Epitaxial growth of a (100) CoSi₂ layer from carbonic cobalt films deposited on (100) Si substrate using an organometallic source

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We report the epitaxial growth of a (100) CoSi₂ layer on Si (100) substrate by the diffusion of Co from an amorphous carbonic cobalt film. The employment of an intermediate buffer layer, usually required between Si and pure Co, was eliminated in this experiment. The amorphous carbonic cobalt film was prepared by the organometallic chemical vapor deposition of cyclopentadienyl dicarbonyl cobalt, Co(η⁵-C₅H₅)(CO)₂ at 350 °C. The carbonic cobalt film was capped by a sputtered Ti layer to avoid oxidation of Co during annealing. A CoSi₂ layer was epitaxially grown on Si (100) by ex situ rapid thermal annealing at 800 °C in N₂ ambient. The supply of Co by diffusion in the carbonic cobalt film seemed to be low enough to form an epitaxial CoSi₂ layer. © 1999 American Institute of Physics. [S0003-6951(99)04207-2]

Epitaxial cobalt disilicide is considered an attractive contact material for submicron devices because of its low resistivity and good thermal stability, easy formation on a narrow Si line, and good shallow junction formation using a silicide-as-doping source (SADS).1 However, the growth of an epitaxial (100) CoSi₂ layer on (100) Si substrate has not been successfully realized by depositing pure Co and annealing due to the formation of CoSi₂ with various orientations such as (110), (100), and (221).2 It was proposed that an epitaxial CoSi₂ layer can be formed by controlling the concentration of Co into (100) Si substrate using a diffusion barrier such as Ti, Ge,3 and a chemical oxide. The formation of epitaxial CoSi₂ on (100) Si has been observed in titanium-interlayer mediated epitaxy (TIME),4 and oxide mediated epitaxy (OME)5 methods. However, it is difficult to control the Co diffusion and to form a thick epitaxial CoSi₂ layer in the interlayer mediated techniques. The techniques also have disadvantages in the multistep process including the deposition of an interlayer and a capping layer, and an in situ first annealing step to avoid cobalt oxidation and to form a high quality epitaxial layer.

We report a new method by which an epitaxial CoSi₂ layer can be grown on (100) Si substrate without employing an interlayer between Co and Si. Instead of pure Co, a Co alloy can be utilized to retard the supply of Co to the Si substrate. For this purpose, an amorphous Co–C alloy film was deposited on a Si substrate by organometallic chemical vapor deposition (OMCVD) of cyclopentadienyl dicarbonyl cobalt, Co(η⁵-C₅H₅)(CO)₂. CVDs using organometallic precursors often do not produce pure metal films at a low temperature due to incomplete decomposition of metal–carbon bonds. The carbon incorporation in deposited films increases as the metal–carbon bond order in compounds increases.6 The OMCVD of Co(η⁵-C₅H₅)(CO)₂ causes carbonic cobalt films, because the cobalt–carbon bond strength in cyclopentadienyl dicarbonyl compounds is stronger than that in other cobalt organometallic compounds.7–10

P-type (100) Si substrates with a resistivity of 5–8 Ω cm were cleaned in a H₂SO₄/H₂O₂ solution, rinsed in deionized water, dipped in HF(1%), rinsed in deionized water, and then loaded into an OMCVD reactor. Carbofilm with 40 nm thickness was deposited from Co(η⁵-C₅H₅)(CO)₂ at 480 mTorr with H₂ carrier gas. The temperatures of bubbler and substrate were 35 and 350 °C, respectively. A Ti capping layer with a 20 nm thickness was deposited on the Co film by a direct current (DC) magnetron sputtering to avoid the oxidation of Co during annealing. Capping layers such as TiN and Ti generally improve the uniformity of CoSi₂ layers on Si substrate.11 Subsequent ex situ rapid thermal annealing (RTA) was carried out in N₂ ambient at temperatures between 500 and 800 °C for 5 min. The crystal structure and microstructure of the film were investigated using x-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. The composition of the film was analyzed by auger electron spectroscopy (AES).

Figure 1 shows the XRD pattern (a) and the AES depth profile (b) of the as-deposited Co film from Co(η⁵-C₅H₅)(CO)₂ precursor. The XRD pattern shows a broad peak with the center at 44–45°. No sharp diffraacted peak was detected, indicating that the as-deposited Co film from Co(η⁵-C₅H₅)(CO)₂ was in an amorphous phase.

![Fig. 1. XRD pattern (a) and AES depth profile (b) of the as-deposited carbonic cobalt film.](image-url)
AES depth profile in Fig. 1(b) indicates that the Co film consists of about 50 at. % Co and about 50 at. % carbon. The carbon incorporation seemed to cause the formation of the amorphous phase.

Figure 2 shows the XRD patterns of the samples annealed by RTA at 500 °C, 600 °C, and 800 °C for 5 min in N₂ ambient. A Ti layer was capped on the as-deposited carbonic cobalt film before the annealing. After annealing at 800 °C, only CoSi₂ (200) and Si (200) peaks without other peaks of CoSi₂ such as (111) and (220) are shown in Fig. 2(c). It is seen that a CoSi₂ layer is formed with a strong (100) preferred orientation on a (100) Si substrate from the carbonic Co layer. The diffracted peak of CoSi₂ (200) is to appear at 600 °C with a very small peak intensity. It is worth noting that the Co–Si reaction does not occur until the temperature exceeds 500 °C. These indicate that the CoSi₂ phase can be formed from the amorphous carbonic cobalt without the transformation of the Co-rich phases such as Co₂Si and CoSi at increasing higher temperature. It is due to the retardation of the Co–Si reaction. During the reaction, the diffusion of Co may be blocked in the amorphous carbonic cobalt film, which retards the reaction between Co and Si. It has been reported that carbon at the interface of silicide/Si could block the Co diffusion path into the Si substrate.

The AES depth profile of the sample annealed by RTA at 800 °C for 5 min in N₂ ambient. The top layer is a TiO layer where the oxygen comes from the environment and is reacted with Ti. The second layer is a carbonic cobalt silicide layer consisting of C, Co, and Si. It can be seen that the annealing lowers the content of Co atoms, while the Si atoms are introduced into the carbonic cobalt layer. It is interesting to note that the ratio of Si/Co in both the carbonic layer and the epitaxial CoSi₂ layer is about 2, apparently satisfying the stoichiometry of CoSi₂. At this composition the diffusion of Co and Si seemed to stop. The first and second layers are amorphous phases because no XRD peaks related with the layers are detected. The third layer is the CoSi₂ layer with a strong (100) preferred orientation on (100) Si substrate. The concentration of Co in the CoSi₂ layer decreases with the sputtering depth, indicating a rough interface between CoSi₂ and the Si substrate. To investigate the CoSi₂/Si interface, the cross-sectional TEM was carried out after annealing at 800 °C.

Figure 4 shows the cross-sectional TEM micrograph (a) of the annealed sample and the diffraction patterns at the CoSi₂/Si interface (b) and at the TiO/C–Co–Si interface (c). In Fig. 4(a), the dark TiO layer, gray C–Co–Si layer, and dark CoSi₂ layers are seen on the Si substrate. The dark CoSi₂ layer has a uniform thickness of about 50 nm with small {111} facets at the CoSi₂/Si interface. It is also found that the discrete CoSi₂ layers with {111} and {100} facets are locally formed in the Si substrate, marked with an arrow in Fig. 4(a). It seems that the discrete CoSi₂ layers grow into the Si substrate below the continuous CoSi₂ layer, resulting in a Co concentration decrease with a depth in the previous AES profile. In Fig. 4(b), the diffracted pattern at the CoSi₂/Si interface shows that the diffracted spots from CoSi₂ and Si almost coincide with each other, which means that an epitaxial (100) CoSi₂ layer was grown on the (100) Si substrate. Figure 4(c) shows a broad-ring pattern from the TiO and carbonic layers. The TEM beam focused on both the TiO and the carbonic layers because the thickness of the carbonic layer was smaller than the beam size. Both the TiO layer and the carbonic layers can be considered as amorphous phases according to XRD and TEM analysis. The epitaxial CoSi₂ layer seems to grow discontinuously on a Si substrate with both {111} and {100} facets because the {111} interface energy of CoSi₂ is lower than (100). However, the precise behavior of the epitaxial growth from the amorphous carbonic cobalt is not yet fully understood, and deserves further investigation for the application to ultralarge scale integration (ULSI).
A high-resolution TEM (HRTEM) micrograph along the (011) zone axis was taken to investigate the coherency of the CoSi₂ and Si layers. The lattice structure image obtained is shown in Fig. 5. An epitaxial (100) CoSi₂ layer with a small {111}-faceted interface is formed on the (100) Si substrate with a sharp silicide–silicon interface. The complete registry of the lattice can be seen across the interface, indicating that the CoSi₂ layer is fully coherent with the Si substrate. Therefore, it can be said that a CoSi₂ layer is epitaxially grown on a (100) Si substrate using an amorphous carbonic Co layer, without an intermediate layer.

The role of the amorphous carbonic layer in the formation of an epitaxial CoSi₂ layer can be ascertained from the following point of view. The key factor in forming an epitaxial CoSi₂ layer on a (100) Si substrate is skipping the Co-rich phases. The initial reaction between pure Co and Si causes the formation of the polycrystalline Co₉Si and CoSi phases, followed by the formation of a polycrystalline CoSi₂ phase. Thus skipping the Co-rich silicide phase is then related to the epitaxial growth of CoSi₂. The chemical oxide in OME, or the Ti layer in TIME, serves as a diffusion barrier with the Co diffusing through it, thereby decreasing the Co concentration to a level where CoSi₂ thermodynamically is favored. The supply of Co from the as-deposited amorphous carbonic Co film into the Si substrate, seems to be suppressed to form an epitaxial CoSi₂ layer on Si as in interlayer-mediated epitaxy.

In conclusion, an epitaxial (100) CoSi₂ layer was grown on a (100) Si substrate by the supply of Co from an amorphous carbonic Co film deposited by OMCVD, without an intermediate layer. This new method of growing a (100) CoSi₂ epitaxial layer may be useful for the process development of Si integrated circuits.