Phases of cobalt-iron ternary disilicides

I. Dézsi,[a] Cs. Fetzer, and I. Szűcs
KFKI Research Institute for Particle and Nuclear Physics, H-1525 Budapest, P.O. Box 49, 114, Hungary

G. Langouche and A. Vantomme
Instituut voor Kern- en Stralingsfysika, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

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Cobalt–iron transition-metal disilicides were investigated by Mössbauer effect and x-ray diffraction in order to determine the concentration range of their homogeneous and separate phase formation. Except at low Co or Fe concentrations, Co and Fe formed separate $CoSi_2$ and $FeSi_2$ phases. Up to 10 at % Co was found soluble in β-$FeSi_2$; Fe dissolved in $CoSi_2$ below 1.5 at % and was positioned at two different sites of cubic symmetry. The results obtained for the phase formation in thin layers of epitaxial $CoSi_2$ on Si implanted with Fe were in agreement with the results obtained for the bulk samples. © *1998 American Institute of Physics.* [S0003-6951(98)01122-X]

In the last decade, interest in metallic silicides has increased considerably because of their potential applications in micro- and optoelectronics.[1–4] Ternary disilicides have been less studied than binary ones, although the former may be of greater importance as doped semiconducting disilicides and may have a beneficial surface effect on the formation of perfect epitaxial layers.

Early Mössbauer studies of ^{57}Co implanted atoms in Si revealed the formation of buried $CoSi_2$ precipitates of fluorite structure.[5] It was surprising to observe not only one single resonance line for iron but, in addition, another ''anomalous'' one.[6] Later when implanting ^{57}Fe in epitaxially grown $CoSi_2$ on Si, the resonance line with the same isomer shift value as for the ''anomalous'' line of ^{57}Co appeared with high relative intensity.[7] Recently, buried ternary Co, Fe silicide phases with fluorite structure were formed[8–10] on implanting Co and Fe in Si at 350 °C. Theoretical calculations for the phase diagram of Co–Fe ternary disilicide[11] suggested that disordered ternary phase in fluorite form could easily be grown above 160 K. However, because of the structural differences of $CoSi_2$ and $FeSi_2$ very low miscibility was expected.[12] In order to learn more about the ternary phase formation between Co, Fe and Si and about the solubility of Fe in $CoSi_2$, we carried out Mössbauer and x-ray diffraction studies on bulk $Fe_xCo_{(1-x)}Si_2$ in a broad concentration range and on thin layers of $Fe_xCo_{(1-x)}Si_2$ formed upon ion implanting and annealing epitaxial $CoSi_2$ on Si.

The bulk ternary disilicide samples were synthesized using 4N metals and Si of very high purity. The elements were melted together four times in an induction oven in vacuum of better than 1×10^{-4} Pa. For the samples of low Fe concentrations ^{57}Fe (enriched to 96%) was used. The weight loss after melting was less than 0.05%. The annealings were made *in vacuo* of $<1\times10^{-4}$ Pa. The $CoSi_2$ layers epitaxially grown on (111) Si with 1000 Å thickness were implanted with ^{57}Fe in the Leuven isotope separator at 80 keV energy at room temperature. The annealings of the samples were made in vacuum of 1×10^{-4} Pa.

The samples were measured by using Mössbauer spectrometers in constant accelerator mode. For the thin layer samples a small sized low background proportional conversion electron counter was used. As single line sources 20–50 mCi ^{57}Co in Rh matrix were used. The measurements were performed at room temperature. The spectra were fitted by using a least squares fitting program allowing fittings in the presence of the distribution of the hyperfine splitting parameters. For x-ray diffraction measurements a Philips vertical powder diffractometer with reflected beam monochromator was used. Cr K_α radiation was used.

The Mössbauer spectra of bulk $Fe_xCo_{(1-x)}$ are shown in Figs. 1(a)–1(e). In Fig. 1(a) the spectrum measured at $x=0.005$ could be fitted by two single lines (SL1 and SL2). For the $Fe_xCo_{(1-x)}Si_2$ bulk samples at low x values the δ

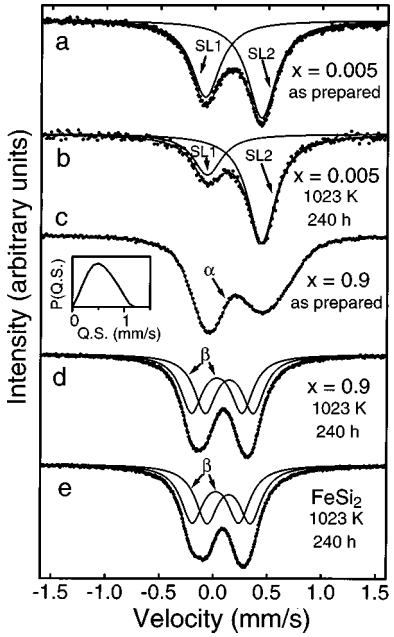

FIG. 1. Mössbauer spectra of $Fe_xCo_{(1-x)}Si_2$.

[a]Also at: Research Institute for Technical Physics and Materials Science; Electronic mail: dezsi@rmki.kfki.hu

values of the single lines agree with the values formerly obtained for the $(^{57}Co)^{57}Fe$ source[5–7] (-0.08 mm/s) (Ref. 13) and for the ^{57}Fe absorber (0.43 mm/s) in the epitaxial $CoSi_2$ layer on the Si surface. In these two different samples both lines were present but with opposite line intensities. For ^{57}Co in $CoSi_2$ and for ^{57}Fe in the $CoSi_2$ layer, the ratios of the relative intensities of SL1 and SL2 were larger than 3 for ^{57}Co and smaller than 1/3 for ^{57}Fe, excluding the fact that the resonance lines belong to a quadrupole doublet. The δ values of the singlets indicate covalently bonded iron atoms. The covalent character of the bonds in $CoSi_2$ was explained theoretically.[14] Both lines can be attributed to iron in sites of cubic symmetry and bonded to Si atoms. $CoSi_2$ has C1 fluorite structure. Because it is a metallic conductor, the appearance of an after effect resulting in anomalous charge state of iron after electron cyclotron (EC) decay can be excluded. Since the SL1 line always appears with very high relative intensity for $(^{57}Co)^{57}Fe$ sources in $CoSi_2$, either diffused or implanted and subsequently annealed,[5–7] this line can be attributed to ^{57}Fe formed after EC decay in the Co lattice position. If Fe were positioned in Si sites, a lower δ value would be expected than the value measured in the Co position because in this case Co atoms are the nearest neighbors of Fe. Since a larger δ value is found, it is highly probable that the iron is positioned in the vacant sites. The higher stability for the iron in this position is shown by the increase of the relative intensity of the SL2 line upon thermal annealing of the as-prepared bulk samples [Fig. 1(b)]. It is probable that this position is also partially populated by Co atoms in pure $CoSi_2$ but because of the random and relatively low population, these atoms have not been observed by other methods as yet. Above $x=0.015$ the spectral shape of the as-prepared samples changed more and more to an asymmetric doublet with different linewidth values. The spectra became very similar to those earlier measured for α-$FeSi_2$.[15,16] These spectra could be fitted by a doublet with distribution in the hyperfine interaction parameters [Fig. 1(c)]. $\langle\delta\rangle=0.22(1)$ mm/s and $\langle\Delta E_Q\rangle=0.54(1)$ mm/s average values were obtained. α-$FeSi_2$ has tetragonal structure[17] $P4/mmm$, in which Fe is surrounded by eight Si atoms. The distribution appears because of the structural vacancies in the α-$FeSi_2$ lattice, thereby resulting in the distribution of the electric field gradient and isomer shift at the iron sites. Only long time annealing (for 750 h) at 1023 K transformed the quadrupole split spectra to the characteristic spectrum of β-$FeSi_2$—the stable phase below 1210 K [Figs. 1(d) and 1(e)]. The transformed spectrum was fitted by considering the two possible pairings of the resonance lines: either the 1,3 and 2,4 or the 1,4 and 2,3 lines for the two doublets.[18,19] In both cases the quality of the fitting was the same. We chose the 1,3, 2,4 pairing to enable direct comparison of the data with the earlier published ones. $\delta_1=0.02(1)$, $\delta_2=0.15(1)$, $\Delta E_{Q1}=0.44(1)$ and $\Delta E_{Q2}=0.41(1)$ values (in mm/s) were found. In the x-ray diffraction patterns of the as-prepared $Fe_xCo_{(1-x)}Si_2$ samples (shown in Fig. 2 for $x=0.5$), two phases ($CoSi_2$ and α-$FeSi_2$) could be identified consistently with the Mössbauer spectra of the samples.

Formation of the separate phases indicates that no homogeneous phase is able to form at $x\gtrsim0.015$. The $\alpha\rightarrow\beta$ transformation kinetics was studied in detail.[20] We realized that

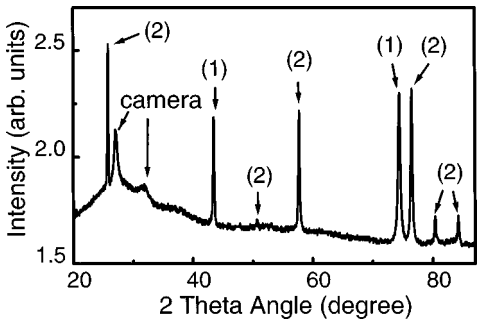

FIG. 2. X-ray diffraction pattern of $Co_{0.5}Fe_{0.5}Si_2$ as-prepared bulk sample: (1) $CoSi_2$, (2) α-$FeSi_2$

the transition rate slowed down considerably when the sample consisted of α-$FeSi_2$ and $CoSi_2$. For $x=0.5$, complete transition could be reached after annealing at 750 °C for 480 h. Therefore, the presence of Co does not decrease the $\beta\rightarrow\alpha$ transition temperature, but the presence of the $CoSi_2$ phase retards the transition. At $x\geqslant0.9$, after long time annealing the spectrum of pure β-$FeSi_2$ appeared. The x-ray diffraction pattern showed only the lines of β-$FeSi_2$, indicating that Co is soluble at $x\geqslant0.9$.

The as-implanted $CoSi_2$ thin layer samples showed quadrupole split doublets [one spectrum of the sample implanted with 6×10^{16} atom/cm^2 dose is shown in Fig. 3(a)] with δ and ΔE_Q values characteristic of ^{57}Fe in the amorphous phase.[21] On annealing at 573 K for 10 min the spectrum of the sample implanted with the lower 3×10^{15} atom/cm^2 dose [Fig. 3(d)], resulted in the spectrum with δ values obtained in the bulk $Fe_xCo_{(1-x)}Si_2$ sample at a low x value. The spectrum of the sample with 6×10^{16} atom/cm^2 dose changed after annealing at 573 K to the asymmetric doublet characteristic of α-$FeSi_2$ and also showed the presence of a fraction of the β-$FeSi_2$ phase [Fig. 3(b)]. After annealing this sample at 1023 K for 240 h, the spectrum changed to that of the pure β-$FeSi_2$ [Fig. 3(c)]. In the sample implanted with 3×10^{15} atom/cm^2 dose, the average number of iron atoms in the 2σ (σ is the straggling) thickness was 0.5 at. %. This value is in the range where the

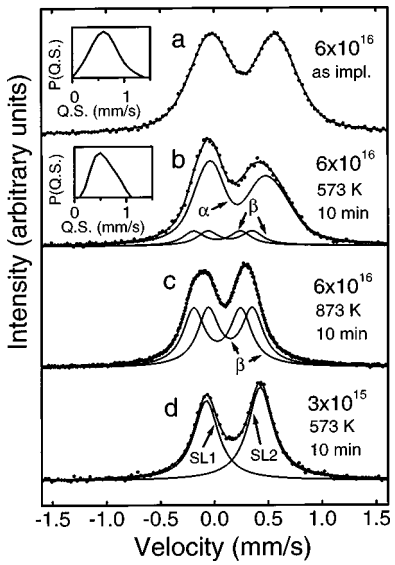

FIG. 3. Mössbauer spectra of ^{57}Fe implanted in epitaxial $CoSi_2$ layer on (111) Si.

iron populates two lattice sites in the $Co_xFe_{(1-x)}Si_2$ bulk samples. At the higher dose value, the relative concentration in 2σ thickness is in the range where phase separation takes place, resulting in α-$FeSi_2$ in the bulk samples. Probably because of the close structural relationship between the cubic fluorite structure and the tetragonal lattice of the α-$FeSi_2$, the α phase forms first at 573 K and only after annealing at 873 K does the orthorhombic β-$FeSi_2$ phase form, which is stable at this temperature.

The results clearly show for Co, Fe and Si ternary phases that a homogeneous single phase may form only in limited concentration ranges.

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