In situ transmission electron microscopy study of the silicidation process in Co thin films on patterned (001) Si substrates

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The results of an in situ transmission electron microscopy study of the formation of Co-silicides on patterned (001) Si substrates are discussed. It is shown that the results of the in situ heating experiments agreed very well with the data based on standard rapid thermal annealing experiments. Fast heating rates resulted in better definition of the silicide lines. Also, better lines were obtained for samples that received already a low-temperature ex situ anneal. A Ti cap layer gave rise to a higher degree of epitaxy in the CoSi$_2$ silicide.

I. INTRODUCTION

Metallic silicide thin films grown on a silicon substrate play an important role in the microelectronic industry. Because of their low resistivity, they are widely used in device applications such as contact materials, interconnects, or gate electrodes. Among these materials, cobalt disilicide has attracted a special interest in the fabrication of advanced submicron devices. Understanding the growth evolution of cobalt silicides in patterned structures with fine lines is not only technologically important, but is also interesting from a purely scientific point of view. Contrary to Ti-silicides, for which a line width dependence of the silicide formation has extensively been reported, CoSi$_2$ formation is generally considered as line width independent, so that it can be applied also in very narrow lines (<0.18 μm). Nevertheless, a few articles reported a dependence of the Co-silicidation on the size of oxide openings. Hsu et al. showed that for rapid thermal annealing (RTA) of 40–60 nm Co layers on (111) Si, B-type epitaxial CoSi$_2$ layers that have a higher faceting for smaller sized oxide windows are formed. Yew et al. reported that epitaxial CoSi$_2$ is formed by RTA of 30 nm TiN and 30 nm Co on (001) Si for linear oxide windows smaller than 0.5 μm, whereas for wider lines only the edges show epitaxial growth while the center is polycrystalline.

There are three known phases of cobalt silicide, CoSi$_2$, with the largest conductivity, has the CaF$_2$ structure, which can be considered as a simple cubic structure for the Si atoms, interpenetrated by a face-centered structure of Co atoms. The lattice parameter is $a = 0.5356$ nm. Because silicon has the diamond structure, with lattice parameter $a = 0.5428$ nm, the lattice mismatch at room temperature is about $-1.2\%$, but disappears at temperatures of 1100 °C because CoSi$_2$ has an approximately 4 times larger linear expansion coefficient than Si. Very good epitaxy of CoSi$_2$ on (111) Si substrates has been reported, when the silicidation reaction took place at temperatures above 500 °C. From a technological point of view, epitaxial layers are, however, not favorable because of the larger stress and the often rough interface on (001) silicon substrates.

Besides CoSi$_2$, Co and Si are known to form two other lower temperature compounds: Co$_2$Si and CoSi. Co$_2$Si is orthorhombic with the following lattice parameters: $a = 0.711$ nm, $b = 0.492$ nm, $c = 0.374$ nm, whereas CoSi has a simple cubic structure with lattice parameter $a = 0.443$ nm.

The in situ production of the silicidation reaction in the electron microscope permits the direct structural investigation of the formation and transformation of the different silicide phases. Such studies have previously been reported for Ti silicidation reactions in active lines. In this article an in situ transmission electron microscopy (TEM) study is reported for cobalt silicidation processes in submicron active lines on patterned (001) silicon substrates. It is one of the goals to verify whether in situ
experiments yield similar results as *ex situ* anneals and can, hence, be used to draw conclusions on the silicidation mechanisms.

II. EXPERIMENTAL

(001) silicon wafers are patterned with a field oxide mask by means of the polyencapsulated local oxidation (PELOX) process, yielding active lines with different widths and spacings in the range of 0.25–10 μm isolated by a 150-nm-thick oxide. Also, larger unpatterned regions are present on the wafers. Subsequently, these wafers are covered with a metal layer consisting of 15 nm Co or 15 nm Co capped with a thin-Ti layer. Some wafers got an RTA treatment at 550 °C for 60 s followed by a wet selective etch to remove the unreacted metal and the Ti-oxide or Ti-nitride formed during the anneal. These annealed samples, CoSi, is formed in the active lines, whereas all metal is removed from the oxide pattern.

Specimens for the *in situ* TEM analysis are prepared in plain view by cutting 3-mm-diameter disks from both the blanket and patterned regions with an ultrasonic cutter. The disks are polished from the backside of the Si wafer by dimpling and subsequently ion milled from the same side until a hole appeared in the middle. *In situ* heating experiments are performed in the Philips CM20 (Eindhoven, the Netherlands) and JEOL 100C (Tokyo, Japan) electron microscopes equipped, respectively, with double- and single-tilt heating holders working up to 1000 °C. The specimen for the *in situ* TEM is fixed on its rim with a Pt washer and screw in a small furnace mounted in the tip of the heating holder. A thermocouple welded to the furnace measures the temperature during the experiments. The furnace is heated by supplying current at a rate that is manually controlled. The stage is water cooled so that the temperature can be maintained at a desired value. The specimen is heated from its edges in the microscope vacuum. Therefore, a firm contact to the furnace is necessary. As this is realized, the difference between the actual temperature of the specimen and the measured one depends on the thermal conductivity of the specimen. Once the temperature of the specimen is stabilized, this difference tends to vanish. It has been observed that at high temperatures (higher than 800 °C), the contact between the specimen and furnace becomes looser, because a difference exists in the dilatation coefficients of the specimen and of the washer and screw. This could give some small differences of a few degrees C between the measured temperature and the actual temperature on the specimen.

III. RESULTS AND DISCUSSION

Several *in situ* heating experiments are performed first on blanket specimens to determine the temperature ranges where the different forms of cobalt silicides are formed in the electron microscope. Figure 1 shows the evolution of the electron diffraction patterns with temperature for the 15 nm Co layer deposited on Si for a blanket specimen. At room temperature, Fig. 1(a), the electron diffraction pattern shows the presence of a polycrystalline hexagonal Co film. The diffraction spots belong to the Si substrate. The cobalt monosilicide (CoSi) is formed first at temperatures around 250 °C. It becomes the prevailing phase relative to the metallic Co at temperatures >300 °C. At 350 °C, Fig. 1(b), CoSi is the dominating phase, as revealed by the first four diffraction rings in the diffraction pattern. Traces of metallic Co are still present, revealed by very faint circles. Further increasing the temperature determines the appearance of the CoSi2 phase around 400 °C. The CoSi2 phase starts growing when the Co supply stops, i.e., when all Co has been converted to CoSi. At the approximate temperature of 500 °C, Fig. 1(c), both CoSi and CoSi2 phases still coexist. The less-continuous diffraction rings indicate that the grain size has increased compared with the 350 °C condition. The electron diffraction pattern shows no texture for the film and no traces of unreacted Co are present anymore. As the temperature is increased to 650–700 °C, only the reflections characteristic for cobalt disilicide remain in the diffraction patterns. The film is fully transformed to CoSi2. Further heating determines the fast growth of the CoSi2 crystallites. At 900 °C, large grains showing different orientations are formed. Figure 1(d) reveals the diffraction pattern of a large crystallite that has grown epitaxially. The crystallographic relations are [001]CoSi2//[001]Si and (200)CoSi2//(400)Si.

Figure 2 shows the TEM images at different temperatures corresponding to the same experiment on a blanket specimen. In Fig. 2(a), the Co thin film is revealed. The layer is continuous polycrystalline with grains of average size of 10 nm. At 350 °C, Fig. 2(b), when CoSi is already formed, the average grain size did not increase significantly. At grain boundaries, the layer looks discontinuous or perhaps thinner. Further increasing the temperature determines the appearance of the CoSi2 phase around 400 °C. As shown in Figs. 1(c) and 2(c) at temperatures of 500 °C, both CoSi and CoSi2 phases coexist. The thin film is polycrystalline and well crystallized. The grain dimensions are rather uniform; their average size is 40 nm. Further heating determines the growth of the CoSi2 crystallites at the expense of the CoSi. At temperatures around 650–700 °C, only cobalt disilicide is present. Figure 2(d) shows the morphology of the film at 900 °C. It consists of large CoSi2 crystallites with dimensions between 150 and 1000 nm. The grains have different orientations, some of which are divided in subgrains by small-angle grain boundaries. The largest ones show well-defined orientations.

In summary, the *in situ* TEM experiments on blanket layers show that the phase transition sequence is the fol-
lowing: CoSi starts to form at 250 °C with coexistence of Co up to 400 °C; at approximately 400 °C cobalt disilicide (CoSi2) appears and coexists with CoSi up to approximately 600 °C. Further specimen heating results in the increase of the CoSi2 crystallite dimensions. At temperatures >800 °C, the growth in size of the CoSi2 crystallites becomes very fast and many of them show epitaxial orientations. Comparison with literature data on the vacuum annealing of Co thin films shows that our transition temperatures are approximately 100 °C lower than reported by Lau et al.9 However, in their experiments, much thicker (one order of magnitude) Co films were deposited on Si. They also showed that Co2Si is the first silicide that formed at 350 °C and that at 375 °C CoSi grew simultaneously with Co2Si until the Co was exhausted. The onset for CoSi2 formation in their experiments was 550 °C. Also van Gurp et al.10 showed that CoSi2 started to grow at 550 °C, after annealing of a 1000-nm Co film. The phase sequence and transition temperatures in our experiments compare much better with the x-ray-diffraction (XRD) studies of a 30-nm Co film on (001) Si annealed for 1 h at temperatures between 500 and 900 °C in a N2/H2 ambient as reported by Bulle-Lieuwma et al.11 They showed the coexistence of CoSi and CoSi2 at 500 °C, with the disilicide starting to nucleate at temperatures of 400–500 °C and the full transformation to CoSi2 at 600 °C. At 900 °C, the CoSi2 in their films exhibited an (011) texture. Sukagawa et al.12 studied the phase transformation of TiN-capped Co (30 nm and 10 nm, respectively) on silicon by XRD and cross-sectional TEM. They found the coexistence of Co2Si, CoSi, and Co in the temperature range 375–425 °C and concluded that the transformation of Co2Si to CoSi started before the transformation of Co to CoSi was completed. Above 450 °C, all Co was reacted, and in the temperature range 475–550 °C CoSi was the only phase present.

Except for the temperature differences, compared with the works of Lau et al.,9 van Gurp et al.,10 and Sukagawa et al.,12 also the formation of Co2Si is not observed in any of the present in situ heating experiments. There is no technical reason why the Co2Si would not be distinguished in the electron diffraction patterns. Maybe the Co2Si forms only in a very narrow temperature or time range so that it transforms too quickly to CoSi to be recognized and is never present in a measurable quantity during the annealing of our thin Co layers. This would imply that the Co2Si almost immediately transforms to

FIG. 1. Electron diffraction patterns from the same region of the blanket specimen showing the phase transformation by in situ heating: (a) RT, Co; (b) 350 °C, CoSi, traces of Co; (c) 500 °C, CoSi2 and CoSi coexist; (d) 900 °C CoSi2.
CoSi, which is in agreement with the results of Sukegawa et al.\textsuperscript{12} that both the Co to Co$_3$Si and the Co$_3$Si to CoSi reactions occur simultaneously. On the other hand, the absence of Co$_3$Si agrees with the XRD results reported by Detavernier et al.\textsuperscript{13,14} for the annealing of thin (<20 nm) Co or Ti-capped Co layers.

It can be concluded that the presence of an unexhausted metal source has a strong influence on the results. On the other hand, it should be realized that in the present experiments because of the backside thinning of the TEM specimens, the silicon source might become exhausted (see further comparison of thinner–thicker specimen regions). Nevertheless, the transition temperatures agree quite well with those reported for the inert annealing of thin Co films. Hence, the temperature reading during the in situ heating cycles can be trusted quite well.

The next step for this in situ study is to find out how the silicidation reaction takes place in narrow structures (submicron lines), which are normally used in the semiconductor devices. In our particular case, the narrow structures consist of groups of 10 lines with equal nominal width and spacing or of isolated lines. The thinning of the specimens for TEM is performed in such a way that a group of such active lines crosses the region transparent to the electron beam more or less parallel with the sloped direction of the specimens.

Different specimens for TEM analysis have been prepared for different heating treatments in the electron microscope. From these experiments some general observations can be outlined. In the active lines, polycrystalline CoSi appears at temperatures between 300 and 400 °C. Also Yew et al.\textsuperscript{4} found that Co, in their case capped with TiN, reacts during the RTA annealing to polycrystalline CoSi in 0.2–2-μm-wide oxide openings at a temperature of 480 °C. In the case of our in situ TEM annealing experiments, polycrystalline CoSi$_2$ starts forming in the narrow lines at temperatures of 500–600 °C, whereas CoSi starts disappearing in the diffraction patterns at temperatures >700 °C. At 800 °C, the only silicide phase present in the active lines is CoSi$_2$. At this temperature, the CoSi$_2$ crystallites grow very fast, some epitaxially, but without forming a single crystalline layer. The CoSi$_2$ grains occur in a large number of orientations. These observations show that Co silicides are in situ formed in the active lines in a similar way as in the blanket specimens, with only one exception: CoSi seems to last at higher temperatures in the

FIG. 2. TEM images at different temperatures, of the regions in the blanket specimen corresponding to the diffraction patterns in Fig. 1, showing the morphology of the film with different silicide phases: (a) Co thin film; (b) CoSi thin film; (c) CoSi and CoSi$_2$ thin film; (d) CoSi$_2$ thin film.
lines than in the blanket layer. Detailed results about the silicide formation in the active lines are given in the following.

In Fig. 3, two TEM images are depicted during a heating cycle up to 800 °C, of a Co–Si specimen with lines, starting from 300 °C, in steps of 100 °C and spending 30 min at each step. At 400 °C, Fig. 3(a), the film that mainly consists of CoSi, starts to shrink from the border of the line. This agglomeration process continues as the temperature is increased. At 700 °C, Fig. 3(b), the layer, which now consists of CoSi₂ with only some traces of CoSi, agglomerates and is no longer present on the borders of the active line. The crystallites are around 100 nm in size. At 800 °C only cobalt disilicide exists. The crystallites double their sizes, whereas the borders of the stripes remain depleted. It is clearly an advantage of the in situ TEM experiments that both the transformation and the agglomeration processes can be directly observed.

Another heating cycle, similar to the previous one but during which each heating step lasted only 5 min, was performed on a Co–Si specimen with lines. In Fig. 4(a) the polycrystalline film of CoSi and CoSi₂ nicely fills the strips, leaving the borders straight. By further heating, at 800 °C, Fig. 4(b), large CoSi₂ crystallites of 200–300 nm

FIG. 3. TEM images showing the silicide formation in the active lines by an in situ annealing at a slow heating rate. Note the agglomeration of CoSi₂ and the roughness of the line borders.

FIG. 4. TEM images showing the silicide formation in active lines by an in situ annealing at a fast heating rate. The borders of the lines are straight.
form a continuous line. The entire line is transformed to CoSi$_2$. Both randomly oriented and epitaxial grains occur. The borders of the lines remain straight in this case. It is clear that, in the previous experimental case, the heating at each temperature step lasted too long and the silicides agglomerated in the middle of the line. A fast heating reduces the agglomeration of the silicide because the total thermal budget decreases.

Finally, the specimens were heated directly at 800 °C, waiting 5 min until the temperature was stabilized, in the aim to form CoSi$_2$ in the lines. Figure 5(a) and 5(b) show the structure of a Co–Si-active line in a thinner and thicker part of the TEM specimen, respectively, and Fig. 5(c) and 5(d) show the structure of a Ti cap–Co–Si line also in thinner and thicker specimen regions. One has to point out that an exact measurement of the specimen thickness is not possible in the TEM. A judgment of the relative thickness between different specimens or specimen regions is based on the intensities in the diffraction pattern. The parts of the specimen referred to as “thicker” are the regions that are typically used to reveal the in situ silicidation reaction. These regions are chosen with the aim to have a larger Si source and, hence, to simulate the behavior during the silicidation on a silicon wafer. In all regions, CoSi$_2$ has been formed directly in a continuous-polycrystalline thin film, but in the thinner parts of the specimen, where less Si substrate is present, CoSi also appears in the diffraction pattern. It indicates that the Si supply is not high enough to transform the whole layer in CoSi$_2$. The crystallite dimensions are much smaller in the thinner part of the specimens, Fig. 5(a) and 5(c) than in the thicker ones, Fig. 5(b) and 5(d). The borders of the lines are better defined for the Co–Si specimen than for the Ti cap–Co–Si one. In the last case, there is a tendency of lateral growth of silicide over the line edges. In standard RTA processing conditions, the lateral overgrowth is suppressed by the use of a Ti or TiN cap. As after the first RTA treatment (at 500–600 °C), the remaining unreacted metal is selectively etched, and no overgrowth can occur anymore during the second RTA anneal. Hence, the situation is different from the single-step in situ experiments.

Figure 6 shows the growth of CoSi$_2$ on active lines that are previously submitted to a low-temperature RTA treatment and selectively etched to remove the unreacted Co so that CoSi is already present before the in situ

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**FIG. 5.** TEM images showing the influence of the Si substrate thickness on the CoSi$_2$ thin film morphology, formed in the active lines by in situ heating at 800 °C: Co on Si line in thinner (a) and thicker (b) parts of the TEM specimen; Ti cap–Co on Si line in thinner (c) and thicker (d) parts of the TEM specimen. Note in (c) and (d) the overgrowth of the CoSi$_2$ at the line borders.
heating experiment [Fig. 6(a)]. As one can see from Fig. 6, all metal has been etched away from the isolation oxide between the lines. Heating experiments are performed in the electron microscope at 520, 720, and 860 °C, lasting 5 min on each step. At temperatures higher than 700 °C, CoSi₂ is fully formed in crystallites of average sizes of 200 nm and with different orientations, filling the line completely. The borders of the lines are straight. By further heating, at temperatures >850 °C, the CoSi₂ starts to agglomerate, making the border of the line rough.

Also, for the initially ex situ RTA annealed Ti cap–Co on Si sample, heating in the microscope in the same way as for the previous experiment to temperatures >700 °C results in active lines consisting of CoSi₂ [Fig. 7]. In this case, however, very large oriented CoSi₂ crystallites are formed. They have the width of the line (500 nm in this case) and are approximately 2000 nm long. As shown in the diffraction pattern, the crystallite in the upper line [Fig. 7(c)] has a [011] orientation [Fig. 7(a)], whereas the crystallite in the line from the middle [Fig. 7(c)], has an [001] orientation [Fig. 7(b)]. Note that one cannot distinguish Si reflections in either of the diffraction patterns. For Fig. 7(b), it is not possible because all reflections are superposed when the [001] zone axes for epitaxial CoSi₂ and Si are parallel. But in Fig. 7(a), except of the [011] CoSi₂ pattern, also the [001] Si substrate pattern should be present. Its absence indicates an almost full consumption of the Si in the silicidation reaction. A high degree of [001] epitaxially oriented grains in the case of Ti cap–Co samples has previously also been reported for ex situ RTA annealing in case of the presence of a thin oxide at the Co–Si interface. The [011] epitaxy for the silicide is less common, but e.g., also reported by Bulle-Lieuwma et al. for inert furnace annealings in N₂–H₂. As one can see in Fig. 7(c), the borders of the lines are very straight and smooth. In Ref. 4 where Co-silicides in lines and holes produced by RTA treatments of TiN–Co starting layers were studied by TEM, it was shown that CoSi₂ grows epitaxially, if the line width is smaller than 500 nm, which was our case. On the other hand, in a TEM study of the epitaxy of CoSi₂ produced by RTA processes in a 1200-nm-wide active line, it has been shown that only the large (approximately 400 nm) CoSi₂ crystallites, which grew near the edges of the line, were epitaxial, whereas the smaller ones in the center of the line were not.

In the last two in situ experiments, we show that the best lines are obtained on wafers that are previously submitted to a one-step RTA and selectively etched so that CoSi is already formed in the lines. By heating in the microscope at temperatures <800 °C, the CoSi film in the active lines transforms completely in a textured CoSi₁ layer, leaving the line border straight. If the temperature is further increased, the CoSi₁ film starts to agglomerate in the center of the line.

IV. CONCLUSIONS

The in situ silicidation of (Ti cap)–Co–Si during observation in a TEM allows the direct investigation of the phase formation, grain growth, and agglomeration processes. The good correspondence of the phase-transition temperatures with comparable ex situ experiments allows concluding that the temperature of the TEM specimen is well controlled. For comparison with ex situ anneals, specimen regions with a thick enough silicon substrate should be considered to avoid effects due to depletion of the silicon source. This implies that the method is only applicable for experiments related to thin metal layers as are relevant for future microelectronic technologies.

The heating experiments show that a better definition of the line edges is obtained by applying a lower total thermal budget, i.e., with a faster heating rate. Also, better lines are obtained for the samples that got the ex situ...
low-temperature RTA anneal and selective etch. This indicates that a surface diffusion on the isolation oxide occurs during the in situ annealing experiments for the samples without RTA anneal.

The Ti cap–Co–Si samples that are RTA annealed at low temperature show more epitaxially oriented grains after the in situ annealing than the samples that did not receive the RTA anneal. This is probably due to a more important reaction of the Ti cap layer with the oxygen contamination in the TEM vacuum, during the relatively slow in situ heating, than the reaction with the oxygen contamination in the ambient, during the fast RTA treatment. Therefore, the gettering role of the Ti for the interfacial oxygen contamination will be less or even absent during the in situ heating experiments.

The ex situ preannealed Ti cap–Co–Si samples also show more epitaxy than the preannealed samples without the Ti cap layer. This is probably related to some trace amounts of Ti remaining in the CoSi formed during the preanneal.

In the present experiments, a slight retardation of the CoSi to CoSi₂ transformation is observed for narrower Co–Si lines. Whether this is related to, e.g., a different contaminant level, a higher stress or some other effect needs further study. In all cases, a line width dependence of the grain growth rate or orientation is not observed.

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