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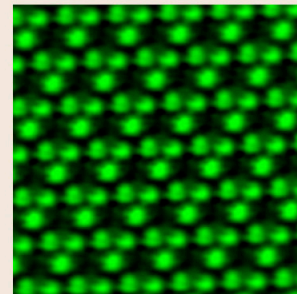
Epitaxial growth of CoSi$_2$ on hydrogen-terminated Si(001)

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We demonstrate that CoSi$_2$ grows epitaxially on H-terminated Si(001) and present the growth mechanism. It was found that direct reaction of Co with Si is suppressed on H-terminated Si below 400 °C. Thus, the hydrogen at the Co/Si interface hinders the formation of Co$_2$Si and CoSi. Upon thermal desorption of hydrogen at around 400–550 °C, CoSi$_2$, which is closely lattice-matched to Si(001), grows on Si(001) and thus, thin epitaxial CoSi$_2$ films are formed on Si(001). The {111}-faceting was completely suppressed in the epitaxial CoSi$_2$/Si(001), leading to the atomically flat interface. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1562335]

A shallow junction is required to minimize punch-through and short-channel effects as the Si metal-oxide semiconductor technology is scaled down to a 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 low resistance and 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$_2$Si 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 a 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 interlayer retards the diffusion of Co until the formation of CoSi$_2$.[5] However, these procedures are not always successful, since 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 relies 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 (0.007 nm/s) onto a heated Si substrate (600 °C). In this method, the

unusually slow deposition rate required is the problem for practical application.

Hydrogen on Si is known to stabilize the Si surface by terminating the dangling bonds[8] and to be thermally stable up to 400–550 °C.[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 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, we investigate reactions of Co on H-terminated Si(001) (H-Si) and demonstrate the epitaxial growth of CoSi$_2$.

Lightly doped *p*-type Si(001) substrates were used in this study. Co was deposited either by an E-gun in a high-vacuum evaporator 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 the evaporator 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 the 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 Rutherford backscattering spectroscopy (RBS)/channeling measurements with 2-MeV He-ion beams. The reaction was examined also by cross-sectional high-resolution transmission electron microscopy (TEM). Electron diffraction for the plan-view specimen was used to identify the silicide phases formed and to investigate the epitaxial relationship between the silicides and Si(001).

We first examined the annealing temperature dependence of Co–Si interface reaction. To make a comparison, thin Co
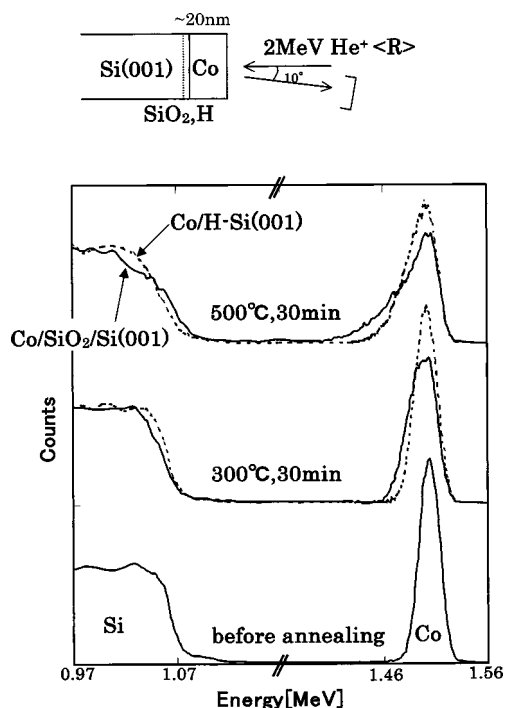

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FIG. 1. RBS spectra of Co/H-Si(001) and Co/Si(001) covered with thin native oxide, before annealing, and annealed at 300 and 500 °C for 30 min.

FIG. 2. Cross-sectional TEM micrographs of (a) Co/bare Si(001) and (b) Co/H-Si(001) annealed at 400 °C for 10 min.

films of ~20-nm thickness were deposited by the E-gun on Si(001), either H-terminated or covered by thin native silicon oxide. The RBS spectra shown in Fig. 1 indicate the striking stability of the Co/H-Si(001) interface against annealing. The specimens were annealed *ex situ* at 300 and 500 °C for 30 min. The random spectrum of the H-terminated specimen annealed at 300 °C exhibits a well-separated Co peak similar to that before annealing, but begins to change at 500 °C. On the other hand, the RBS spectra of specimen covered with thin native silicon oxide change even at 300 °C, showing the onset of silicidation. These results indicate that the thin native silicon oxide is not sufficiently thick enough to prevent the Co diffusion for the present annealing process.

Next, we investigated the low-temperature reaction between Co and Si 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 °C and cooling down to room temperature. The Co film is ~1.3 nm thick. The specimens were annealed at 400 °C for 10 min. The TEM micrographs in Fig. 2(a) and 2(b) clearly show the difference in Co reactions with Si on H-Si(001) and on bare Si(001). In the TEM micrograph of bare Si shown in Fig. 2(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. 2(b), the texture of Co thin film is similar to that of the as-deposited specimen. Thus, no reaction occurs between Co and H-Si(001) at 400 °C. These results show that the formation of low-temperature Co silicide phases is hindered on H-Si(001), and presents the possibility of direct growth of $CoSi_2$ on Si(001).

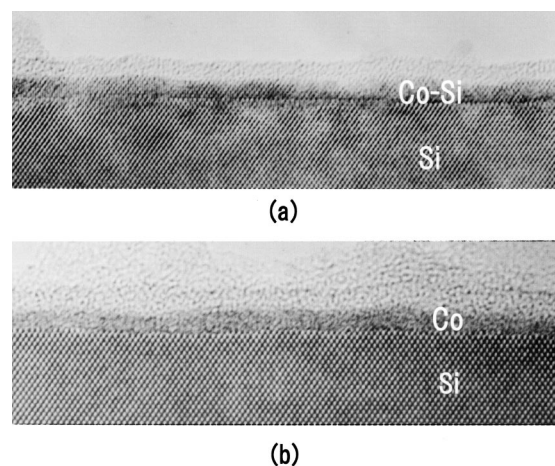Based on these results, we have tried epitaxial growth of $CoSi_2$ thin films. Co was deposited on H-Si(001) at room temperature in a MBE chamber and *in situ* annealed at 650 °C for 10 min. The Co thickness is ~1.2 nm. In RHEED observations, the polycrystalline diffraction pattern at room temperature persisted during low-temperature annealing, but it turned into a well-ordered one, with streaks above about 500 °C, suggesting epitaxial growth. Consistent with the RHEED observations, the cross-sectional TEM micrograph and the plan-view diffraction pattern in the inset shown in Fig. 3 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 $(001)_{Si} \| (001)_{CoSi_2}$ and $[110]_{Si} \| [110]_{CoSi_2}$. It is also noticed that the epitaxial $CoSi_2$/Si(001) interface is atomically flat.

As shown in Fig. 4, cracks along the $\langle 110 \rangle$ directions were observed in some parts of specimens. Since $CoSi_2$ is lattice-matched to Si at ~1100 °C and has smaller lattice constant than Si below that temperature, $CoSi_2$ formed on Si is always under tensile stress; the stress becomes larger as the temperature is decreased. Some amount of the tensile stress may be relaxed by introduction of misfit dislocations. However cracks result when the temperature is lowered rapidly before the sufficient relaxation of the stress.

The hydrogen atoms on the Si surface terminate dangling bonds and stabilize the surface.[8] It was observed for a
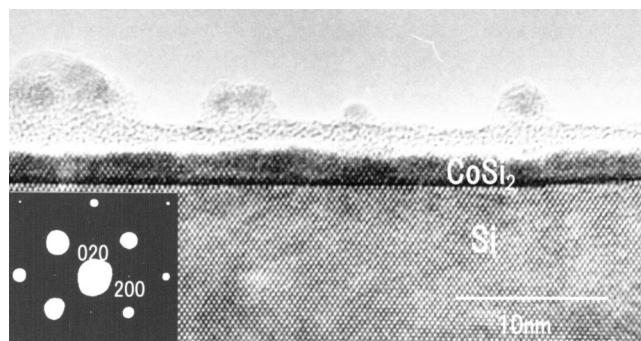

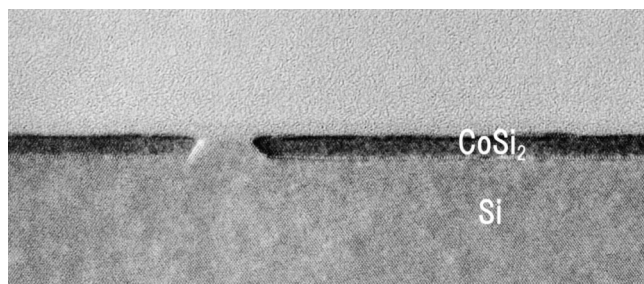FIG. 3. Cross-sectional TEM micrograph of Co/H-Si(001) annealed at 650 °C for 10 min., and the diffraction pattern.

FIG. 4. Cross-sectional TEM micrograph showing a crack along the [110] direction.

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 in the 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 the Si(001) surface up to 400–550 °C 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 400–550 °C, 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, that is, silicidation. Since the formation temperature of $CoSi_2$ is close to that 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 {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 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}$_{CoSi_2}$/{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)$_{CoSi_2}$/(001)$_{Si}$ interface is stabilized, with no possibility of formation of the {111} interface.

In summary, we have shown that $CoSi_2$ can be epitaxially grown on hydrogen-terminated Si(001) and that 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). In the present process, the presence of hydrogen on the Si surface is crucial. For the practical application of this method to Si LSI process, some technique to preserve the hydrogen on the Si surface must be devised in the practical deposition technique such as sputtering.

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