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XPS investigations of FeSi, $FeSi_2$ and Fe implanted in Si and Ge

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Abstract. Polycrystalline FeSi and $FeSi_2$ samples have been examined by ESCA experiments. The valence band spectra show features that can be attributed to bonding and non-bonding states, as is the case for other transition metal silicides, where bonding is expressed in terms of hybridisation. Furthermore we have investigated the photoelectron spectra of samples of Si and Ge implanted with Fe at an energy of 40 keV in order to draw some conclusions regarding the character of the Fe–Si bonding in the disordered layer. The concentration of Fe as a function of the sample depth was also determined and compared with the results of Monte Carlo calculations.

1. Introduction

In recent years, transition metal silicides have attracted considerable attention mostly because of their possible practical applications (Murarka 1983, Murarka 1986). It is also important to understand their electronic structure (Rubloff 1983, Kinsinger *et al* 1988, Speier *et al* 1989). To a great extent it is only the properties of the silicide/silicon interface and silicide formation at interfaces that have been examined (Grunthaner *et al* 1982, Franciosi *et al* 1981), but the bulk silicides have also been investigated in order to obtain more insight into the chemical bonding. Implanted silicon layers may also have technical importance, as one can produce buried silicide layers by subsequent annealing, and these can be used to build metal base transistors (White *et al* 1987, van Ommen *et al* 1988). FeSi, in particular, has been investigated because of its temperature induced paramagnetic moment (Oh *et al* 1987). Furthermore, β-$FeSi_2$ is a very promising thermoelectric material (Sekiguchi *et al* 1988).

Photoemission spectroscopy is an important method for acquiring information on the chemical bonding, especially in connection with calculations of the density of states (Speier *et al* 1989, Bisi and Calandra 1981, Weaver *et al* 1984). In addition, one can obtain information about important technical properties of the silicides, for example the Schottky barrier heights of the silicide/silicon interfaces, from core level spectroscopy (Hara and Ohdomari 1988, Hirose *et al* 1988).

We became interested in samples where Fe has been implanted in a Si or Ge target and compared their bonding characteristics to the stoichiometric crystalline phases.

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2. Experimental details

Fe-silicides of various stoichiometries were prepared by melting Fe and Si of 99.99% purity in an electron beam furnace. After melting the samples were homogenised and the $FeSi_2$ samples annealed at 800 °C for 24 h to form the perfect β-$FeSi_2$ structure.

Si (Wacker Electronics) and Ge (Hoboken) of high resistivity (more than 600 Ω cm) were implanted with Fe in the Leuven Isotope Separator to a dose of 4×10^{16} atoms cm^{-2} at 40 keV. The depth distribution of the Fe in Si was checked by Rutherford backscattering in the Leuven Pelletron with a He^+ beam.

The photoemission data have been recorded with a HP 5950 A ESCA spectrometer with a monochromatised Al Kα x-ray source with a photon energy of 1.487 keV and an energy resolution of 0.6 eV. The base pressure during the measurements was in the 10^{-10} mbar range.

Before measurements the FeSi and $FeSi_2$ samples were scraped *in situ* with a fine diamond file to remove surface contaminations. Afterwards the cleanness of the samples was checked by spectroscopy of the oxygen 1s and the carbon 1s signals.

To obtain a depth profile of the implanted samples, several layers were gradually removed by 1.5 keV argon sputtering. We calculated the sputtered layer thickness from the sputtering times and currents by using data from oxidised Si and Ge samples and assuming that the sputter yields for the oxide would be the same as for the pure material. The Fe concentration values were determined from the intensity ratios of the Fe 2p and Si 2p core level spectra, using the Fe 2p/Si 2p intensity ratio of the FeSi sample as a standard. Since we did not measure a Fe–Ge compound of known stoichiometry, we used data tables (Elliot *et al* 1983) based on cross-section calculations to determine the Fe concentration in Ge.

The values of the concentrations determined in these ways had to be corrected because of preferential sputtering effects (Liau *et al* 1979, Castro and Ballesteros 1988). The factor for the correction was determined by sputtering FeSi, and comparing the Fe 2p/Si 2p intensity ratios with the unsputtered one. In this way we found a sputter ratio of 2.0(3) for Si/Fe.

3. Results

The greatest insight into the nature of the chemical bonds in the silicides is obtained from spectroscopy measurements of the valence bands and comparing them with those of the pure constituents. This is shown in figure 1 with an arbitrary intensity scale for each spectrum. Here one has to be aware that the photoemission cross-sections for the 3d electrons are much larger than for the Si 3s and 3p electrons when using Al Kα radiation. All spectra have been background corrected.

The Fe valence band is dominated by structure A, which is produced by the emission of electrons from the Fe 3d states. The peaks labelled B, C and D in the Si valence band correspond to the emission of electrons from Si 3s, Si 3p and a mixture of Si 3s and 3p states, respectively (Tersoff and Hamann 1983).

The dominant Fe 3d derived structure in the silicides shows a shift to a higher binding energy with respect to the pure Fe. The magnitude of the shift is 0.4 eV for $FeSi_2$ and 0.2 eV for FeSi. The structures appear 1.2 and 1.0 eV below the Fermi energy. One can recognise a shoulder at a binding energy 2 eV higher and this can be attributed to hybridised Fe 3d–Si 3p states.

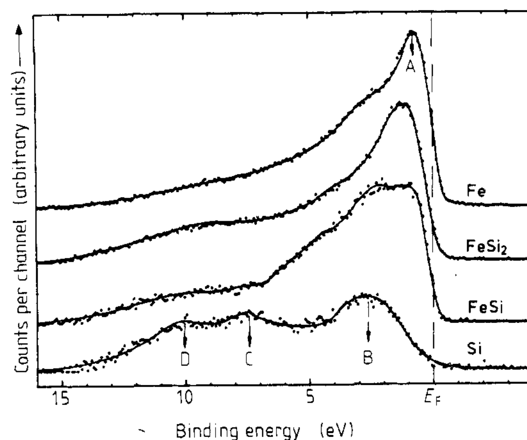

Figure 1. XPS valence band spectra of Fe, Si, $FeSi_2$ and FeSi shown on an arbitrary scale. See text for the explanation points A to D.

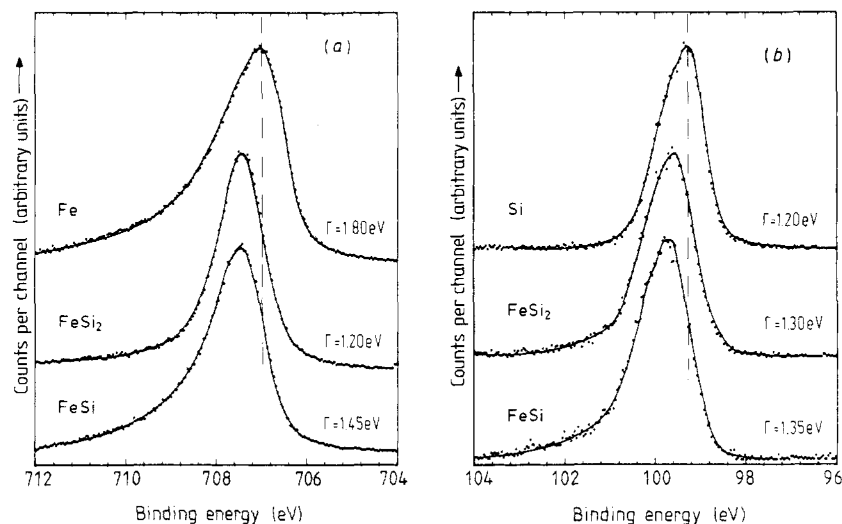

Figure 2. (*a*) Fe $2p_{3/2}$ core level spectra for Fe, $FeSi_2$ and FeSi. Γ is the full width at half-maximum. (*b*) Si 2p core level spectra for Si, $FeSi_2$ and FeSi. Γ is the full width at half-maximum.

Changes in the binding energy can also be seen in the core level spectra of Fe and Si compared to the pure constituents. This is shown for the Fe $2p_{3/2}$ line (figure 2(*a*)) and for the Si 2p line (figure 2(*b*)). The Fe $2p_{3/2}$ line shifts by 0.4 eV to a higher binding energy in $FeSi_2$ as well as in FeSi. Furthermore, the core lines become narrower. The value for the full width at half-maximum (FWHM) is reduced from 1.80 eV for pure Fe to 1.20 eV for $FeSi_2$, which indicates a strongly reduced line asymmetry in the silicides.

Shifts of almost the same magnitude are seen in figure 2(*b*) for the Si 2p spectra of FeSi and $FeSi_2$ and can be compared to that for pure Si, where the lines shift to a higher binding energy. The measured energy shifts are in reasonable agreement with those of

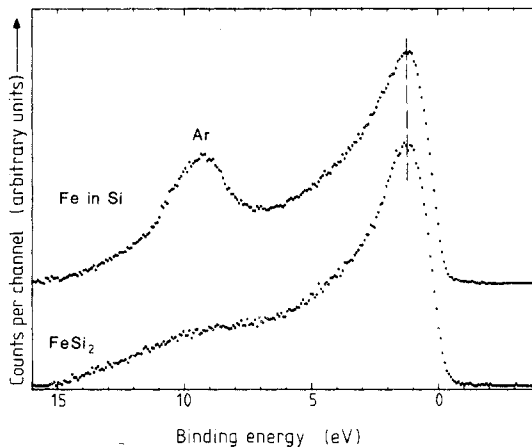

Figure 3. XPS valence band spectra for $FeSi_2$ and Fe implanted in Si. The Fe concentration is 14.5 at.%.

Egert and Panzer (1984), who reported values in the order of 0.30 eV. The difference of 0.1 eV may be due to the determination of the zero-point of the energy scale. The spectra of the Fe in Si are very similar to those of $FeSi_2$, as has been found for the case of Co in Si and $CoSi_2$ (Kinsinger *et al* 1988). Figure 3 shows a comparison of the valence bands. The peak in the spectrum of Fe in Si which appears 9 to 10 eV below E_F arises from Ar 3p emission which is due to the diffusion of argon into the sample during the sputter process. One can see that the dominating structures for Fe in Si and $FeSi_2$ have the same binding energy. We have found the same behaviour for the core level spectra. The energy positions as well as the line shapes are almost the same for both the Fe $2p_{3/2}$ and the Si 2p levels.

Figure 4 shows the depth profiles of the Fe implanted in Si and Ge. The implantation energy was 40 keV, and the dose was 4×10^{16} atoms cm^{-2}. For Fe in Si we have determined a maximum Fe concentration of 14.5 at.% at a depth of 21 nm. The measured profile is asymmetric with a tail to larger depths, and the width is 16.5 nm.

For Fe in Ge the profile looks quite different. The depth of the maximum Fe concentration (12.5 at.%) is only about 6 nm with a high Fe concentration very close to the sample surface.

4. Discussion

In recent years many photoemission experiments on transition metal silicides with various photon energies (XPS, UPS, synchrotron) have been reported. Furthermore, to complete the understanding of the electronic structure, BIS experiments have given insight into the nature of the antibonding states above the Fermi energy (Speier *et al* 1989, Azizan *et al* 1986, Sarma *et al* 1985). Together with these experimental techniques, a number of bandstructure calculations, mostly for the disilicides of Co and Ni, have been performed (Tersoff and Hamann 1983, Lambrecht *et al* 1987, Mattheiss and Hamann 1988, Newcombe and Lonzarich 1988). Recently, there has been an extensive study experimentally as well as theoretically on a number of disilicides and monosilicides

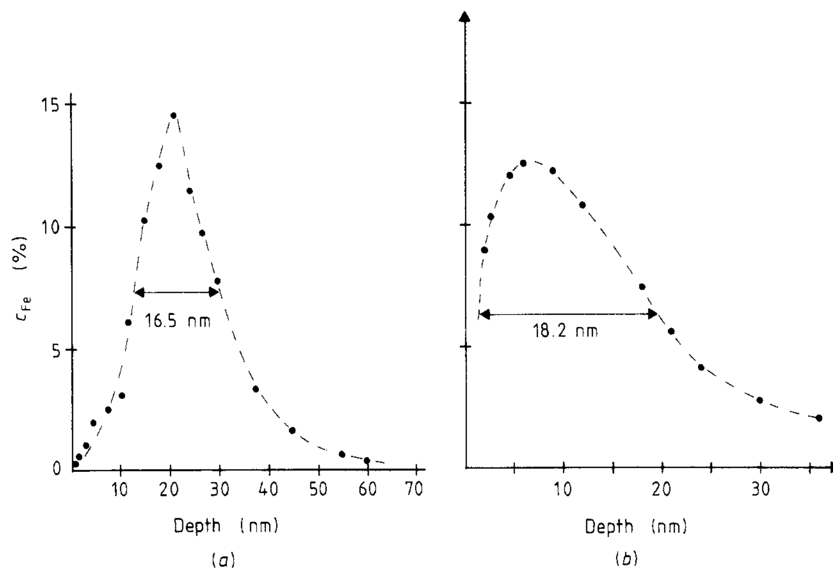

Figure 4. (*a*) The depth profile of Fe implanted in Si determined by XPS. (*b*) The depth profile of Fe implanted in Ge determined by XPS.

(Speier *et al* 1989). These investigations led to the following picture for the chemical bonding in the transition metal silicides: the bonding is expressed in terms of hybridisation between the metal d and the silicon p electrons and, in addition, the silicon s electrons seem to be involved in the bonding (Speier *et al* 1989), at least for the disilicides $CoSi_2$ and $NiSi_2$ (Tersoff and Hamann 1983). This leads to bonding states several eV below E_F, antibonding states above E_F and so-called non-bonding states in between. The same behaviour was found for Co-germanides (Kinsinger *et al* 1988). The XPS valence bands for the Fe-silicides are dominated by the non-bonding states, while the bonding states, which have mostly p-characteristics, appear as a shoulder 2 eV below the non-bonding peak. The energy of this non-bonding peak in FeSi (1.0 eV) is comparable to the value found in UV-induced photoemission experiments (Kakizaki *et al* 1982). Self-consistent ASW calculations predict the binding energy values of the bonding and non-bonding states quite well (Speier *et al* 1989, Weaver *et al* 1984).

The energy shifts in the core levels are due to changes in the chemical environment of the atoms. Changes in the chemical surroundings of the atoms lead to changes in the initial state orbital energies of the electrons, but an interpretation of these chemical shifts is complicated because of the screening effects associated with the creation of a photohole.

The Fe 2p core level lines show a substantial reduction of their half-widths from 1.80 eV for pure Fe to 1.20 eV for $FeSi_2$. This behaviour has also been reported by Egert and Panzer (1984). This narrowing of the lines is due to a decrease in the Fe density of states (DOS) at the Fermi level. It is known that an increase of the DOS at the Fermi edge leads to an increasing asymmetry of the core level lines due to the response of the conduction electrons to the creation of the photohole (e.g. Wertheim and Citrin 1979).

An interesting point is the striking similarity between the spectra of the samples, where Fe has been implanted into Si, and those of $FeSi_2$. This has also been found for

Co implanted in Si and Co implanted in Ge and the products have been compared to $CoSi_2$ and $CoGe_2$, respectively (Kinsinger *et al* 1988). The valence bands look very similar, and the core levels show the same positions and line shapes as in $FeSi_2$. This leads to the assumption that the chemical environment of the Fe atoms in these samples is quite similar, although the maximum percentage of Fe in the implanted sample is less than half the value in $FeSi_2$. Recent Mössbauer studies of Si implanted with Fe have shown that the ^{57}Fe isomer shift value of the implanted samples agrees quite well with that of β-$FeSi_2$. From these values, together with the quadrupole splittings, which are different for the implanted samples and the crystalline phases, it was concluded that the Fe–Si bonding is similar but has a different geometric and atomic configuration around the Fe atoms (Peiqun *et al* 1989). The same conclusion concerning the Fe–Si bonding can be drawn from our XPS data.

The experimentally determined depth profiles differ from those that have been determined by Monte Carlo calculations for the implantation process using standard procedures (Ziegler *et al* 1985). This is especially the case for Fe implanted in Ge, of which we have examined several samples with similar results. Monte Carlo calculations predict the value for the depth of maximum concentration at 25.5 nm and a half-width of 13.6 nm. The predictions for the depth of maximum concentration and the half-width for Fe in Si are 37.9 nm and 14.4 nm, respectively.

The asymmetry of the profiles can be explained by atomic mixing of the constituents during the sputter process (Liau *et al* 1979). However, the calculated profiles predict, especially for the case of Fe in Ge, the maximum concentrations at a larger depth than observed here. At the moment, we have no explanation for this difference, however, it might possibly be due to diffusion processes, especially for Fe in Ge, caused by local heating either during the implantation process itself or afterwards during the sputter process. For the case of Fe in Si, our depth profile was in reasonable agreement with the Rutherford backscattering results.

5. Conclusions

Our ESCA experiments on FeSi, $FeSi_2$ and Fe implanted in Si and Ge showed the following results:

(i) The bonding can be expressed in terms of the hybridisation of metal 3d and Si 3p and 3s states, as is the case for other transition metal silicides.

(ii) The spectra of Fe implanted in Si are very similar to those of $FeSi_2$, indicating that the chemical bonding is of the same type.

(iii) Experimentally determined depth profiles differ from calculated ones, especially for the case of Fe in Ge.

References

Azizan M, Baptist R, Chauvet G and Nguyen Tan T A 1986 *Solid State Commun.* **57** 1–3
Bisi O and Calandra C 1981 *J. Phys. C: Solid State Phys.* **14** 5479–94
Castro G R and Ballesteros A 1988 *Surf. Sci.* **204** 415–27
Egert B and Panzer G 1984 *Phys. Rev.* B **29** 2091–101
Elliot I, Doyle C and Andrade J D 1983 *J. Electron Spectrosc. Relat. Phenom.* **28** 303–16
Franciosi A, Peterman D J and Weaver J H 1981 *J. Vac. Sci. Technol.* **19** 657–60

Grunthaner P J, Grunthaner D J and Madhukar A 1982 *J. Vac. Sci. Technol.* **20** 680–83
Hara S and Ohdomari I 1988 *Phys. Rev.* B **38** 7554–57
Hirose K, Ohdomari I and Masayuki U 1988 *Phys. Rev.* B **37** 6929–32
Kakizaki A, Sugawara H, Nagakura I, Ishikawa Y, Komatsubara T and Ishii T 1982 *J. Phys. Soc. Japan* **51** 2597–603
Kinsinger V, Dézsi I, Steiner P and Langouche G 1988 *J. Phys. F: Met. Phys.* **18** 1515–26
Lambrecht W R L, Christensen N E and Blöchl P 1987 *Phys. Rev.* B **36** 2493–503
Liau Z L, Tsaur B Y and Mayer J W 1979 *J. Vac. Sci. Technol.* **16** 121–27
Mattheiss L F and Hamann D R 1988 *Phys. Rev.* B **37** 10623–27
Murarka S P 1983 *Silicides for VLSI Applications* (New York: Academic)
—— 1986 *J. Vac. Sci. Technol.* B **4** 1325–31
Newcombe G C F and Lonzarich G G 1988 *Phys. Rev.* B **37** 10619–22
Oh S J, Allen J W and Lawrence J M 1987 *Phys. Rev.* B **35** 2267–72
Peiqun Z, Urhahn L, Dézsi I and Langouche G 1989 *Proc. Int. Conf. on the Application of the Mössbauer Effect* (Budapest, 1989)
Rubloff G W 1983 *Surf. Sci.* **132** 268–314
Sarma D D, Hillebrecht F U, Campagna M, Carbone C, Nogami J, Lindau I, Barbee T W, Braicovich L, Abbati I and de Michelis B 1985 *Z. Phys.* B **59** 159–65
Sekiguchi S, Sugai T, Hanamura T, Kikuchi T, Matsuo M and Tanaino T 1988 *Proc. JIMIS; Trans. Japan. Inst. Met. Suppl.* **29** 343–6
Speier W, van Leuken E, Fuggle J C, Sarma D D, Kumar L, Dauth B and Buschow K H J 1989 *Phys. Rev.* B **39** 6008–16
Tersoff J and Hamann D R 1983 *Phys. Rev.* B **28** 1168–70
van Ommen A H, Ottenheim J J M, Theunissen A M L and Mouwen A G 1988 *Appl. Phys. Lett.* **53** 669–71
Weaver J H, Franciosi A and Moruzzi V L 1984 *Phys. Rev.* B **29** 3293–302
Wertheim G K and Citrin P H 1979 *Photoemission in Solids I (Springer Topics in Applied Physics* 26) ed L Ley and M Cardona (Berlin: Springer)
White A E, Short K T, Dynes R C, Garno J P and Gibson J M 1987 *Appl. Phys. Lett.* **50** 95–97
Ziegler J F, Biersack J P and Littmark U 1985 *The Stopping and Range of Ions in Solids* (New York: Pergamon)