Growth of single-crystal columns of $CoSi_2$ embedded in epitaxial Si on Si(111) by molecular beam epitaxy

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The codeposition of Si and Co on a heated Si(111) substrate is found to result in epitaxial columns of $CoSi_2$ if the Si:Co ratio is greater than approximately 3:1. These columns are surrounded by a Si matrix which shows bulk-like crystalline quality based on transmission electron microscopy and ion channeling. This phenomenon has been studied as functions of substrate temperature and Si:Co ratio. Samples with columns ranging in average diameter from approximately 25 to 130 nm have been produced.

Epitaxial growth of $CoSi_2$ on Si has been actively studied for several years, and high quality films have been grown on Si[1–3] and overgrown with epitaxial Si.[3] The disilicide phase is stable to high temperatures and lattice matches to Si to 1.2% at room temperature. As the cubic-fluorite structure of $CoSi_2$ and the diamond structure of Si are both face-centered-cubic structures, epitaxy on a number of crystallographic planes is feasible. While the best epitaxial quality has been demonstrated on Si (111), single-crystal growth has also been demonstrated on Si (100) and Si (110).[4]

One of the first techniques used to grow $CoSi_2$ was coevaporation of Si and Co in stoichiometric ratio on a heated Si substrate. This was found to yield films with good crystalline quality but a high density of pinholes[5,6] and has been replaced with more elaborate techniques involving room-temperature deposition.[1,2,3,7] The subject of this letter is codeposition on a heated substrate, but at Si:Co ratios which are silicon rich (i.e., significantly greater than 2:1). This technique yields the unique result of columns of single-crystal $CoSi_2$ surrounded by epitaxial Si.

Two-in.-diam *p*-type (111) oriented Si wafers cut on-axis to within a half degree were cleaned by a technique referred to as the "spin clean."[8] All of the samples described in this letter were taken from the same wafer lot, chemically cleaned *ex situ* simultaneously, and grown consecutively over a five day period. A protective chemical oxide was removed with an HF:ethanol solution in a dry-nitrogen glove box on the same day as the growth. A Riber EVA 320 molecular beam epitaxy (MBE) system was used, where Si and Co are evaporated from separate electron beam sources. On each sample, a 50-nm-thick silicon buffer layer was grown prior to deposition of the Si/Co layer, while all Si/Co layers were deposited to a Si thickness of 100 nm. Substrate temperature was controlled with a thermocouple placed behind the sample. Reported temperatures are infrared pyrometry values at the start of the Si/Co deposition, and the silicon buffer layers were grown at the same temperatures as the Si/Co layers. All samples were analyzed *in situ* by reflection high-energy electron diffraction (RHEED), and *ex situ* by transmission electron microscopy (TEM) and Rutherford backscattering/channeling (RBS).

Samples were grown with varying Si:Co ratios and substrate temperatures, but with a fixed Si deposition rate of 1.0 Å/s. With a Si:Co ratio of 12:1, substrate temperatures of 640, 700, and 800 °C were employed, and ratios of 3:1 and 60:1 were also used at 700 °C. All of the samples exhibit $CoSi_2$ columns surrounded by a silicon matrix except for the 3:1 sample, in which the $CoSi_2$ regions are coalesced. Planar TEM micrographs of these samples are shown in Fig. 1. The average diameter of the columns ranges from approximately 25 nm [Fig. 1(a)] to approximately 130 nm [Fig. 1(c)]. Cross-sectional TEM analysis shows that the $CoSi_2$ columns extend from the buffer layer to the top surface of the epitaxial Co/Si layer, as seen in Fig. 2. Planar TEM micrographs reveal a hexagonal faceting, while cross-sectional micrographs show that not all of the sidewalls are vertical but exhibit faceting on inclined planes. RHEED patterns ranged from streaks (normally obtained for single-crystal $CoSi_2$ layers) to 7×7 reconstructions. This indicates that good epitaxy is achieved, and that in some cases sufficiently large areas of high quality silicon exist to allow reconstruction.

The epitaxial silicon between the columns is free of extended defects based on TEM except for the sample grown at the lowest temperature, 640 °C. This sample shows a high density of microtwins in the silicon, visible in Figs. 1(a) and 2(a). No misfit dislocations were observed at the interface between the columns and the buffer layers. The majority of the samples exhibited only type *B* $CoSi_2$, where the silicide lattice is rotated 180° about the [111] surface normal with respect to the silicon substrate. However, some type *A* columns (unrotated) were observed in the 12:1 sample grown at 700 °C.

RBS/channeling analysis confirms the high quality of the epitaxial silicon, with the channeling minimum yield χ_{min} measured along the [111] growth axis in the silicon ranging from 1.9 to 8.9% (Table I). Note that the silicon yield is due both to epitaxial silicon between the columns and silicon atoms constituent in the $CoSi_2$. Low channeling mini-

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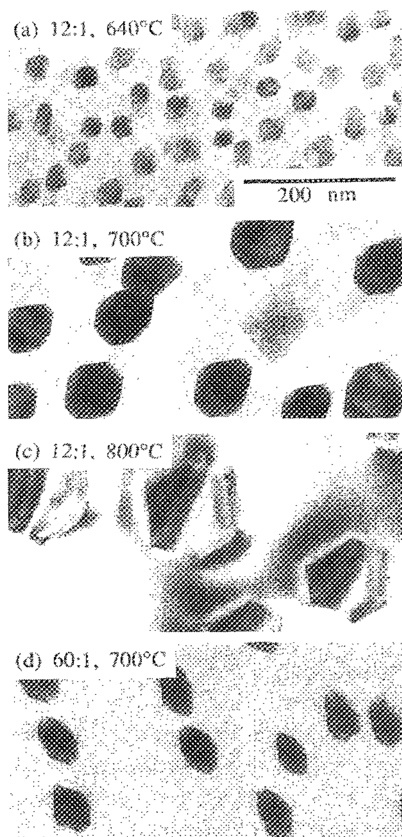

FIG. 1. Planar TEM micrographs of samples produced by codeposition of Si and Co on a heated Si(111) substrate for (a) a Si:Co ratio of 12:1 at 640 °C, (b) a Si:Co ratio of 12:1 at 700 °C, (c) a Si:Co ratio of 12:1 at 800 °C, (d) a Si:Co ratio of 3:1 at 700 °C, and (e) a Si:Co ratio of 60:1 at 700 °C. The lighter $CoSi_2$ grain to the right of center in (b) has the type *A* orientation, while the rest of the grains in that micrograph have the type *B* orientation. All four micrographs are at the same magnification.

mum yields in the Co indicate excellent crystalline quality in the $CoSi_2$ as well. RBS data were taken with normally incident 2 MeV He^+ ions, and the detector was placed at an angle of 10° from the wafer surface for optimum depth resolution.

Diodes have been fabricated from this material by evaporating Co through a shadow mask to contact the tops of the columns. Rectification was observed for all of the columnar samples, as shown in Fig. 3 for the sample grown at 640 °C with a 12:1 ratio. The relatively large reverse leakage observed could be due to several factors, including surface leakage (as no precautions such as guard rings were employed), unintentional doping of the intrinsic silicon matrix surrounding the columns, and a small percentage of leaky regions of the columnar structures. It is not known at this time whether or not these latter two are present.

From Figs. 1(a)–1(c), increasing the substrate temperature is seen to result in a greater separation of the columns as well as larger diameters. Given the spacing of the column centers, of course, the diameter is determined by the Si:Co ratio. From Figs. 1(b) and 1(d), increasing the Si:Co ratio is seen to decrease the column diameter without changing the spacing. The height of the columns is apparently dictated by the thickness of the epitaxial deposit, which was 100 nm in all of the samples grown to date. Thus the column spacing, diameter, and height may all be controlled independently by appropriate choice of the growth parameters.

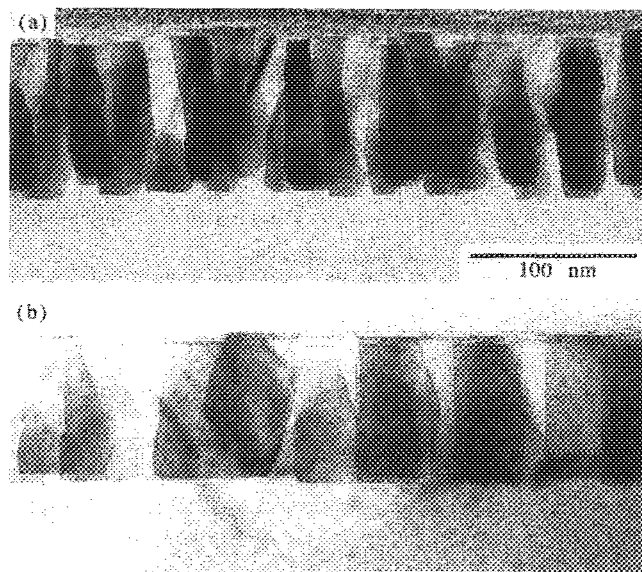

FIG. 2. Cross-sectional TEM micrographs of samples with Si:Co ratios of 12:1 grown at (a) 640 °C and (b) 700 °C, looking down a [110] direction. The material on top of the columns is epoxy used in the TEM sample preparation. The variation in the vertical position of the bottoms of the columns is due to a slight tilt of the samples with respect to the electron beam. The inclined planes in (a) are probably microtwins in the epitaxial silicon. The diamond-shaped $CoSi_2$ grain just to the left of center in (b) has the type *A* orientation, while the other grains have the type *B* orientation. Both micrographs are at the same magnification.

The fact that planar interfaces are obtained for $CoSi_2$ growth on Si(111) while {111} faceting is observed on Si(100)[9] suggests that the {111} interface is the lowest energy plane for $CoSi_2$/Si. There are three {111} planes at angles of 71° from the wafer surface (111) plane. A type *A* column, such as that seen in Fig. 2(b), could form interfaces strictly on these planes. The shape of the observed type *A* column is consistent with this. However, a type *B* column only has a single {111} plane in common with the silicon, namely, the wafer surface (111) plane. Thus the sidewalls of the type *B* columns have to form on other planes, which, as seen in Fig. 2, are sometimes vertical and sometimes inclined. This argument would favor the type *A* orientation; however, the orientation is probably determined by the initial nucleation of $CoSi_2$, at which time the sidewalls are not present.

The growth of these structures may be divided into two distinct processes, nucleation of $CoSi_2$ on the silicon buffer layer and growth of $CoSi_2$ grains. The fact that the spacing of

TABLE I. Selected data on the samples discussed in the text. The Si:Co ratio is taken from RBS measurements, and the channeling minimum yields are taken just behind the surface peaks. The average diameter and spacing of the columns are obtained from planar TEM micrographs. The last column gives the percentage of columns with the type *A* orientation as revealed by planar TEM.

Growth T (°C)	Si:Co ratio	Average diameter (nm)	Average spacing (nm)	χ_{min} of Co (%)	χ_{min} of Si (%)	Percent type *A*
640	12:1	27	79	5.2 ± 0.6	8.9 ± 0.4	< 1
700	12:1	69	118	4.0 ± 0.5	3.1 ± 0.2	15
700	60:1	45	127	4.5 ± 0.9	1.9 ± 0.2	< 1
800	12:1	132	228	7.1 ± 0.7	4.1 ± 0.3	< 1

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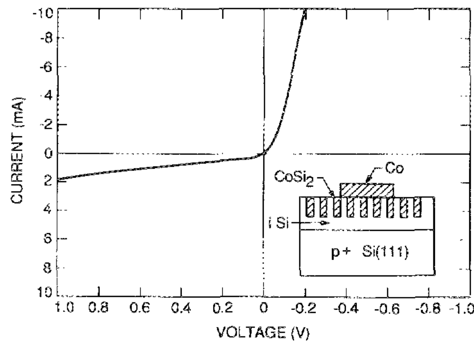

FIG. 3. Current-voltage characteristic for a diode formed by depositing Co on top of a $CoSi_2$/Si columnar structure grown with a Si:Co ratio of 12:1 at 640 °C. The inset shows a schematic drawing of the diode structure. The area of the Co pad is 2.2×10^{-3} cm^2, while the surface area of the columns is roughly 3.5 times this. Voltage is applied to the Co pad with the substrate grounded.

the columns increases with substrate temperature suggests that the initial nucleation is governed by diffusion distances of Co atoms during the initial stages of the deposition, rather than by atomic steps or impurities in the buffer layer. Once these nuclei are established, a columnar structure will be obtained if surface-diffusing Co atoms preferentially attach to existing $CoSi_2$ nuclei rather than nucleating additional $CoSi_2$ regions on the epitaxial Si. Alternatively, the initial density of $CoSi_2$ islands could be much higher than the final density of columns, with the latter determined by the bulk diffusion rate of Co at various temperatures. Such consumption of smaller $CoSi_2$ grains by larger grains has been observed in the annealing of Co implanted silicon.[10]

This phenomenon of columnar growth may be exhibited by a large class of two-component systems. However, to achieve low-defect material, a reasonable epitaxial match will probably be necessary. For the columns to have vertical sidewalls, low-energy interfaces parallel to the substrate normal are required. Additional restrictions peculiar to specific classes of materials can also be deduced. For example, in the case of silicon/silicide systems, the silicide phase must, in addition to being epitaxial, be the most silicon-rich phase.

Structurally, these materials are similar to bulk-grown, directionally solidified, metal/semiconductor eutectic composites. Examples of these materials include $TiGe_2$/Ge,[11] NiSb/InSb,[12] and most notably $CoSi_2$/Si.[13] Differences between the present work and these earlier studied include the fact that this work deals with epitaxial thin films as opposed to bulk materials, an epitaxial match between the metal and semiconductor only in the case of $CoSi_2$/Si, and much smaller dimensions for this work (roughly 20–200 nm as opposed to 1–10 μm for bulk materials). In addition to bulk composities, submicron-periodicity lamellar Si/$CoSi_2$ structures have been formed on SiO_2 by directional solidification of eutectic thin films with a scanned laser beam.[13] An earlier study demonstrated lamellar CoSi/$CoSi_2$ structures formed with a scanned laser beam.[14] The $CoSi_2$ and silicon regions in the more recent study are columnar in cross section, but contain a high density of crystallographic faults and do not have the same crystallographic orientation.

In summary, single-crystal columns of $CoSi_2$ have been produced on Si(111) substrates, where the columns are surrounded by epitaxial silicon. The column diameter and spacing may be controlled independently via the Si:Co ratio and the growth temperature, respectively. To the best of our knowledge, this is the first report of metallic epitaxial columns in a metal/semiconductor system.

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