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Surface segregation of arsenic in iron

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The surface of polycrystalline iron covered by segregated arsenic, phosphorus and sulphur was analysed in a combined electron spectroscopic study by means of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The saturation coverage of arsenic at 1033 K was determined as 0.33 ± 0.02 monolayer. Sulphur, arsenic and phosphorus segregate in competition. A relation giving the surface coverage from the XPS intensity of adsorbed element is deduced from the experiments and is also calculated. Experimental and calculated values are found to be in relatively good agreement.

1. Introduction

Segregation of non-metallic impurities to transition metal surfaces can play an important role in surface based phenomena such as chemisorption, corrosion, adhesion and catalytic processes. Numerous segregation studies of metalloids of group VA (N, P, Sb) on iron surface utilizing surface sensitive methods have been performed during the last decade [1, 2]. It has been shown that even for very low concentrations in bulk (trace quantities), the impurity can enrich the surface up to the coverages of one monolayer.

In the present work surface segregation of arsenic to the surface of iron was investigated using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). From the phase diagram of the As–Fe system [3] it is obvious that up to several per cent of arsenic, As in α-Fe forms a solid solution. Simple criteria [4, 5], notably the lower melting point of arsenic and its greater atomic radius than iron, give a relatively high driving force for surface segregation. Mixing and segregation of arsenic in an Fe metal overlayer on a GaAs substrate has been investigated [6]. However, to our knowledge, no experiments on bulk iron samples focused on the surface enrichment in arsenic during heating have been published. In a short letter, evidence of surface segregation of arsenic in iron, studied by XPS, has already been presented [7]. Co-segregation of sulphur and phosphorus present as impurities in the iron sample was observed. In the present work, the detailed procedure used in this XPS study is explained. A complementary AES study of the segregation of arsenic in iron is also presented; to achieve this, careful cleaning of the sample was done in order to minimize the quantities of sulphur and phosphorus in the bulk. This procedure allowed us to establish the arsenic coverage at the thermal equilibrium (complete monolayer). The quantitative treatment of the XPS and AES results is developed. Attention was focused on the calibration of the XPS intensity of one arsenic monolayer. The experimental value is compared to the theoretical value calculated using values of photoionization cross-section from Scofield [8].

2. Experimental procedure

The solid solution of arsenic in iron was prepared from pure iron. Approximately 300 p.p.m. of powdered arsenic was set into a hole in a cylindrical shaped piece of iron and the whole was melted and homogenized under a neutral atmosphere. Three slices (for AES, XPS and chemical analysis), approximately 0.9 mm thick, were cut from the centre of the cylinder. The chemical analysis of one piece gave the following results (percentage in atomic values): As, 225 p.p.m.; P, 67 p.p.m. and S, 11 p.p.m. After mechanical polishing, two samples were introduced into ultrahigh vacuum (UHV) chambers.

The experiments were performed in two independent systems: AES and XPS. AES measurements were carried out in a Varian UHV chamber pumped by a $200\,\mathrm{l\,s^{-1}}$ ion pump (Riber) and equipped with a cylindrical mirror analyser (CMA) with integrated electron gun (Riber, model OPC 105) working in the dN/dE mode, a manipulator of high precision TUM-3 (Riber) and an ion bombardment gun (Varian, model 981). The base pressure was lower than 5×10^{-7} Pa. The residual gases could be analysed by a VG ARGA plus partial and total pressure analyser.

The sample was spot-welded to two (ϕ 0.5 mm) tungsten wires, 30 mm long, and the ends of the wires were connected to the manipulator handle. Such construction allows heating of the sample by ac current passing through the holder. The temperature was controlled by a Pt–PtRh10% thermocouple, spot welded to the rear surface of the sample. The uncertainty in the absolute temperature measurements was estimated as ± 10 K. The alternating current used in

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TABLE I Kinetic energies (KE) and relative intensities of Auger transitions under investigations; the intensities are normalized to the Ag MNN transition [13]

Element	Transition	KE (eV)	Relative intensity	Λ, monolayers
Fe(L)	MVV	47	0.36	1.17
Fe(H)	LMM	651	0.20	3.70
As	MVV	31	0.05	1.22
P	LVV	123	0.24	1.63
S	LVV	152	0.65	1.80

L, the Auger peak at low kinetic energy.
H, at high kinetic energy.
Λ, the electron escape depth calculated from Seah and Dench [14] formula for CMA.

TABLE II Binding energies, BE, in eV for principal peaks of analysed elements by XPS

Element	Line	BE, this work	BE, other works
^{6}C	1s	284.5	284.6^{a}
^{7}N	1s	403.0	402.0 [16]
^{8}O	1s	531.8	531.7^{a}
^{14}Si	2p	–	102.0 [16]
^{15}P	2p	129.0	133.0 [16]
^{16}S	2p	161.9	162.1^{a}
^{26}Fe	$2p_{3/2}$	706.9	707.0^{a}
^{33}As	$2p_{3/2}$	1322.8	1323.1 [15]

^{a} Values determined in this laboratory in other experiments.

heating the sample caused only negligible distortions of the measured electron energy spectrum and the Auger spectra could be registered at a given temperature without switching off the current. The spectra in the 20–1300 eV range were measured by exciting the sample with a beam of 0.9 mA cm^{-2} of 2 keV electrons using 3 V peak-to-peak modulation amplitude. In order to maintain reproducible analytic conditions, the sample position and the CMA settings were tuned in the way to give optimum intensity and symmetry at the proper energy of the elastic peak of reflected primary electrons. The Auger transitions of the elements measured during the study are shown in Table I. It is seen that the intensity of the arsenic MVV transition relative to the iron MVV is $\simeq 0.13$. The relative intensity of the arsenic LMM transition at 1230 eV, not presented here, is smaller. This shows that arsenic has very low sensitivity in AES.

After degassing, the surface of the sample contained typical contaminants, carbon, oxygen, phosphorus, sulphur and nitrogen. To clean the surface, the sample was heated in the AES chamber. During heating, as indicated by the Auger spectrum, some fraction of the carbon, sulphur, phosphorus and oxygen were removed by desorption. After 1 h of heating at 1103 K sulphur remained on the surface. Prolonged heating at this temperature caused an increase of the Auger peak-to-peak (p/p) height of the sulphur. A prolonged heating at lower temperature, e.g. at 923 K for 24 h, did not change the state of the surface. The sample was then exposed to oxygen at room temperature (RT). After one dose of 600 L (60 s, 1.33×10^{-3} Pa), the sample was heated to 1103 K for 30 min. Initially, the sulphur from the surface was removed as SO and/or SO_2 and the rest of oxygen by desorption. Next, at this temperature, sulphur started to segregate to the surface and the exposure to oxygen was repeated. Three such cycles depleted the surface region of contaminants, not only of sulphur, but of phosphorus, carbon and nitrogen as well. The Auger peaks were reduced to the noise level of the spectrum and a small arsenic peak at 31 eV appeared.

The segregation experiment in the AES chamber was performed in the increasing temperature mode. The temperature of the sample was increased from RT to the desired value, the temperature was then maintained for several hours and Auger spectra were recorded. Next, the sample temperature was increased and the procedure repeated. The sample was heated successively at 863 K for 6 h, at 913 K for 12 h, at 963 K for 12 h, at 1033 K for 7 h and finally at 1073 K for 23 h.

XPS measurements were made with a VG Escalab MK II spectrometer with standard equipment using an AlK$_{\alpha}$ ($h\upsilon = 1486.6$ eV) anode and a hemispherical electron energy analyser operating in the constant pass energy mode. The base pressure was lower than 5×10^{-7} Pa. The spectrometer was calibrated using Au $4f_{7/2}$ and Cu $2p_{3/2}$ photoelectron lines at 83.8 ± 0.1 eV and 932.7 ± 0.1 eV, respectively. The detection angle was normal to the surface. Experimental results were analysed using a DEC Micro/PDP-11 computer and VG Scientific model VGS 500 data processing software.

The sample was mounted on a molybdenum holder using tantalum clips. The holder could be heated and the sample temperature was determined by means of an optical pyrometer [7]. Wide range spectra of the 20–1350 eV energy range as well as spectra of the regions of interest, i.e. iron, Fe $2p_{3/2}$, arsenic As $2p_{3/2}$, and regions of common impurities: carbon, C 1s, sulphur, S 2p, phosphorus, P 2p, silicon, Si 2p, nitrogen, N 1s and oxygen, O 1s, were recorded during the study using 50 eV pass energy in the electron energy analyser (Table II).

The sample surface was cleaned in the XPS chamber by ion argon bombardment (approx. 1 μA cm^{-2}, 2 keV). After several cycles of ion sputtering, the XPS spectrum from the surface contained only residual peaks of carbon and oxygen. The kinetics of segregation were followed at 873 and 973 K.

3. Calculation of surface coverage

Evaluation of the surface coverage was performed on the basis of the formulation concerning the submonolayer region [9]. When the substrate is covered by adsorbed (or segregated) atoms, an adsorbate coverage can be expressed as a fraction of the substrate monolayer $\tau = N_a/N_b$, where N_a is the surface density of adsorbed atoms and N_b is the surface density of substrate atoms. The surface coverage can be expressed also in terms of the surface density of adsorbed atoms at saturation layer N_a^{sat}, i.e. $\Theta = N_a/N_a^{sat}$, on condition that the N_a^{sat} is known for the surface under investigation or can be easily determined from the experiment. Usually $N_a^{sat} \leqslant N_b$ which through the relation $\tau = \Theta N_a^{sat}/N_b$ gives $\tau \leqslant \Theta$ for the same surface density of adsorbed atoms.

In the submonolayer region ($0 \leqslant \tau \leqslant 1$) the Auger or the photoelectron intensities of the adsorbate I_a and the substrate I_b can be written as

$$I_a(\tau) = J_a^1 \tau \tag{1}$$

$$I_b(\tau) = I_b^0 [(1 - \tau) + \tau \exp(-1/\Lambda_b^a)] \tag{2}$$

where J_a^1 denotes the adsorbate intensity coming from one monolayer of adsorbate ($\tau = 1$) and I_b^0 the substrate intensity for the clean ($\tau = 0$) surface; Λ_b^a is the electron escape depth of the substrate Auger electrons in the adsorbate in units of monolayers. Λ is related geometrically to the attenuation length, λ; for the VG Escalab spectrometer simply by $\Lambda = \lambda$ and for CMA conditions by $\Lambda = 0.74\lambda$. λ depends on the kinetic energy of the electrons and on the matrix. Using first principles method [10], Equations 1 and 2 can be rewritten as a function of Θ

$$I_a(\Theta_a) = I_a^1\Theta_a = FY_a^1N_a = FY_a^1N_a^{sat}\Theta_a \tag{3}$$

$$\begin{aligned} I_b(\Theta_a) &= I_b^0\{1 - (N_a^{sat}/N_b)\Theta_a[1 - \exp(-1/\Lambda_b^a)]\} \\ &= FD_b\Lambda_b^bY_b\{1 - (N_a^{sat}/N_b) \\ &\qquad \times \Theta_a[1 - \exp(-1/\Lambda_b^a)]\} \end{aligned} \tag{4}$$

where I_a^1 denotes the Auger or the photoelectron intensity of the saturation layer of the adsorbate ($\Theta = 1$), F is a constant for the given analysis condition, Y_a^1 is the surface atomic yield factor (the superscript denotes that it refers to the layer of adsorbate), D_b is the atomic bulk density of the substrate, Λ_b^b is the electron escape depth from the substrate in the substrate and Y_b is the atomic yield factor of the substrate, defined as

$$Y_b = \sigma_b T(KE_b) \tag{5}$$

where σ_b is the cross-section for Auger or photoelectron emission and the term $T(KE_b)$ denotes the dependence of the transmission function T, on kinetic energy of emitted electrons KE_b. For the VG Escalab spectrometer used in experiment, the transmission function was determined as $T = f\sigma_b(KE_b)^{-0.54}$, where f is a constant [11]. Y_a^1 differs markedly from Y_a and the surface atomic yield factor cannot be calculated from Equation 5, it should be determined from an experiment with a calibrated quantity of the adsorbate.

Quantification in AES and XPS can be accomplished through the ratio between the monitored signals. Two kind of ratios, different in principle, are important: the ratio of low to high kinetic energy signals of one element and the ratio of adsorbate to substrate signals. When the substrate has two Auger or photoelectron transitions of different energy, the energy dependence of Λ gives a convenient method for the determination of coverage. Using Equation 2, the ratio of low (L) to high (H) energy signals, R, can be expressed as

$$R = \frac{I_L}{I_H}(\tau) = \frac{I_L^0}{I_H^0}\frac{1 - \tau\alpha_L}{1 - \tau\alpha_H} = R_0\frac{1 - \tau\alpha_L}{1 - \tau\alpha_H}, \tag{6}$$

where $\alpha_{L,H} = 1 - \exp(-1/\Lambda_{L,H})$ and R_0 is the ratio for the clean surface. Solving Equation 6 for τ we have

$$\tau = \frac{R_0 - R}{R_0\alpha_L - R\alpha_H} \tag{7}$$

Equation 7 is very useful and it can be used to determine of the coverage τ from the substrate signals only [12].

The ratio of the adsorbate to the substrate signal, I_a/I_b, has no simple linear relation with the coverage [12] as can be seen from Equations 3 and 4. The ratio of the signals can be written as

$$\begin{aligned} i_a(\Theta_a) &= \frac{I_a}{I_b}(\Theta_a) \\ &= \Theta_a\frac{I_a^1}{I_b^0}[1 - (N_a^{sat}/N_b)\Theta_a\alpha_b^a]^{-1} \\ &= \Theta_a\frac{I_a^1}{I_b^0}A(\Theta_a, \alpha_b^a) \end{aligned} \tag{8}$$

where $\alpha_b^a = 1 - \exp(-1/\Lambda_b^a)$, and the third term of multiplication, the attenuation factor A, depends on Θ and α_b^a; A is very close to 1 and usually it is not taken into account. Equation 8 can be rearranged into the form

$$\Theta_a = i_a(\Theta_a)[I_a^1/I_b^0 + (N_a^{sat}/N_b)\alpha_b^a i_a(\Theta_a)]^{-1} \tag{9}$$

When several elements are present on the surface, the substrate intensity in Equation 9 depends on the total adsorbate coverage, $\Theta = \Sigma\Theta_a$, instead of Θ_a. Hence, the attenuation factor A in Equation 8 has no explicit Θ_a dependence, and Equation 9 can be written in a simplified form

$$\Theta_a = i_a(\Theta_a)/i_a(1) = i_a(\Theta_a)[(I_a^1/I_b^0)A(\Theta, \alpha_b^a)]^{-1} \tag{10}$$

The above equations can readily be used for determination of Θ_a on condition that the ratio I_a^1/I_b^0 is known. This ratio can be determined in an independent calibration experiment; it comes directly through Equation 8 for given data of $i_a(\Theta_a)$ and Θ_a. For several elements presented on the surface ($a = x, y, \ldots$), Θ_a can be found using Equation 10 on condition that I_x^1/I_b^0, I_y^1/I_b^0, ..., ratios, and the total coverage Θ are known. The calibration procedure of one element, I_x^1/I_b^0, may be enough because the relationship for the second element, y, can be written

$$\frac{I_y^1}{I_b^0} = \frac{I_y^1}{I_x^1}\frac{I_x^1}{I_b^0} = \frac{I_x^1}{I_b^0}\frac{N_y^{sat}Y_y^1}{N_x^{sat}Y_x^1} \tag{11}$$

Under approximation of the same proportionality k-coefficient between the yield factors ($Y^1 = kY$) for any transition, i.e. $Y_y^1/Y_x^1 = Y_y/Y_x$, Equation 11 reduces to

$$\frac{I_y^1}{I_b^0} = \frac{I_x^1}{I_b^0}\frac{N_y^{sat}}{N_x^{sat}}\frac{\sigma_y T(KE_y)}{\sigma_x T(KE_x)} \tag{12}$$

From Equation 12 the value of I_y^1/I_b^0 can be found using theoretical values on the cross-section and the ratio of transmission function which for the VG Escalab spectrometer is $T(KE_y)/T(KE_x) = (KE_x/KE_y)^{0.54}$. The second condition, i.e. knowledge of Θ, is difficult to fulfil. One solution is to use a so-called self-consistent procedure. In the first step, Θ_a ($a = x, y, \ldots$) is calculated from simplified formulae (e.g. from Equation 8 with $A = 1$ or from Equation 9) giving the total coverage $\Theta = \Sigma\Theta_a$. In the second step, Θ_a is determined using the above value of Θ, through accurate solutions of Equation 10. Then, iteration can be repeated until good convergence between successive coverages is obtained.

4. Results and discussion

4.1. AES study

At temperatures of 863, 913, 963 and 1033 K, segregation of arsenic was observed only. This result confirmed that the adopted cleaning procedure was properly chosen. When the sample was annealed at 1073 K, the arsenic signal decreased slowly with time (arsenic was still present after 1.5 h of heating) and the sulphur signal increased (Fig. 1). Although the rates of each event were different – arsenic diffused to the surface much faster than sulphur – this behaviour shows competition between arsenic and sulphur segregation. The Auger p/p heights from the spectra taken at the end of heating time of each temperature were considered quantitatively. Because the Auger electrons come from some depth of the sample, the composition of the segregated region should be calculated assuming a model for the surface region. Here, the monolayer model was adopted, i.e. a model in which the segregating component exists only in the outermost atomic layer and the composition of subsequent layers corresponds to the bulk. Although the very small As MVV at 31 eV peak was noticeable in the Auger spectrum (Fig. 1), quantitative analysis on the basis of the peak introduces a large error. For this reason, Equation 7 was taken to quantify the surface coverage using the ratio of the low energy Fe MVV at 47 eV to the high energy Fe LMM at 651 eV auger peak. τ was determined as expressing the coverage in terms of the surface density of Fe monolayer, $N_{Fe} = 19.2 \times 10^{14}$ at cm^{-2} (i.e. $1/a^2$ for $a = 0.228$ nm). The results are summarized in Table III.

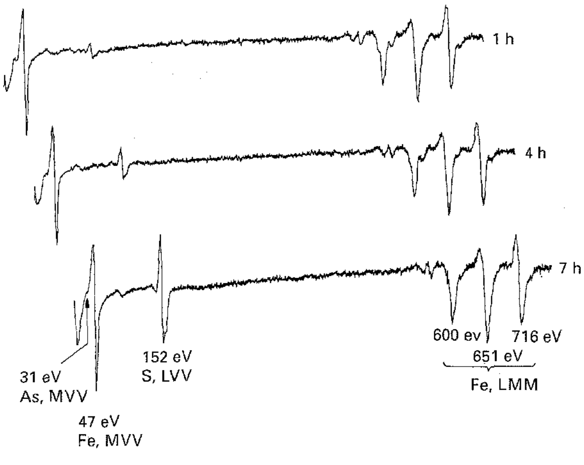

Figure 1 Auger spectra of arsenic doped iron sample for heating at 1073 K (800 °C). Competition between arsenic and sulphur is evident from the spectra.

TABLE III Values of the p/p heights of the Auger transition and corresponding total surface concentration of segregants for arsenic doped iron sample after heating in different temperatures

Temperature (K)	t_h (h)	As	Fe_L	S	Fe_H	R	τ
863	6	2.0	60.7	–	36.0	1.686	0.13
913	12	2.5	69.3	–	42.3	1.639	0.20
963	12	2.0	57.0	–	36.6	1.557	0.32
1033	7	1.3	54.4	–	35.2	1.545	0.34
1073	1.5	1.5	52.0	6.0	33.0	1.576	0.29
1073	22	–	60.0	48.0	40.0	1.500	0.40

t_h, time of heating.
As(MVV) 31 eV.
Fe_L(MVV) 47 eV.
S(LVV) 152 eV.
Fe_H(LMM) 651 eV.
$r = Fe_L/Fe_H$.
τ, total coverage.
Melting point of iron $T_M = 1809$ K (1536 °C).
The Fe_L/Fe_H ratio for the clean surface was found to be $R_0 = 1.764$.

At a temperature of 963 K the surface segregation kinetics was very fast [7]. At this temperature and at 1033 K, thermodynamic equilibrium was achieved, that is, the saturation layer of arsenic was segregated. The surface coverage of arsenic was determined as $\tau = 0.32 - 0.34$ at saturation. At lower temperatures (863 and 913 K), the kinetics of segregation were slower and the equilibrium was not achieved yet at the end of the experiment. The results belong to the diffusion limited region of surface segregation [17]. After one hour of heating at 1073 K the surface coverage of arsenic was lower than that at 960 K, which agrees with a lowering equilibrium surface concentration at higher temperatures in the Langmuir–MacLean model of segregation [18]. During prolonged heating, sulphur segregated and displaced arsenic from the surface; this shows on the repulsive interaction between S and As that As was repelled from the surface sites. After 22 h of heating, arsenic was dissolved in the bulk and the surface was covered only by sulphur. The calculated sulphur coverage $\tau = 0.40$ is close to the saturation value in the sulphur–iron system found by Berthier and Oudar [19], i.e. to the density of sulphur monolayer, $N_S^{sat} = 7.9 \times 10^{14}$ at cm^{-2} ($\tau = 0.41$). This result validates the segregation model assumed in calculation. Although a segregated atom can block many inequivalent sites around the one which is occupied, it is believed that, due to the similar saturation coverages, the As and S segregate to the same surface sites.

In conclusion, the present results show that: (i) arsenic segregates to the surface of iron and the surface coverage at the monolayer is $\tau = 0.33$; (ii) arsenic and sulphur segregate to the same surface sites and (iii) compared to the sulphur coverage ($\tau = 0.40$), one can deduce that arsenic segregates in 80% of the sulphur sites.

4.2. XPS study

The peak of arsenic As $2p_{3/2}$ was observed at the binding energy of 1322.8 eV, which agrees very well with the published data for elemental arsenic [15] (Table II). The peak of As 3d at 41.6 eV was registered here at 42 eV with a smaller relative intensity (I(As 3d)/I(As $2p_{3/2}$)$\simeq$0.05) than reported in the literature: I(As 3d)/I(As $2p_{3/2}$)$\simeq$0.073 [16], σ(As 3d)/σ(As $2p_{3/2}$)$\simeq$0.066 [8]. For the above reason, the As $2p_{3/2}$ peak was chosen to quantify.

At 973 K, the surface segregation of arsenic and sulphur was observed [7] on the sample surface with very rapid kinetics (a few minutes). The spectra of Fe $2p_{3/2}$, As $2p_{3/2}$ and the S 2p, representing surface composition, obtained during segregation at that temperature are presented in Fig. 2. After one minute of heating, the I(S)/I(Fe) ratio did not vary longer with time. The attained value of 0.011 is inferior to the value obtained at the complete sulphur monolayer of 0.0217 [20]. This confirms the suggestion that arsenic segregates to the same sites as sulphur. The I(As)/I(Fe) ratio reached a plateau after approximately 20 min, which indicates that the thermodynamic bulk–surface equilibrium was attained.

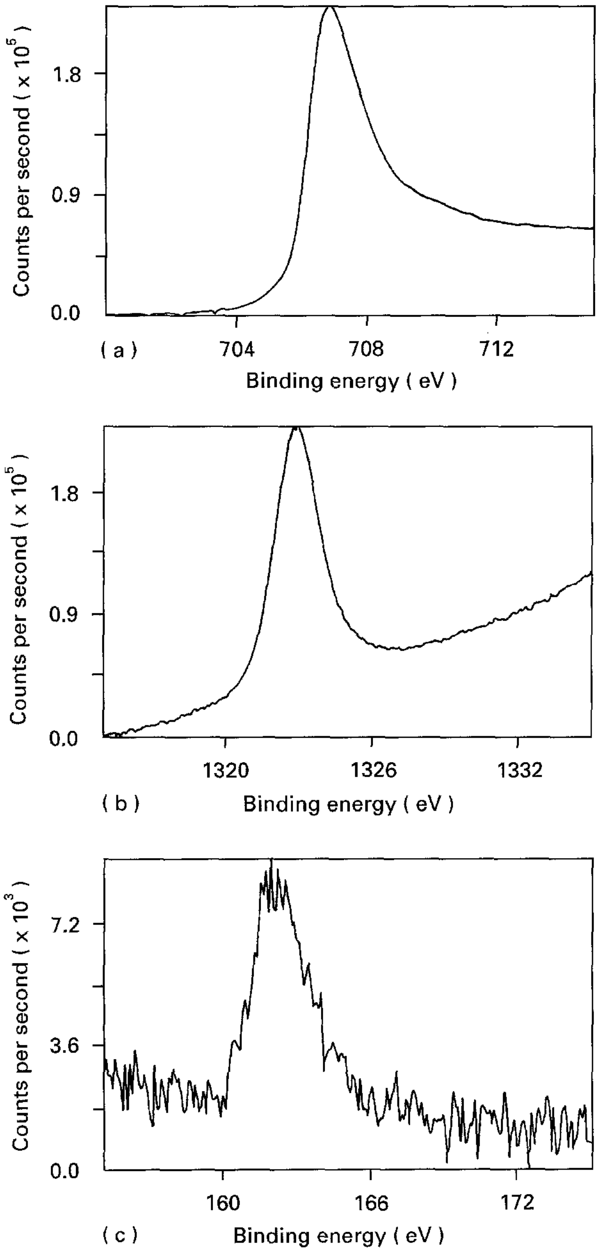

Figure 2 Photoelectron spectra of the region of (a) Fe $2p_{3/2}$, (b) As $2p_{3/2}$ and (c) S 2p obtained during segregation at 973 K (700 °C) from an iron sample doped with arsenic.

TABLE IV Ratio of the intensities of the photoelectron lines, I_a/I_b, obtained at the end of heating the sample at given temperature in UHV conditions

Temperature (K)	I_{As}/I_{Fe}	I_S/I_{Fe}	I_P/I_{Fe}
873	0.11[a] (10 h)	0.005[a] (10 h)	0.005[b] (7 min)
973	0.22[b] (35 min)	0.011[b] (1 min)	–

[a] The surface-bulk equilibrium was not attained in time showed in the parenthesis.

[b] At the thermodynamical equilibrium.

At 873 K apart from sulphur and arsenic, the co-segregation of phosphorus to the surface was observed. The phosphorus signal achieved a plateau more rapidly than those of sulphur and arsenic. It is known from the literature, that phosphorus segregates in iron at this temperature and that the thermal equilibrium (phosphorus monolayer) is attained after less than 10 min [1]. The appearance of phosphorus on the sample surface at 873 K indicates that phosphorus was not removed from the subsurface region during the cleaning procedure used. After 10 h of heating, the intensities of the S 2p and the As $2p_{3/2}$ photoelectron lines were still changing. The surface was not yet in equilibrium with the bulk. The results are shown in Table IV.

The XPS results confirm that: (i) As segregates to the iron surface at 973 K and 873 K and (ii) As and S segregate competitively. In addition, it is shown that the kinetics of segregation is rapid at 973 and slower at 873 K.

4.3. Discussion

The XPS and AES experiments have both shown that arsenic segregates at the surface of iron and that arsenic with sulphur segregates competitively. The lower saturation coverage of arsenic than that of sulphur can be explained in terms of stronger As–As repulsive lateral interaction than S–S on the surface. With increasing temperature the following order could be written: arsenic, sulphur and phosphorus segregate (873 K), sulphur and arsenic (973 K) and then only sulphur (1073 K). Because the sulphur content of the sample is much lower than its arsenic content, at 973 K the segregation of sulphur is favoured over the segregation of arsenic. Phosphorus is known to segregate on iron at temperature of 973 K [1]. The absence of phosphorus segregation at this temperature shows that phosphorus segregates in competition with sulphur and arsenic.

It was assumed that the segregation phenomena are concentrated in the top atomic layer whereas the composition of the other layers is homogeneous and equal to the bulk composition. The coverages of As, S and

TABLE V The parameters used in quantitative XPS; density of monolayer is expressed in at cm^{-2}

Element/line	ML density	σ	KE (eV)	λ
Fe $2p_{3/2}$	19.2×10^{14}		755.8	5.45
As $2p_{3/2}$	6.3×10^{14} (this work)	36.98×10^{14}	159.9	
S 2p	7.9×10^{14} [20]	2.281×10^{14}	1320.8	
P 2p	9.6×10^{14} [1]	1.162×10^{14}	1353.7	

σ, the photoionization cross-section in barn, for sulphur and phosphorus, the lines $2p_{1/2}$ and $2p_{3/2}$ are inseparable and the cross-section was determined from the sum $\sigma(2p) = \sigma(2p_{1/2}) + \sigma(2p_{3/2})$ of the values given by Scofield [8].
KE, the kinetic energy of photoelectron
λ, the electron escape depth in monolayers calculated using Seah and Dench formula [14] and applied to iron.

P at 873 K and of As and S at 973 K were determined from XPS intensities using experimental calibration by calculations on the base of equations given in the previous paragraph. The parameters used for quantification are collected in Table V. For a complete monolayer of sulphur ($\Theta_S = 1$) on a polycrystalline iron surface, the ratio of XPS signals is given by Grimal and Marcus [20] as $i_S(1) = [I(\mathrm{S2p})/I(\mathrm{Fe2p_{3/2}})]$ $(\Theta_s = 1) = 0.0217$. Then, the ratio of $I_S^1/I_{Fe}^0 = 0.202$ was found for $\alpha_{Fe} = 1 - \exp(-1/\lambda_{Fe}) = 0.168$ and the data from Table V using Equation 8. To obtain the ratios I_{As}^1/I_{Fe}^0 and I_P^1/I_{Fe}^0 Equation 12 was used. Taking $N_{As}^{sat} = N_S^{sat}, N_P^{sat} = N_S^{sat}$ and cross-section values from Table V the ratios of $I_{As}^1/I_{Fe}^0 = 1.02$ and $I_P^1/I_{Fe}^0 = 0.0142$ were calculated.

When several elements are present on the surface, the coverage of one of them can be determined from the ratio of signals, i_a, in three different ways. The simplest way is to use an equation which does not take account of the attenuation of substrate signal, i.e. Equation 8 for $A = 1$. Equation 9 takes account of the attenuation of substrate signal by only this element. Finally, the most accurate way is to use an equation which takes into account attenuation of substrate signal by all elements presented on the surface (Equation 10). The last procedure is the best of all, but it needs the value of total coverage and use of an iteration method described earlier.

At 973 K both arsenic and sulphur were present on the surface at the thermal equilibrium. Taking into account (AES results) that arsenic can occupy 80% of the sites compared to sulphur, it can be shown $\Theta_{As} = 0.8(1 - \Theta_S)$ at thermodynamic equilibrium. Adopting Equation 9 for sulphur, the coverage of $\Theta_S = 0.52$ ($\tau_S = 0.21$) was obtained and in consequence $\Theta_{As} = 0.38$ ($\tau_{As} = 0.16$), where Θ_a is the coverage expressed in terms of the density of sulphur monolayer and τ_a in terms of the density of the iron monolayer. On the other hand, the calculated ratio of I_{As}^1/I_{Fe}^0 by Equation 12 and inserted into Equation 9 gave the coverage of $\Theta_{As} = 0.21$ ($\tau_{As} = 0.09$). For results obtained after heating at 873 K, the same calculations were made under the assumption that phosphorus segregates to the same sites as sulphur on iron [1]. The coverages were found using Equation 9 as: $\Theta_{As} = 0.11$ ($\tau_{As} = 0.05$), $\Theta_S = 0.24$ ($\tau_S = 0.10$) and $\Theta_P = 0.34$ ($\tau_P = 0.14$).

The above coverages were taken as the starting parameters for iteration. For segregation at 973 K, $\Theta_{As} = 0.20$ and $\Theta_S = 0.52$ were found by inserting the total coverage of $\Theta = 0.21 + 0.52 = 0.73$ into Equation 10. By analogy for segregation at 873 K, $\Theta_{As} = 0.10$, $\Theta_S = 0.24$ and $\Theta_P = 0.34$ were calculated using the total coverage of $\Theta = 0.11 + 0.24 + 0.34 = 0.69$ in Equation 10. It can be seen that the iteration did not improve the determined values of coverages, the change of the Θs lies within the limits of experimental error. In conclusion, the procedure involving an approximation to Equation 9 was exact enough for the case of the interface under investigation.

5. Conclusion

The following conclusions can be drawn:

1. Because of low yield of the As MVV (31 eV) transition and As LMM (1228 eV) a very small Auger peak of arsenic in the spectrum can be detected starting from coverages of approximately $\tau = 0.3$ HML. This implies, that for small surface coverages, AES is insensitive for arsenic contamination.
2. Arsenic, sulphur and phosphorus segregate in competition at 873 K (600 °C) and arsenic and sulphur segregate at 973 K (700 °C). Segregation of sulphur is highly favoured at 973 K (700 °C) over segregation of arsenic.
3. Due to the higher heat of sulphur segregation, the surface of iron after heating above 1073 K (800 °C) contains only sulphur.
4. For arsenic, a bulk concentration of 0.0225 at % and sample temperature around 1033 K (760 °C), gives a saturation coverage of $\tau = 0.33$ HML.

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