Transmission electron microscopic study of $CoSi_2$ epitaxial growth on hydrogen-terminated Si(001)

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Epitaxial growth of $CoSi_2$ on H-terminated Si(001) was studied by transmission electron microscopy and the epitaxial growth mechanism was presented. Direct reaction of Co with Si is suppressed on H-terminated Si below 400℃. Thus, the hydrogen at the Co/Si interface hinders the formation of low-temperature Co_2Si and CoSi phases. Upon thermal desorption of hydrogen at around 400−550℃, $CoSi_2$, which is closely lattice-matched to Si(001), grows on Si(001) and thin epitaxial $CoSi_2$ films are formed on Si(001). The {111}-faceting is completely suppressed in the epitaxial $CoSi_2$/Si(001), leading to the atomically flat interface between $CoSi_2$ and Si(001)

Key word: silicide, $CoSi_2$, hydrogen-termination, Si(100), TEM

1. Introduction

Shallow junction is required to minimize punch through and short channel effects as the Si MOS technology is scaled down to deep submicron regime. At the shallow junction, the self-aligned-silicide (SALICIDE) process is used to reduce the parasitic resistance. Cobalt silicide ($CoSi_2$) is the most promising material for the SALICIDE process, because of the lower resistance and the possibility of epitaxial growth on Si(001)(1). However, the conventional direct silicidation process leads to polycrystalline $CoSi_2$ films, since the low temperature phase Co_2Si and CoSi, which are not lattice-matched to Si(001), are first formed(2). The resulting films may have poor thermal stability and rough interfaces with {111}-faceting(3).

Epitaxial $CoSi_2$ has been grown on Si(001) using Ti(4) or SiO_2 (5) interlayer between Co and Si. In the case of the Ti interlayer, the reacted layer with Si was suggested to retard the Co-diffusion(6). The mechanism of the epitaxial growth is thus considered to be due to the skipping of the low temperature Co silicide phases; the presence of the SiO_2 or Ti-reacted interlayer retards the diffusion of Co until the formation of $CoSi_2$ (5). However, these procedures are not always successful, since the careful controls of the interlayer thickness, the quality of SiO_2 and the annealing temperature were needed. The narrow process window is due to the difficulty in precise control of the Co-diffusion for different annealing processes.

There has been another approach for the direct epitaxial growth of $CoSi_2$ on Si(001),which relys on the mechanism of concentration-controlled phase selection of silicide during reactive deposition(7). The epitaxial growth of $CoSi_2$/Si(001) was achieved when depositing Co sufficiently slowly (0.007nm/s) onto a heated Si substrate(600℃). In this method, the unusually slow deposition rate is the problem for the practical application.

Hydrogen on Si is known to stabilize the Si surface by terminating the dangling bonds(8) and be thermally stable up to 400℃−550℃(9). Co and Ni are very reactive with bare Si surfaces and the silicides are formed even at room temperature(10). The reaction was found to be prohibited on the

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hydrogen-terminated Si (11-14). Thus, the surface terminating hydrogen, which may be present on Si surfaces after deposition of metal atoms, is expected to suppress the formation of low temperature Co silicide phases upon annealing. In this study, the reaction of Co on H-terminated Si(001) (H-Si) is investigated to form the epitaxial $CoSi_2$ layers on Si.

2. Expriment

Lightly doped p-type Si(001) substrates were used in this study. Co was deposited either by an E-gun in a high vacuum evaporater or by K-cells in a molecular beam epitaxy (MBE) chamber. Before loading, the Si surfaces were chemically cleaned and some of them were H-terminated by dipping them into a 10% HF solution(8). The specimens prepared in an evaporater were ex-situ annealed in an electric furnace in a pure He ambient. The specimens deposited in a MBE chamber were in-situ annealed and Co-Si reaction was examined by reflection high energy electron diffraction (RHEED) during annealing.

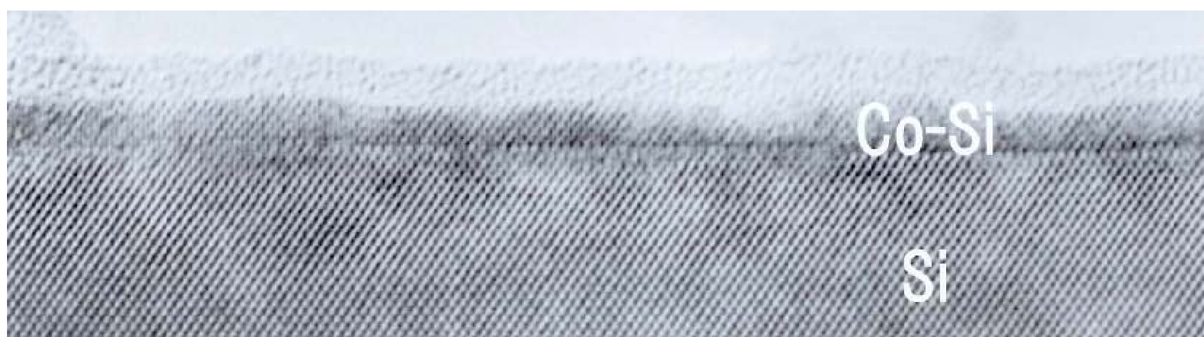
The interface reaction between Co and Si in annealed specimens was studied by cross-sectional high resolution transmission electron microscopy (TEM). Electron diffraction for plan view specimen was used to identify the silicide phases formed and to investigate the epitaxial relationship between the silicides and Si(001).

3. Results

The low temperature reaction between Co and Si was first examined using cross-sectional TEM. Co was deposited at room temperature by MBE either on H-Si(001) or on bare Si(001) which is prepared by thermally desorbing hydrogen of H-Si(001) at around 700℃ and cooling down to room temperature. The Co film is ～1.3nm thick. The specimens were annealed at 400℃ for 10 minutes. The TEM micrographs in Fig. 1(a) and (b) clearly show the difference in Co reaction with Si between on H-Si(001) and on bare Si(001). In the TEM micrograph of bare Si shown in Fig. 1(a), the lattice fringes are observed in the Co-Si reacted thin film showing the formation of silicides in the annealed layer; the observed lattice fringe in the thin layer corresponds to (101) plane of Co_2Si. On the other hand, in the TEM micrograph of H-Si(001) shown in Fig. 1(b), the texture of Co thin film is similar to that of as-deposited specimen. Thus, no reaction occurs between Co and H-Si(001) at 400℃. These results show that the formation of low temperature Co silicide phases is hindered on H-Si(001) and present the possibility of direct growth of $CoSi_2$ on Si(001).

Based on the above results, the epitaxial growth of $CoSi_2$ thin films was investigated. Co was deposited on H-Si(001) at room temperature in a MBE chamber and in-situ annealed at 650℃ for 10 min. The Co thickness is ～1.2nm. In RHEED observations, the polycrystalline diffraction pattern at room temperature persisted during low temperature annealing, but it turned into well ordered one with streaks above about 500℃ suggesting epitaxial growth of the Co-Si reacted layer on Si. Consistent with the RHEED observations, the cross-sectional TEM micrograph and the plan view transmission diffraction pattern in the inset shown in Fig.2 demonstrates the formation of epitaxial thin $CoSi_2$ layer on Si(001); the 111-fringes in the Si substrate extend into the $CoSi_2$ layer showing the epitaxial growth of $CoSi_2$. In the diffraction pattern, only the {200} spots of $CoSi_2$ were observed except for Si diffraction spots. Thus, the epitaxial relationship of the $CoSi_2$ to Si(001) is $(001)_{Si}$ // $(001)_{CoSi2}$ and $[110]_{Si}$ // $[110]_{CoSi2}$. It is also noticed that the epitaxial $CoSi_2$/Si(001) interface is atomically flat.

As shown in Fig.3, cracks along the ⟨110⟩ directions were observed in some parts of specimens.



(a)

(b)

Fig. 1 Cross-sectional TEM micrographs of Co/bare Si(001) (a) and Co/H-Si(001) annealed at 400℃ for 10 min.(b).

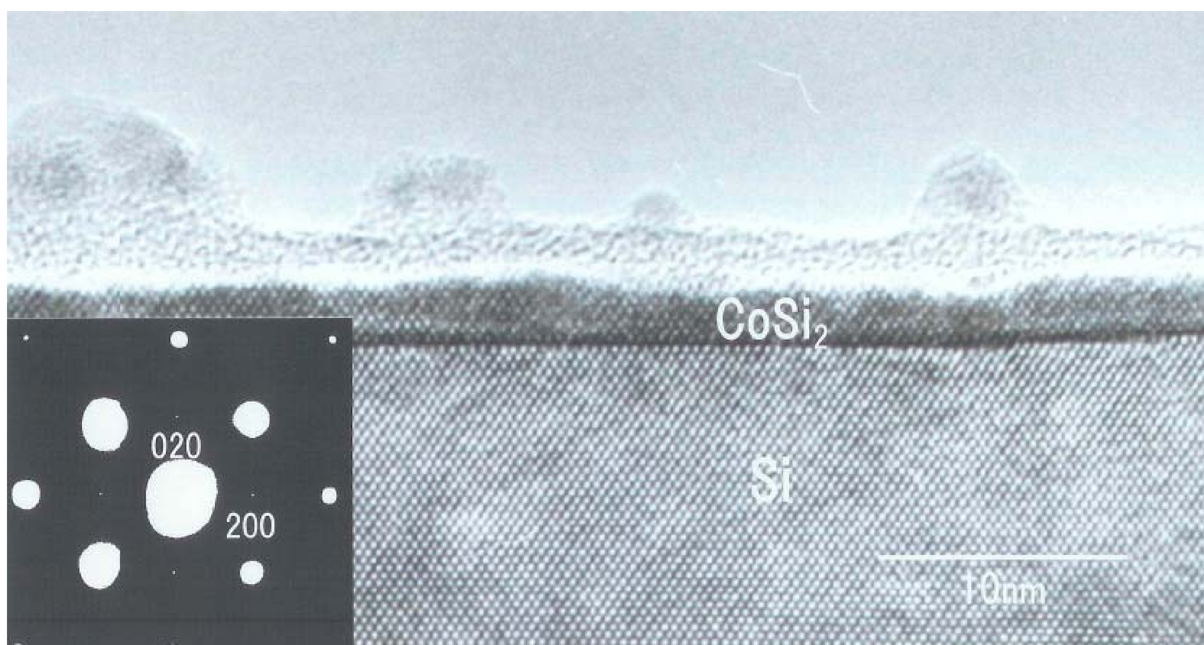


Fig. 2 Cross-sectional TEM micrograph of Co/H-Si(001) annealed at 650℃ for 10 min. and the plan-view transmission diffraction pattern.

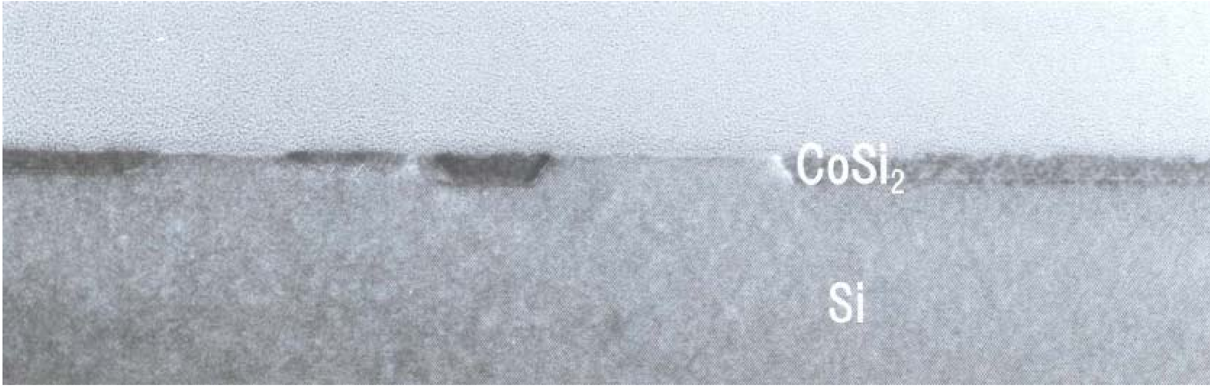


Fig. 3 Cross-sectional TEM micrograph showing cracks along the [110] direction.

4. Discussion

The hydrogen atoms on Si surface terminate dangling bonds and stabilize the surface; the 10% HF-treated Si(001) surfaces show both monohydride and dihydride termination (8). It was observed for a Ni/H-Si(111) system that Ni atoms deposited first diffuse into Si to form a thin Ni-diffused layer (Ni-Si) leaving the hydrogen on top of the Si surface(14). Co atoms are considered to behave similarly for Co/H-Si(001) system. Furthermore, Co atoms deposited subsequently may pile up on the surface terminated by hydrogen. Thus, we suppose that a Co/H-Si/Co-Si/Si interface structure is formed at room temperature. On the other hand, surface terminating hydrogen on Si(001) was found to stay at least partially on Si(001) surface up to 400℃－550℃ until it thermally desorbs(9). The hydrogen in the buried Co/H-Si/Co-Si/Si interface is also expected to stay in the interface up to the same temperature. Then, the hydrogen hinders the Co-Si reaction suppressing the formation of low temperature Co silicides phases upon annealing. At 400C－550℃, it is very likely that the hydrogen in the buried interface of Co/H-Si/Co-Si/Si thermally desorbs leading to the onset of Co/Si reaction, i.e., silicidation. Since the formation temperature of $CoSi_2$ is close to the above temperature, $CoSi_2$ begins to grow epitaxially. Thus, the skipping mechanism for epitaxial $CoSi_2$ growth works for Co/H-Si in any annealing process.

The formation of cracks shows the $CoSi_2$ is under strong tensile stress at room temperature. Since $CoSi_2$ is lattice-matched to Si at～1100℃ and has smaller lattice constant than Si below that temperature, the epitaxial $CoSi_2$ formed on Si is always under tensile stress; the stress becomes largest at room temperature(a_{CoSi2}=0.5365nm and a_{Si}=0.5431nm at room temperature). Thus, the presence of the cracks in the $CoSi_2$ films is the natural consequence of epitaxial growth of $CoSi_2$ and suggests the difficulty in growing thick epitaxial $CoSi_2$.

The formation of {111}-facet in the $CoSi_2$/Si(001) interface has been a serious problem for a shallow junction. As our results show, no {111}-faceting was observed and the interface was flat in an atomic scale. Thus, the faceting is related to the formation of polycrystalline silicides in the initial silicidation. Since the grains in the polycrystalline Co_2Si silicide have various orientations, some grains may have {111}silicide/$\{111\}_{Si}$ interface. As the temperature is raised to the formation temperature of $CoSi_2$, these grains grow preferentially with the {111} facet, since the $\{111\}_{CoSi2}$/$\{111\}_{Si}$ interface has very low free energy(15). This leads to the heavily {111} faceted interface. On the other hand, once the epitaxial

growth of $CoSi_2$ occurs on Si(001), the $(001)_{CoSi2}$ $/(001)_{Si}$ interface is stabilized, with no possibility of formation of the {111} interface.

5. Conclusions

It has been demonstrated that $CoSi_2$ can be epitaxially grown on hydrogen-terminated Si(001) and the interface is atomically flat. The hydrogen, which is present on the Si surface, is suggested to suppress the formation of low temperature phases of Co-rich silicides, leading to the direct epitaxial growth of $CoSi_2$ on Si(001).

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