Formation and evolution of epitaxial Co_5Ge_7 film on Ge (001) surface by solid-state reaction in an *in situ* ultrahigh-vacuum transmission electron microscope

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A thin metallic cobalt (Co) layer was deposited on a single-crystal Ge (001) surface at room temperature by the electron-beam evaporation of a pure Co metal source in an ultrahigh-vacuum transmission electron microscope. The formation and epitaxial growth of a cobalt germanide Co_5Ge_7 phase on the Ge (001) surface was studied *in situ* by gradually heating the sample from room temperature to ~350 °C. The occurrence of an epitaxial hexagonal-close-packed Co and the reaction between Co and Ge were observed at ~225 °C. After annealing at ~300 °C for 26.5 h, a continuous epitaxial Co_5Ge_7 film formed on the Ge (001) substrate. With further annealing at a higher temperature, the continuous Co_5Ge_7 layer broke up and formed three-dimensional islands in order to relieve the strain energy in the epitaxial Co_5Ge_7 layer. Two epitaxial relationships between Co_5Ge_7 and Ge, i.e., $Co_5Ge_7\langle 110\rangle(001)//Ge\langle 100\rangle(001)$ and $Co_5Ge_7\langle 001\rangle(110)//Ge\langle 100\rangle(001)$ were found by electron diffraction. © *2005 American Institute of Physics.*
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Si-based transistor technology is approaching its limit to achieve enhanced transistor speed for next-generation complementary metal-oxide-semiconductor (CMOS) applications. Channel mobility is a major challenge for scaled silicon devices to meet the requirements of sub-45 nm device geometries. To continue the improvement of device speed, alternative high-mobility materials have been considered essential for the CMOS technology to reach the roadmap targets set by the International Technology Roadmap for Semiconductors.[1] Currently, the most well-studied and widely accepted method to enhance carrier mobility is strained silicon technology.[2] Ge recently attracted considerable attention due to its high carrier mobility and the introduction of the next generation of high-k dielectric materials. Both p- and n-channel Ge-metal-oxide-semiconductor field effect transistors (MOSFETs) with significantly enhanced channel mobilities have been demonstrated recently.[3,4] Now, considerable efforts are put toward Ge wafer fabrication and device development by semiconductor industries.

Ge-based CMOS technology is still in a very early stage. There are many key issues to be addressed and resolved. One important issue is the formation of suitable local metal-semiconductor contact. Similar to the case in a Si-based CMOS transistor where self-aligned metal silicide layer presents in the gate, source, and drain electrode areas, self-aligned metal germanides will be used as contact materials in the future Ge-based MOSFET structures as well. The use of self-aligned silicides and germanides for contact metallization and local wiring is a response to the continued decreasing of the MOSFET structure size that requires minimized parasitic contact and series resistances in the gate and source/drain regions to enhance the device speed. Compared with silicides that have been extensively investigated in the past,[5] the formation of germanides on single-crystal Ge surface has attracted less attention.

Some earlier studies on cobalt germanides originated from the fact that cobalt germanides, especially $CoGe_2$, can be used as contact materials in $Si_{1-x}Ge_x$ and GaAs systems.[6,7] Solid-state reaction by thermal annealing of a thin Co layer on Ge showed that Co_5Ge_7 will form at a temperature around 300 °C, and then transform to $CoGe_2$ at temperature above 425 °C.[6] For contact applications, epitaxial growth is preferred to remove grain boundaries and to reduce interface roughness. Localized epitaxial growth of Co_5Ge_7 and $CoGe_2$ on single-crystal Ge (111) was observed by transmission electron microscopy (TEM).[8] Epitaxial growth of Co_5Ge_7 and $CoGe_2$ islands on a strained Ge epilayer on Si (001) was studied by scanning tunneling microscopy and reflection high-energy electron diffraction.[9]

In this letter, we report an *in situ* ultrahigh-vacuum (UHV) TEM investigation of the formation of epitaxial Co_5Ge_7 on a single-crystal Ge (001) substrate by the deposition of Co on Ge at room temperature followed by annealing at a high temperature.

A JEOL-2010 transmission electron microscope modified for the *in situ* deposition of materials under UHV conditions was used to study the formation and growth of germanide during the solid-state reaction. An electron transparent substrate was prepared by mechanical polishing and Ar^+-ion milling of a (001)-oriented single-crystal Ge wafer from the back side. The Ge substrate was mounted on the top of a conductive silicon support to enable *in situ* heating. To remove oxygen molecules adsorbed on the Ge surface, the substrate was *in situ* annealed at ~325 °C for 20 min. The deposition of Co on Ge was performed after the sub-

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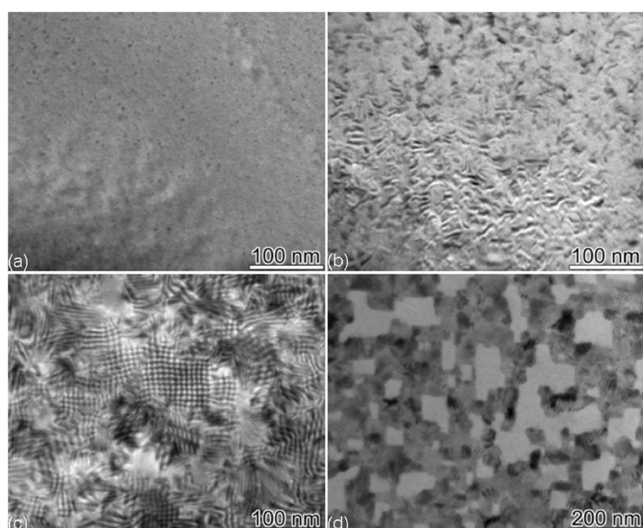

FIG. 1. TEM images showing the morphology of a Co film deposited on the Ge (001) surface at annealing at 125 °C (a), 225 °C (b), 300 °C (c), and 350 °C (d).

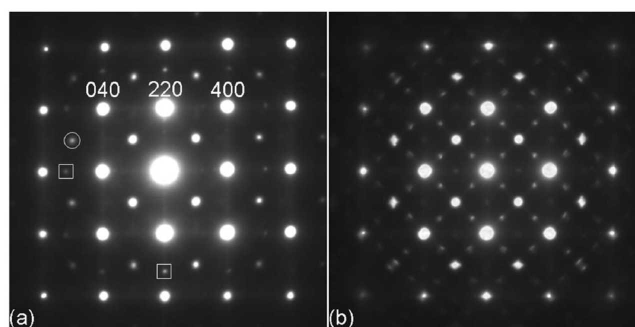

FIG. 2. Electron diffraction patterns corresponding to Figs. 1(b) and 1(c), respectively.

strate was cooled down to room temperature. The total deposition time was 3 h. Atomic Co flux was generated by the electron-beam evaporation of a high-purity Co rod from an evaporator attached to the microscope above the sample stage. The growth rate was approximately 2 nm per hour that was calibrated by *ex situ* Rutherford backscattering spectroscopy. After deposition, the sample was gradually annealed to a maximum temperature at 350 °C. During the annealing period, a GATAN DualVision™ digital camera was used to record both TEM images and selected area electron diffraction (SAED) patterns.

A uniform Co film was deposited on the Ge (001) surface within 3 h. The TEM image shows that the Co film consists of nanocrystalline particles that are few nanometers in size. Electron diffraction shows a broad ring pattern due to the small sizes of the Co crystallites.

The specimen was then gradually heated to several selected temperatures and remained long enough at each temperature to allow a possible reaction to occur. Figure 1 shows four typical TEM images representing the morphology change of the sample during the annealing. Figure 1(a) is a TEM image taken after annealing at ~125 °C for 1.5 h. The morphology did not show any difference from that at room temperature. When the temperature was increased to ~225 °C, a ripplelike pattern quickly appeared in the whole specimen, as shown in Fig. 1(b). The ripple pattern remains the same even after annealing the sample for 3 h. After further annealing at ~300 °C for 26.5 h, the ripple pattern gradually changes into a more regular Moiré pattern, as shown in Fig. 1(c). After further annealing at ~325 °C for 47 h and then at ~350 °C for 0.5 h, a mosaic pattern was formed on the surface, as shown in Fig. 1(d). The morphology changes described above are caused by the formation of a cobalt germanide phase through the solid-state reaction between Co and Ge.

The crystal structure and orientation of the cobalt germanide phase is determined by electron diffraction patterns that were recorded during the annealing process. Figure 2 is a SAED pattern corresponding to Fig. 1(b) with the electron beam along the Ge [001] zone axis. The very intense spots are from the single-crystal Ge substrate (a=0.5658 nm). The spots marked by squares are from metallic hexagonal-close-packed (hcp)-Co with the [210] zone axis parallel to the electron beam. The epitaxial orientation relationship between hcp-Co and Ge is hcp-Co $\langle 002\rangle(10\bar{1}0)\|\mathrm{Ge}\langle 220\rangle(001)$. A 90° rotation of the hcp-Co structure along the surface normal of the specimen will produce an equivalent epitaxial orientation relationship. As will be discussed later, the formation of the metallic hcp-Co phase is due to the agglomeration of Co nanoparticles. The circled spots located at Ge 200 reflections are from the cobalt germanide phase due to a solid-state reaction between Ge and Co.

During annealing at ~300 °C, the electron diffraction pattern of the specimen changes gradually from Fig. 2(a) to Fig. 2(b). More diffraction spots appear during the annealing. It was found that the reflections of the hcp-Co phase in Fig. 2(a) disappear in Fig. 2(b). It is interesting to find that the electron diffraction pattern in Fig. 2(b) is exactly the same as the one obtained in our previous studies of the reactive deposition of Co on the Ge (001) surface,[10] in which the epitaxial growth of Co_5Ge_7 was determined. This means that the cobalt germanide formed in the present solid-state reaction also has the Co_5Ge_7 phase with the orientation relationships of Co_5Ge_7 $\langle 110\rangle(001)\|\mathrm{Ge}\langle 100\rangle(001)$ and $Co_5Ge_7\langle 001\rangle(110)\|\mathrm{Ge}\langle 100\rangle(001)$. A detailed analysis of the electron diffraction pattern can be found in our previous paper.[10] The electron diffraction pattern in Fig. 2(b) will remain unchanged with annealing at ~350 °C.

The above results clearly show the formation of an epitaxial Co_5Ge_7 phase on the Ge (001) surface by the thermal annealing at temperatures up to 350 °C. Annealing temperature and time are two key factors that control the solid-state reaction process between a metal and a substrate, as well as the final product. A higher temperature will provide more thermal energy to assist atom diffusion to overcome diffusion barrier. The lattice parameter for Ge is larger than that of Si, so in general the diffusion of an atom in Ge should be easier than in Si. It was reported that Co atoms will diffuse into the bulk Ge (001) surface at a relatively low temperature (~150 °C), in comparison with the diffusion of Co into Si (350 °C).[11]

At room temperature, the diffusion of the deposited Co atoms on the Ge surface is limited. As a result, a uniform Co film consisting of small clusters is formed, revealed by TEM images and electron diffraction patterns. Although photoelectron spectroscopic study indicated the formation of germanides when Co was deposited on the Ge (001) surface at room temperature,[11] we did not find any evidence of this from TEM images and electron diffraction patterns. Figure

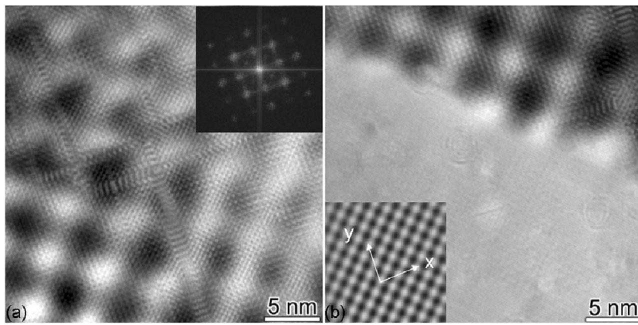

FIG. 3. High-resolution TEM images showing (a) Moiré patterns due to the overlap of Co_5Ge_7 with the Ge (001) substrate and (b) phase boundary between Co_5Ge_7 and Ge after the transition from a continuous film to 3D islands.

1(a) shows that annealing at 125 °C does not cause any visible reaction between Co and Ge.

At 225 °C, two reactions took place. One was that small Co clusters agglomerated into the bigger patches of the hcp-Co phase. The epitaxial orientation relationship is hcp-$Co\langle 002\rangle(10\bar{1}0)\|Ge\langle 220\rangle(001)$ that can be identified in Fig. 2(a). The other was that Co atoms diffused into the Ge substrate to form a cobalt-germanium intermixing layer. The strong spots located at the Ge 200 reflection spots in Fig. 2(a) should come from this layer. This layer may be a solid solution of Co in Ge with Co atoms randomly distributed in the substitutional or interstitial sites of the diamond structure of Ge. No evidence for the formation of the Co_5Ge_7 phase was found during annealing up to 225 °C. Thus, the annealing at 225 °C was not enough to promote the reaction of Co with Ge.

The disappearance of the reflection spots of the hcp-Co phase at 300 °C [Figs. 2(a) and 2(b)] indicates that the Co film has been consumed due to the reaction with Ge to form the Co_5Ge_7 phase. At the same time, regular Moiré patterns gradually appear, as shown in Fig. 1(c). The formation of Moiré pattern is due to the overlap of two crystalline materials with different lattice parameters and/or different orientations, in this case, Co_5Ge_7 on top of the Ge substrate. A regular Moiré pattern reveals that the crystallinity of the cobalt germanide phase increases with a long-time annealing, and a well-defined orientation relationship between the Co_5Ge_7 phase and the Ge substrate has been established.

A high-resolution TEM image of the Moiré pattern is shown in Fig. 3(a). The inset on the top-right-hand side corner is the corresponding fast Fourier transformation (FFT) pattern. Both the image and FFT pattern indicate an epitaxial orientation with $Co_5Ge_7\langle 110\rangle(001)\|Ge\langle 100\rangle(001)$.

It is seen in Fig. 1(c) that there are some blank areas in the specimen. Electron diffraction patterns taken from those areas only show the reflection spots from the Ge substrate, which indicates that the initial continuous Co_5Ge_7 film has broken, leaving the underlying Ge substrate exposed in some area. After annealing at 350 °C, the Co_5Ge_7 film further breaks into three-dimensional (3D) islands as shown in Fig. 1(d), in which the dark regions are Co_5Ge_7, while the bright regions correspond to the Ge substrate. The Co_5Ge_7 islands are interconnected. It appears that the exposed Ge regions are rectangular in shape with sharp straight boundaries separating the Ge substrate and the Co_5Ge_7 islands. Figure 3(b) is a high-resolution TEM image of such a boundary, in which the blank area is Ge with barely seen faint lattice images. The inset in the bottom-right-hand side corner is a Fourier filtered image of the Ge lattice with enhanced contrast. Using the lattice image of Ge as a reference, the orientation of the Co_5Ge_7 island edges is determined to be along the $Ge\langle 110\rangle$ directions.

The driving force for the transformation from a continuous Co_5Ge_7 film to 3D islands is caused by the minimization of the strain and interface energy. For the epitaxial growth with $Co_5Ge_7\langle 110\rangle(001)\|Ge\langle 010\rangle(001)$, there will be -4.5% lattice mismatch along the $\langle 110\rangle$ directions of Ge. The Co_5Ge_7 layer will experience an in-plane tensile stress from the Ge matrix. The reduction in interface and/or surface area can lower the free energy of the system, which will result in a morphology transition from Fig. 1(c) to Fig. 1(d). It is obvious that the interface area in Fig. 1(d) is smaller than that in Fig. 1(c). After the Co film is completely transformed into Co_5Ge_7, its total volume is constant. If the Co_5Ge_7 layer reduces its coverage area on the Ge surface, then its thickness will be increased. This process is controlled by the diffusion of the Co_5Ge_7 phase and occurs more easily at a higher temperature. This explains why the formation of 3D Co_5Ge_7 islands is slow at 300 °C [Fig. 1(c)], which becomes much faster at 350 °C [Fig. 1(d)].

In conclusion, the epitaxial growth of Co_5Ge_7 on Ge(001) was achieved by the solid-state reaction of a deposited Co layer with the Ge single-crystal substrate in an *in situ* UHV transmission electron microscope. The epitaxial orientation relationships were identified to be $Co_5Ge_7\langle 110\rangle(001)\|Ge\langle 100\rangle(001)$ and $Co_5Ge_7\langle 001\rangle\times(110)\|Ge\langle 100\rangle(001)$. Below 125 °C, the deposited Co layer consists of randomly orientated nanoclusters. A significant reaction between Co and Ge took place at $\sim$225 °C. The formation of a continuous Co_5Ge_7 film was obtained by annealing at $\sim$300 °C. Further annealing at 350 °C resulted in a transition from the continuous Co_5Ge_7 film to 3D islands with their edges parallel to the $Ge\langle 110\rangle$ directions.

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