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EXAFS and XRD studies of phase formations of Co in reactions with Si–Ge alloys

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Abstract

Using EXAFS and XRD techniques, we have investigated the phase formation of Co/SiGe structures at several annealing temperatures. For the Co/$Si_{0.80}Ge_{0.20}$ samples annealed from 400°C to 600°C, Co($Si_{1-y}Ge_y$) phases with $y \sim 0.10$ were identified and the coordination number of Si around Co increases as the annealing temperature increases. For the sample annealed at 700°C, only the $CoSi_2$ phase was formed. These results indicate a preferential Co–Si reaction when annealing the Co/SiGe structure.

Knowledge about reactions between metal thin films and epitaxial $Si_{1-x}Ge_x$ is essential for application of $Si_{1-x}Ge_x$ devices [1]. We have investigated the phase formation of Co reaction with SiGe alloys under different annealing processes.

$Si_{0.80}Ge_{0.20}$ alloys of 800 Å in thickness were used for the study of Co–SiGe reactions under UHV annealing conditions. For each sample, a 200 Å Co layer was deposited onto room temperature alloys. The metallized sample was then annealed for 20 min in situ at a specific temperature ranging from 300°C to 700°C.

The phases of the annealed samples were determined using XRD and EXAFS techniques. The EXAFS experiments were carried out at beam line X-11A at the NSLS at Brookhaven National Laboratory. Two flat Si (1 1 1) crystals were used as the monochromator. Harmonics were rejected by detuning the beam intensity to 60% of its peak intensity. The XAFS signals were collected in the total electron yield mode and data were analyzed using the standard University of Washington package.

The X-ray diffraction patterns of Co/$Si_{0.80}Ge_{0.20}$ samples annealed from 400°C to 600°C show the same features as those of CoSi (viz. the cubic FeSi structure) formed by annealing Co/Si at 375°C (not shown). This suggests that the reacted layers at these temperatures have the FeSi structure. However, the peak positions of (2 1 0) and (2 1 1) lines have shifted to lower angle in comparison with those of CoSi. This shift can be associated with an expansion of inter-plane spacing of the corresponding diffraction planes. The natural assumption is that the compounds formed at these temperatures are Co($Si_{1-y}Ge_y$), which has a larger lattice constant than CoSi. However, it is also possible that the reacted layer is strained CoSi because the lattice constant of CoSi is about 20% less than that of Si. In our case, these two possibilities cannot be distinguished from the X-ray diffraction patterns. For the Co/$Si_{0.80}Ge_{0.20}$ sample annealed at 700°C, X-ray diffraction indicates the formation of $CoSi_2$.

The local atomic environment around the Co atom was obtained from the Co K-edge EXAFS. Fourier transforms of Co K-edge k^2-weighted EXAFS oscillations spectra of the Co/$Si_{0.80}Ge_{0.20}$ samples are shown in Fig. 1. These EXAFS data were collected with the electric field, $\boldsymbol{E}$, of the incident X-ray parallel to the sample surface, i.e. (1 0 0) plane of the Si substrate. To obtain

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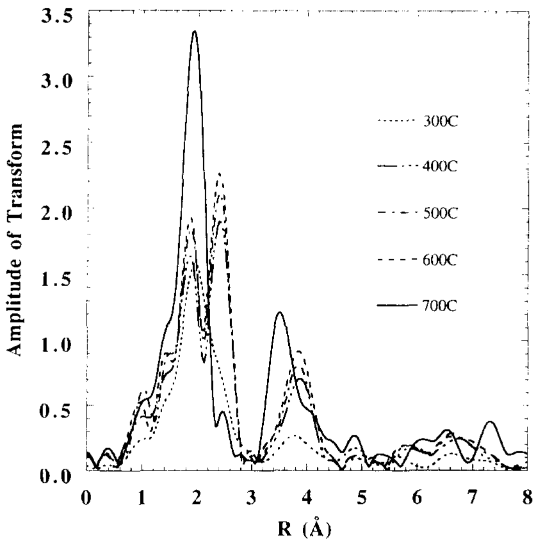

Fig. 1. The Fourier transforms of k^2-weighted EXAFS oscillations from 3 to 12 $Å^{-1}$ of the Co/$Si_{0.80}Ge_{0.20}$ samples annealed at several different temperatures (without phase correction).

Table 1
The Coordination number (N), bond length (R), and DW factor (σ^2) of Co/$Si_{0.80}Ge_{0.20}$ samples annealed at various temperatures obtained from EXAFS measurements

Sample	N	R (Å)	σ^2 ($\times 10^{-4}$ Å^2)
First shell Co–Si			
400°C	5.9 ± 0.5	2.31 ± 0.01	60 ± 10
500°C	6.4 ± 0.5	2.32 ± 0.01	58 ± 10
600°C	6.7 ± 0.5	2.32 ± 0.01	59 ± 10
CoSi	7.0 ± 0.5	2.32 ± 0.01	57 ± 10
700°C	8.2 ± 0.5	2.31 ± 0.01	40 ± 5
$CoSi_2$	8.0 ± 0.5	2.30 ± 0.01	34 ± 5
Second shell Co–Co			
400°C	5.4 ± 0.5	2.73 ± 0.01	67 ± 10
500°C	5.6 ± 0.5	2.73 ± 0.01	62 ± 10
600°C	5.9 ± 0.5	2.71 ± 0.01	60 ± 10
CoSi	6.0 ± 0.5	2.71 ± 0.01	60 ± 10

quantitative EXAFS structural parameters, standard EXAFS fittings were performed. The fitting results are listed in Table 1. No statistic significant Ge was found. As we can see from Table 1, the coordination numbers of first shell Si and second shell Co increase as the annealing temperature increases while the Debye–Waller factor of both the Co–Si and Co–Co bonds decrease. This indicates that, in this temperature range, the higher the annealing temperature, the more the Co reacts with the SiGe alloy and the more ordered the resulting film becomes.

To check if the thin films formed about 500°C are strained, we have also measured EXAFS of the 500°C annealed sample with ***E*** perpendicular to the sample surface. If the thin film is strained, its lattice no longer has cubic symmetry. In this case, there would be some measurable differences between the bond lengths or the coordination numbers obtained from the two set of EXAFS data, which were collected with ***E*** parallel and ***E*** perpendicular to the sample surface, respectively. However, no such differences were obtained from our fitting results. This indicates that the resulting films are not strained. Therefore, the line shifts in the X-ray diffraction patterns are caused by the formation of $Co(Si_{1-y}Ge_y)$. From their X-ray diffraction peak positions, we found that the Ge composition y is 12% for the 400°C sample and 8% for the 600°C sample, respectively. These y values are considerably less than those of the original epitaxial $Si_{0.80}Ge_{0.20}$ layer. This result suggests that only part of the Ge atoms in the original $Si_{0.80}Ge_{0.20}$ layer had reacted with Co during the annealing while the remaining Ge atoms had segregated out. From thermodynamic data, it is known that Si is more reactive than Ge with Co [2]. Thus we suggest that the preferential reaction of Co with Si is responsible for the low Ge composition in the formed compound $Co(Si_{1-y}Ge_y)$. The structural differences between $CoSi_2$ and $CoGe_2$ and the thermodynamically favored Co–Si reaction may explain why only a $CoSi_2$ phase was formed in the 700°C annealed Co/$Si_{0.80}Ge_{0.20}$ sample.

References

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[2] F.R. De Boer et al. (eds.), Cohesion in Metals: Transition Metal Alloys (North-Holland, Amsterdam, 1988).