MCD9, an x-ray tube with a double anode used as a source of MgK_α x-ray radiation, and a Microfocus EK-12-M electron gun (STAIB Instruments) used for excitation of the electron energy loss spectra. To remove surface impurities, argon Ar^+ ion etching (with accelerating voltage of 2.5 kV and ion current of 15 µA) was performed using a PU-IQE 12/38 SPECS scanning ion gun directly in the spectrometer chamber before the registration of the spectra.

2. EXPERIMENTAL RESULTS

The binding energies of the photoelectron $2p$ Fe and $2p$ Si lines of iron monosilicide and $2p$ Fe lines of metallic iron measured after cleaning of the surface with ion etching were determined. The x-ray photoelectron spectra were obtained with the use of MgK_α radiation with energy of 1253.6 eV. Si and Fe atomic concentrations were determined from the panoramic spectra by the method of sensitivity coefficients of the elements after subtraction of the noise background using the Shirley method. The ratio of iron and silicon atomic concentrations was 0.45:0.55, which is close to the composition of the initial mixture of the alloy. The binding energies of the $2p_{3/2}$ Fe doublet line and $2p_{1/2}$ Fe iron monosilicide line were 706.9 and 720.0 eV, respectively. These values were practically identical to those of metallic iron (707.0 and 720.1 eV) (Fig. 1). The obtained binding energies were in agreement with the literature data for iron silicides [4] and confirmed that it was difficult to identify FeSi by its chemical shift.

The experimental reflection electron energy loss spectra in the integral form (Fig. 2a) were obtained in the region located 150 eV below the elastic peak with a step of 0.1 eV. The primary electron energies were 300, 600, 1200, 1900, and 3000 eV. Three energy peaks were resolved in the integral REEL spectra: the intensive peak with energy of (21.0 ± 0.1) eV and the less intensive peak with energy (42.6 ± 0.6) eV corresponding to the excitation of the single ($\hbar\omega_p$) and double ($2\hbar\omega_p$) bulk plasmon in iron monosilicide [6, 8, 9], respectively, as well as the peak with energy of (55.9 ± 0.7) eV corresponding to single-electron transition M_{23} [8]. The energies of the loss peaks were practically independent of the primary electron energy; their values averaged over all E_0 are shown in the figure.
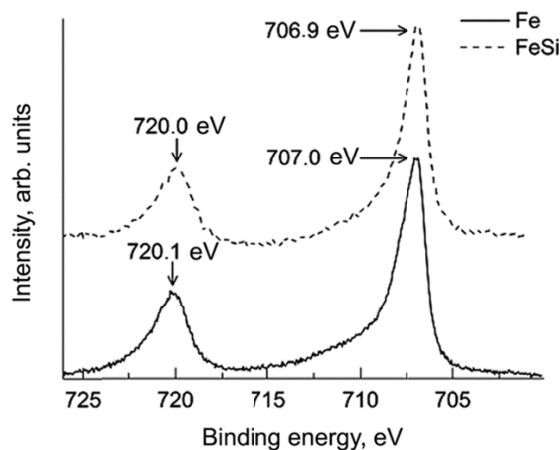
Fig. 1. XPS spectra in the region of 2*p* Fe lines of silicide FeSi and elementary Fe.
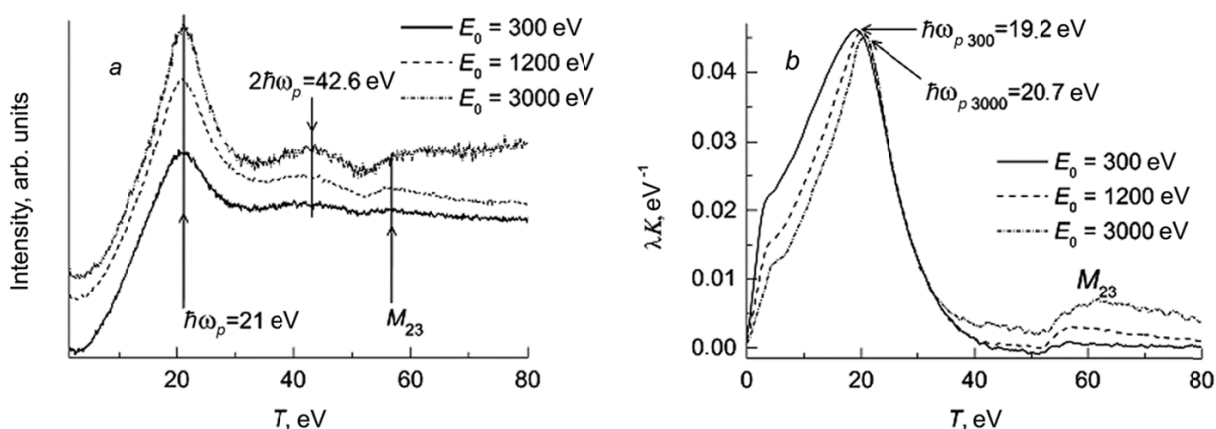

Fig. 2. REEL (*a*) and inelastic electron scattering cross section spectra of FeSi (*b*).

The inelastic electron scattering cross section spectra were retrieved from the experimental REEL spectra using the software package *Quantitative Analysis of Surfaces by Electron Spectroscopy Cross Section determined by Reflection Electron Energy Loss Spectrum (QUASES^{TM} XS REELS)* [13] according to the algorithm proposed in [10]. These spectra determine the probability of the energy loss *T* in the case of single electron scattering per inelastic electron mean free path per unit of energy. The maxima in the $K\lambda$-spectra determine the probabilities of energy losses for single surface or bulk excitations. The absolute intensities of energy losses in the spectra of inelastic electron scattering cross section allow the spectra of various materials (including those obtained by different authors) to be compared and analyzed without pre-processing and normalization.

The inelastic electron scattering cross section spectra of FeSi contain peaks corresponding to the excitation of bulk plasmon with average energy of (20.1 ± 0.6) eV and single-electron transition M_{23} with average energy of (55.7 ± 1.2) eV (Fig. 2*b*). At low energies, a special feature was observed at energy of about 4.5 eV. Unlike the REEL spectra, energy losses for multiple bulk plasmon excitation were absent in the FeSi $K\lambda$-spectra, and the background noise of inelastic electrons has already been subtracted. The intensities of the bulk plasmon and of the peak M_{23} increased with primary electron energy.

The surface plasmon was unresolved in the FeSi $K\lambda$-spectra, but its presence was manifested through the FWHM decreasing from 21.2 to 15.3 eV with increasing primary electron energy from 300 to 3000 eV. Wherein, the bulk plasmon intensity increased compared to the surface plasmon; therefore, the intensity at low energies decreased,
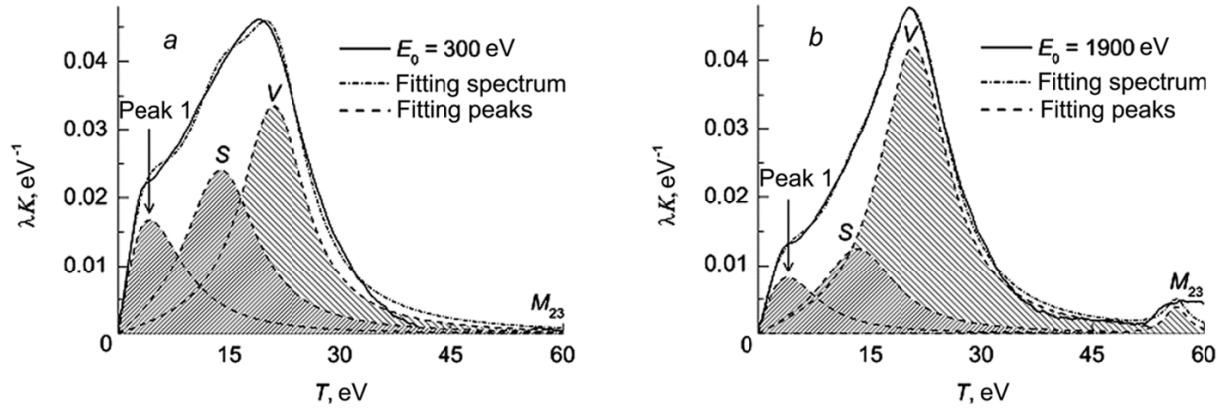
Fig. 3. Fine structure of the inelastic electron scattering cross section of FeSi obtained at primary electron energies of 300 (*a*) and 1900 eV (*b*).

and the maximal inelastic FeSi electron scattering cross section increased from 19.2 eV at primary electron energy of 300 eV to 20.7 eV at primary electron energy of 3000 eV (Fig. 2*b*). Thus, the inelastic electron scattering cross section spectra are more sensitive to a change in the primary electron energy than the REEL spectra. This fact can be caused by the increasing intensity of surface excitations due to the subtraction of the background noise of multiple inelastic electron scattering.

The processes of energy losses forming the FeSi inelastic electron scattering cross section spectrum were analyzed using the approximation of the FeSi spectra by the three-parameter Lorentzian-like Tougaard peaks [14, 15]:

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

The parameters *B*, *C*, and *D* determine the peak intensity, position, and width, respectively; the parameter *D* also indirectly affects the peak position and intensity. In [14, 15] the inelastic electron scattering cross section of Si were approximated by the Tougaard functions. Figure 3 shows the result of approximation of the inelastic electron scattering cross section spectra of FeSi at primary electron energies of 300 and 1900 eV.

Since an analysis of the $K\lambda$-spectra of FeSi revealed contributions of four peaks – bulk (*V*), surface (*S*), weak low-energy (peak 1), and M_{23} – four peaks were used for the approximation (Fig. 3). The parameters of the Tougaard peaks were chosen to achieve a minimal standard deviation between the fitting and experimental spectra. The decomposition of the inelastic electron scattering cross section spectra into the loss peaks allowed the energy of the peaks to be determined more accurately by analyzing the processes of energy losses individually rather than for the initial spectrum representing their superposition. The average fitting peak energies were (4.3 ± 0.3), (13.5 ± 0.6), (20.9 ± 0.1), and (55.0 ± 3.7) eV, that is, the standard deviations of energy were less than those determined from the initial $K\lambda$-spectra. The ratio of the bulk to surface plasmon energies was 1.55, which is close to $\sqrt{2}$ corresponding to the free electron gas approximation [6]. Previously the fine structures of the inelastic electron scattering cross sections of Fe, disilicide $FeSi_2$, and Si were investigated in [14]. The bulk plasmon energies determined from the fine structures of the spectra of Fe, $FeSi_2$, and Si were (22.5 ± 0.4), (21.08 ± 0.03), and (16.9 ± 0.1) eV, respectively. Thus, the bulk plasmon energy determined from the fine structure of the inelastic electron scattering cross section spectra is more sensitive to the composition of iron silicides than the chemical shifts in the XPS spectra. This fact allows the decomposition of the $K\lambda$-spectra into the loss peaks to be used for an analysis of elemental composition of ferrosilicon structures. Figure 4 shows the dependence of the fitting peak areas determining the intensity of excitation on the primary electron energy.
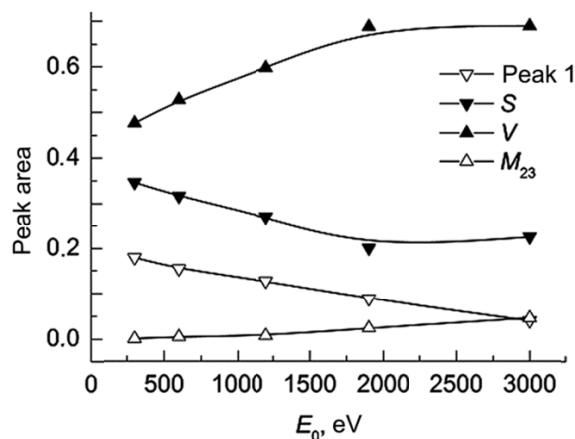
Fig. 4. Dependence of the fitting peak areas on the primary electron energy.

The dependence of the fitting peak areas on the primary electron energy allows the loss peak nature to be determined. Peak S and peak 1 have monotonically decreasing dependences reflecting their surface nature, whereas peaks V and M_{23} have increasing dependences characteristic for the bulk losses. The fine structure of the inelastic electron scattering cross section spectra allows the unresolved peak energies to be determined, contributions of the individual processes to the resulting $K\lambda$-spectrum to be estimated quantitatively, and hence can be used for characterization of iron silicides of different compositions.

CONCLUSIONS

Iron monosilicide FeSi has been investigated by the methods of x-ray photoelectron spectroscopy, reflection electron energy loss spectroscopy, and inelastic electron scattering cross section spectroscopy. It was shown that the binding energies of $2p$ Fe photoelectron lines of FeSi differ slightly from the binding energies of pure Fe that hindered identification of iron monosilicide from the chemical shift. The comparative analysis of the inelastic electron scattering cross section spectra and of the REEL spectra showed that the inelastic electron scattering cross section spectra were more sensitive to a change in the primary electron energy and allowed not only energies, but also intensities of losses to be analyzed. The fine structure of the inelastic electron scattering cross section spectra was analyzed by their decomposition into the elementary Tougaard peaks. The nature of the elementary peaks was determined and the unresolved peaks were identified. The bulk plasmon energy determined from the fine structure of the inelastic electron scattering cross section was more sensitive to the composition of iron silicides than the binding energy in the XPR spectra. This fact allows decomposition of the $K\lambda$-spectra into the loss peaks to be used for the elementary analysis of ferrosilicon structures.

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