Co silicide formation on SiGeC/Si and SiGe/Si layers

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The reaction of Co with epitaxial SiGeC/Si layers is investigated and compared to the reaction of Co with SiGe/Si layers. The sequence of phase formation is the same as the reaction of Co with monocrystalline Si, however, cobalt disilicide is formed at much higher temperatures. The presence of C further delays the disilicide formation, as a result of C accumulation at the silicide/substrate interface during the reaction, which blocks the Co diffusion paths. The $CoSi_2$ layers thus formed exhibit a preferential $(h00)$ orientation. The slow supply of Co atoms to the silicide/Si interface, due to the blocking of Co diffusion paths by Ge and C, is believed to be the reason for this epitaxial alignment. © *1997 American Institute of Physics.* [S0003-6951(97)00610-4]

Growth of strained SiGe alloys offers the possibility of band gap engineering for silicon-based devices. The equilibrium critical thickness of a pseudomorphic SiGe layer depends on the total strain energy in the layer and restricts the applications where high Ge concentrations are needed. Addition of substitutional carbon to a SiGe alloy gives an extra degree of freedom to control the band gap. Moreover, the strain introduced by the Ge atoms can be compensated by C atoms, which are smaller than Ge and Si atoms, resulting in a critical thickness that can be drastically increased. Silicide formation on SiGe alloys has been studied for low-resistance ohmic contacts and as contacts for Schottky barrier infrared detectors. Reaction of metals such as Pt,[1–3] Pd,[1,3,4] Ti,[5] and Co[6–9] with SiGe layers have been reported. Among the various silicides, $CoSi_2$ is a very attractive material due to its low resistivity and possibility of self-aligned formation at relatively low temperatures. The aim of this work is to investigate the reaction of Co with strained $Si_{1-x-y}Ge_xC_y$, and to compare the results to reaction of Co with $Si_{1-x}Ge_x$.

The SiGe and SiGeC layers used in this work were grown by rapid thermal chemical vapor deposition (RTCVD) on 4 in. *n*-type Si (100) substrates. Details of the deposition system are described elsewhere.[10] 35 nm of undoped $Si_{1-x}Ge_x$ or 32 nm of $Si_{1-x-y}Ge_xC_y$ were deposited at 625 °C from dichlorosilane, germane, and methylsilane (the C precursor). Ge contents were 20% for the SiGe layer and 18% for the SiGeC layer, as determined from Rutherford backscattering spectroscopy (RBS) and the nominal C content was 0.9%. A 6 in. *n*-type Si (100) wafer was used as a control sample. Prior to cobalt deposition, the wafers were cleaned in an H_2SO_4/H_2O_2 solution followed by an HF dip.

Subsequently, 17 nm of Co was sputter deposited. Reaction of Co with Si, SiGe, and SiGeC was performed by isochronal (30 s) annealing in a rapid thermal processor (RTP) in N_2 ambient at temperatures ranging from 500 to 1000 °C. The samples were characterized by x-ray diffraction (XRD) using Cu $k\alpha$ radiation, Rutherford backscattering, and channeling spectrometry, secondary ion mass spectroscopy (SIMS), and four point probe for sheet resistance measurements.

The phase formation sequence during reaction of Co with $Si_{0.8}Ge_{0.2}$ and $Si_{0.811}Ge_{0.18}C_{0.009}$ and the crystallographic orientation of the silicides formed were monitored by symmetric x-ray diffraction in the θ-2θ geometry. XRD spectra of 17 nm Co on $Si_{0.8}Ge_{0.2}$ (not shown) and on $Si_{0.811}Ge_{0.18}C_{0.009}$ (Fig. 1) after annealing for 30 s at different temperatures showed that after 500 °C the predominant phase is Co_2Si in both cases, although the presence of the
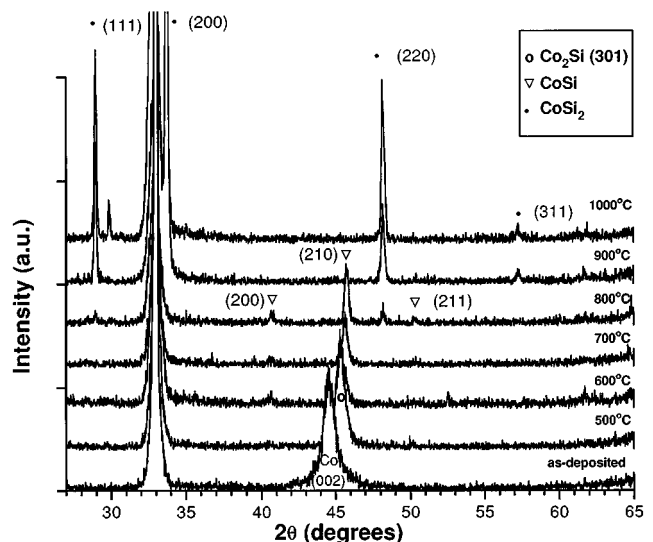

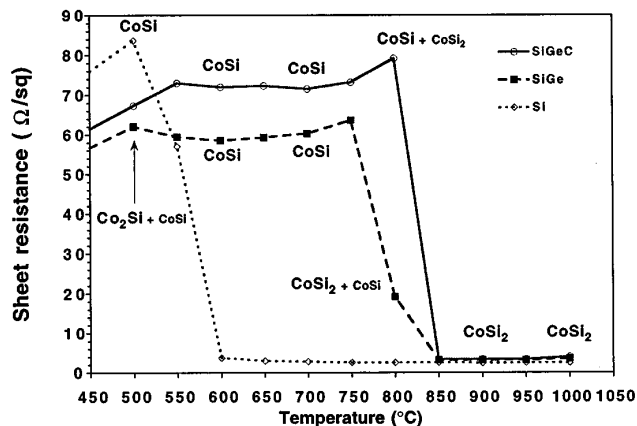FIG. 1. XRD spectra of 17 nm Co deposited on SiGeC after annealing at different temperatures for 30 s.

FIG. 2. Sheet resistance measurements of 17 nm of Co deposited on Si, SiGe, and SiGeC after 30 s annealing at different temperatures.

FIG. 3. ^{4}He backscattering spectra of 17 nm of Co deposited on SiGeC after annealing at different temperatures for 30 s.

monosilicide (CoSi) can be observed. Further annealing at 600 and 700 °C results in a full transformation to CoSi. At 800 °C both the mono- and the disilicide phases can be identified, with the CoSi$_2$ peaks being much more intense in the case of the reaction on SiGe than on SiGeC, indicating the presence of a higher fraction of this phase in the former film. Moreover, the (200) and (400) orientations of the disilicide are very pronounced in the case of SiGe, but are not observed in the SiGeC case. Finally, after annealing at 900 and 1000 °C, only the disilicide phase is present. By comparing the intensity of the diffraction peaks, a preferential (h00) orientation is observed for both substrates at these temperatures. The reaction of a Co layer with monocrystalline Si (not shown) has the same phase sequence, Co→Co$_2$Si →CoSi→CoSi$_2$, but the formation temperatures are significantly lower. At 500 °C only CoSi could be identified by XRD and after 700 °C the film is completely converted to CoSi$_2$. The preferential (h00) orientation of the disilicide observed for the reaction on SiGe and on SiGeC does not occur when monocrystalline Si (100) is used as a substrate. The formation of Co(Si$_{1-y}$Ge$_y$) ternary compounds have been previously suggested for the reaction of Co with SiGe, based on shifts of the position of the CoSi peaks in XRD spectra, which can be associated with an expansion of the CoSi lattice.[6,9] No such shifts were observed in our XRD spectra, most likely because the increase of the lattice parameter of the reacted film was too small to be resolved by our XRD system. The SiGe and SiGeC layers are totally consumed during the reaction, in addition to some Si from the substrate. The incorporation of Si from the substrate may result in a low fraction of Ge (and C) in the monosilicide phase, thus not changing significantly the CoSi lattice. However, we cannot exclude the possible presence of this ternary phase in the initial stages of the reaction. One plausible explanation for the observed retardation of the disilicide formation is that the Ge is expelled from the Co–Si–Ge compound and decorates the grain boundaries, thus lowering the reaction rate.

The sheet resistance of 17 nm Co on Si, SiGe, and SiGeC as a function of the annealing temperature is shown in Fig. 2. The phases identified by XRD for the respective temperatures are indicated in the figure. Both CoSi which has a resistivity of 100–150 $\mu\Omega$ cm, and CoSi$_2$, with a resistivity
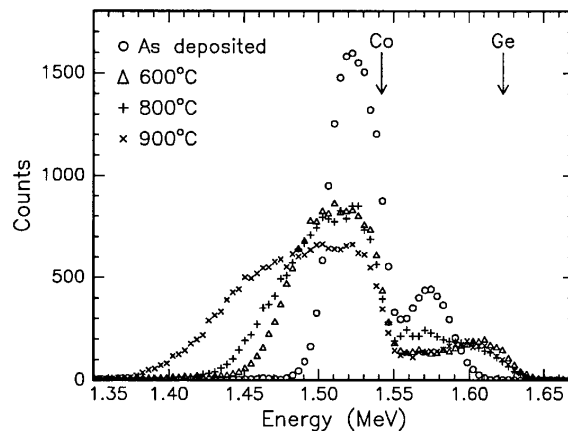
of 14–17 $\mu\Omega$ cm, are formed at higher temperatures on SiGe and SiGeC than on pure Si substrates. The resistance results confirm the retardation of the silicide formation on SiGe and SiGeC compared to Si, as observed by XRD. The delay in the disilicide formation is even more pronounced when SiGeC is used. At 800 °C a clear difference between the films formed on SiGe and SiGeC can be observed. The silicide formed on SiGe shows a sheet resistance value of approximately 19 Ω/sq, whereas the one formed on SiGeC has a sheet resistance value of 80 Ω/sq, indicating the presence of a larger fraction of a low resistivity phase in the former case. The sheet resistance of the final disilicide is the highest when formed on SiGeC, ~3.42 Ω/sq. slightly lower when formed on SiGe, ~3.24 Ω/sq, and has the lowest value for monocrystalline Si, ~2.52 Ω/sq.

Information about composition and distribution of the elements as a function of depth was obtained by RBS. RBS analysis of 17 nm Co as-deposited and after annealing at 600, 800, and 900 °C on SiGe (not shown) and on SiGeC (Fig. 3) was done using a 2 MeV ^{4}He beam. The sample normal was tilted 60° from the incident beam to increase the depth resolution. The scattering angle of the detected particles is 5°. After annealing of Co on SiGe at 600 °C, the layer formed consists of Co(Si$_{1-y}$Ge$_y$), with a higher Si content than in the initial alloy (80%). The results also indicate a pile-up of Ge both at the surface and silicide/substrate interface. At higher temperatures a bilayer structure is formed, consisting of substrate/CoSi$_2$/CoSi, with the relative thickness of the layers depending on the annealing temperature. Annealing at 800 °C results in a film which is predominantly CoSi$_2$ and a small fraction of CoSi on top, and with Ge being more uniformly distributed in the film. These results are in line with the expulsion of Ge from the Si–Ge–Co compound and subsequent formation of the disilicide, as suggested above. After annealing at 900 °C, only CoSi$_2$ is formed and the Ge is equally distributed throughout the layer. The evolution of the reaction of Co deposited on SiGeC is very similar, as can be seen in Fig. 3. For the sake of clarity, only the energy window corresponding to backscattering from Co and Ge is shown. The spectrum of the sample annealed at 600 °C shows the same features as the sample on SiGe, i.e., Co(Si$_{1-y}$Ge$_y$) which is Si enriched. Unlike the SiGe case,

annealing at a temperature of 800 °C results in the formation of $CoSi+Ge$, with a pile-up of Ge at the interface. Also, the onset of the $CoSi_2$ formation can be observed at the interface (energy ≈ 1.46 MeV). A total conversion to $CoSi_2$ occurs at 900 °C and the surface is Ge enriched. From RBS, no information on the chemical nature of the Ge-containing phases can be obtained. These results are in agreement with the XRD and sheet resistance measurements.

Additional SIMS measurements yielded information about the distribution of the C atoms, the concentration of which is too low to be detected with RBS. SIMS analysis indicates that, initially, carbon piles-up at the silicide/substrate interface (after annealing at 650 °C). For higher temperatures (800 °C), it diffuses towards the surface of the film, finally accumulating at the top surface and smearing out in depth in the silicide layer (950 °C). The accumulation of C at the silicide/substrate interface is thought to be responsible for the extra delay of $CoSi_2$ formation compared to silicidation on SiGe, although the role of the C atoms in this retardation is not yet fully understood. At high temperatures (>800 °C) carbon can precipitate and form interstitial clusters or SiC. It is speculated that these precipitates can block Co diffusion paths, slowing the reaction even more than in the SiGe case.

Channeling spectrometry of the SiGe sample annealed at 900 °C was done to study the crystalline quality of the disilicide layer. The results show a minimum backscattering yield of 60% in the Co and Si signals, and 41% in the Ge signal, confirming the highly (h00) oriented texture of the $CoSi_2$ layer, as enunciated from the XRD measurements. This observation is opposed to the solid phase reaction of Co on Si (100), which results in polycrystalline $CoSi_2$ layers. However, formation of epitaxial $CoSi_2$ layers on (100) Si has been shown when a Ti/Co bilayer is used[11] or when Co is deposited very slowly onto a hot substrate.[12,13] The key to this process seems to be the rate of Co supply. If the supply of Co atoms to the silicide/Si interface is slow enough and the temperature is high enough, such that the Co consumption is larger than the supply, the disilicide is likely to be epitaxial. The fact that the $CoSi_2$ formed on both SiGe and SiGeC exhibits $\langle 100 \rangle$ epitaxial alignment further supports the idea that the supply of Co to the silicide/Si interface is slowed down, as a result of Ge expulsion from the $Co(Si_{1-y}Ge_y)$ compound, and the C pile-up at the interface in the case of SiGeC, as suggested above.

The reaction of Co with SiGe and SiGeC layers has been investigated. It was found that the presence of C retards the formation of the disilicide phase. During the reaction, C piles up at the silicide/substrate interface which is believed to block the Co diffusion paths. The precise role of the C atoms in this retardation is not yet fully understood and is a subject that deserves further investigation. Moreover, the $CoSi_2$ layers formed show a preferential (h00) orientation. This epitaxial alignment can be a result of the slow supply of Co atoms to the silicide/Si interface, caused by the blocking of Co diffusion paths by Ge and C.

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