# Formations and morphological stabilities of ultrathin $CoSi_2$ films*

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In this paper we investigate the formations and morphological stabilities of Co-silicide films using 1–8-nm thick Co layers sputter-deposited on silicon (100) substrates. These ultrathin Co-silicide films are formed via solid-state reaction of the deposited Co films with Si substrate at annealing temperatures from 450 °C to 850 °C. For a Co layer with a thickness no larger than 1 nm, epitaxially aligned $CoSi_2$ films readily grow on silicon (100) substrate and exhibit good morphological stabilities up to 600 °C. For a Co layer thicker than 1 nm, polycrystalline CoSi and $CoSi_2$ films are observed. The critical thickness below which epitaxially aligned $CoSi_2$ film prevails is smaller than the reported critical thickness of the Ni layer for epitaxial alignment of $NiSi_2$ on silicon (100) substrate. The larger lattice mismatch between the $CoSi_2$ film and the silicon substrate is the root cause for the smaller critical thickness of the Co layer.

**Keywords:** silicide, epitaxial alignment, ultrathin film

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## 1. Introduction

Nickel and Cobalt silicides are widely used in today's silicon-based integrated circuits as contacts and local interconnects.[1−4] The formation of ultrathin Ni-silicide film via a solid-state reaction of a deposited Ni thin film with Si(100) substrate is recently found to critically depend on the initial Ni film thickness.[2,3] For Ni films above 4 nm in thickness, the usual phase formation sequence prevails with the formation of $Ni_2Si$ followed by NiSi preceding that of $NiSi_2$ that is the most Si-rich phase in the Ni–Si binary phase diagram.[4] The transition from NiSi to $NiSi_2$ does not occur until the formation temperature is raised above 700 °C.[5] When the starting Ni films are below 4 nm in thickness, epitaxially aligned $NiSi_2$ films immediately grow below 500 °C. This distinct growth behaviour directly affects the morphological stability of the resulting Ni-silicide film at an elevated temperature such that the NiSi and resultant $NiSi_2$ formed using the relatively thick Ni films are polycrystalline and thereby easily agglomerating above 500 °C, while the epitaxially aligned $NiSi_2$ formed using the thinner Ni films can withstand treatments up to 850 °C. Here, the symbol "$NiSi_2$" is used for the sake of discussion of the epitaxially aligned films since the exact atomic composition in such an ultrathin Ni-silicide film is yet to be confirmed.[2,3,6] Nonetheless, this strong thickness dependency is interpreted as a consequence of the interfacial energy being of growing importance for smaller film thicknesses.[2] In view of the great structural and chemical similarities between Co and Ni as well as between their silicides especially the disilicides, i.e., $CoSi_2$ and $NiSi_2$, similar thickness dependences of phase formation and morphological stability should be observed in the growth of Co-silicide films. Unfortunately, epitaxial growth of a $CoSi_2$ film on a Si(100) substrate has proven very difficult.[7−9] One of the methods to promote $CoSi_2$ epitaxy on Si(100) substrates is to use a thin interlayer between the Co film and the Si substrate.[7] Some later studies have shown that very thin Co film with only one monolayer (ML) could transform into a $CoSi_2$-like layer even at room temperature.[7,10] But for a thicker Co layer sputter-deposited on Si(100), it is still not easy to obtain the

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expected epitaxially aligned $CoSi_2$ film for a Co–Si binary system.[9]

Up to date, there have been few studies dealing with the phase formation and morphological stability of ultrathin Co-silicide film. Furthermore, identification of phase formation in ultrathin silicide film is frequently a major challenge and a combination of several characterization methods is necessary. The present work offers a systematic investigation of the phase formation and subsequent morphological stability of Co-silicide films starting from 1-nm to 8-nm thick Co films deposited by magnetron sputter deposition.

## 2. Experiment

Silicon wafers, which are (100) oriented and of p-type with resistivity in a range of 20 Ω·cm–40 Ω·cm, were used as a substrate material. After standard wafer cleaning and removal of native oxide in dilute HF (5% in $H_2O$), the wafers were loaded into a sputter-deposition chamber for a series of Co depositions at room temperature (nominal) using an elemental target of Co. Details about the deposition process are found elsewhere.[11] The deposition rate of Co was 0.014 nm/s and the target thicknesses (nominal) ranged from 1 nm to 8 nm. These wafers were then sliced into small pieces of 2 cm × 2 cm in size for subsequent anneals in a rapid thermal processing (RTP) chamber at temperatures ranging from 450 °C to 850 °C. All anneals were performed in a $N_2$ atmosphere and lasted 30 s. The samples were characterized using four-point probes for sheet resistance ($R_s$), micro-Raman spectroscopy (MRS), X-ray diffraction (XRD) for phase formation, and high-resolution transmission electron microscopy (HR-TEM) for lattice imaging and interface morphology.

## 3. Results and discussion

Figure 1 shows the variations of the product of $R_s$ of silicide film and thickness of the deposited Co layer, $t_{Co}$, with RTP temperature ($T_{RTP}$). Since the precise thickness information is unavailable *a priori* for the Co-silicides formed, it is informative to use this $R_s \times t_{Co}$ product instead of $R_s$. The product $R_s \times t_{Co}$ provides some resistivity information about the silicide films but it is smaller than the true resistivity by a factor corresponding to the volume expansion from metal to silicide. In Fig. 1, the formed Co-silicide films show two distinct annealing behaviors as $t_{Co}$ varies from 1 nm to 8 nm. When $t_{Co} > 1$ nm, $R_s \times t_{Co}$ decreases sharply at a temperature above 500 °C and this occurs at higher temperatures for thicker films. The $R_s \times t_{Co}$ step in the low temperature range is associated with a phase change from the high-resistivity CoSi to the low-resistivity $CoSi_2$. This phase change follows the usual $Co_2Si$–CoSi–$CoSi_2$ formation sequence with all silicide films in the polycrystalline (poly) form.[7–9] The steepness increases of $R_s$ in the high temperature range is caused by a capillary effect leading to agglomeration of the formed silicide films, and the onset of this steepness increase continually decreases with film thickness decreasing except for silicide films with $t_{Co} = 1$ nm.[2,3] In contrast, $R_s \times t_{Co}$ keeps decreasing for the films formed with $t_{Co} = 1$ nm when the $T_{RTP}$ increases up to 600 °C. Above this temperature, an increase in $R_s \times t_{Co}$ is found because of the agglomeration of the silicide films. However, the films formed with $t_{Co} = 2$ nm begin to agglomerate at a temperature above 550 °C. The improved thermal stability of a Co-silicide film with $t_{Co} = 1$ nm ought to be a result of an epitaxial alignment of the silicide film to the Si(100) substrate because the epitaxial silicide is capable of forming with excellent uniformity and thermal stability.[12,13]

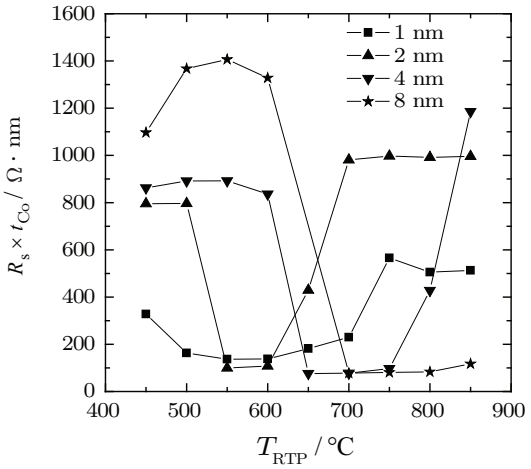



**Fig. 1.** Variations of $R_s \times t_{Co}$ with RTP temperature for silicidation at different values of metal thickness ($t_{Co}$). The behaviour of the Co-silicide film with $t_{Co} = 1$ nm is distinctly different from those of Co-silicide films with $t_{Co}$ being equal to and more than 2 nm: Co-silicide films with $t_{Co}$ being 1 nm and 2 nm act as a watershed in behaviour.

Such an epitaxial aligned silicide has been reported for $NiSi_2$ layers with $t_{Ni} \leq 4$ nm previously.[2] As is well known, both $CoSi_2$ and $NiSi_2$ share the same crystallographic structure (face-centred cubic) with

Si, and the values of lattice parameter $a$ at room temperature for $CoSi_2$, $NiSi_2$, and Si are 0.5364, 0.5406, and 0.5431 nm, respectively. The minor difference in $a$ between $CoSi_2$ and Si could diminish at elevated temperatures for silicide formation because the thermal expansion coefficient of $CoSi_2$ ($\sim 12 \times 10^{-6}$ K$^{-1}$) is larger than that of Si ($\sim 3 \times 10^{-6}$ K$^{-1}$).[14] In view of the structural and geometrical similarities of $CoSi_2$ and $NiSi_2$,[15] one would expect to observe the $CoSi_2$ (200) and (400) peaks from XRD patterns for $CoSi_2$ film formed with $t_{Co} = 4$ nm. However, as revealed by XRD and MRS analyses in Figs. 2(a) and 2(b), CoSi grows at a low RTP temperature for these samples with $t_{Co} = 4$ nm, and then poly $CoSi_2$ film, dominated by components with (111) and (220) orientations, is grown when $T_{RTP}$ increases. The larger lattice mismatch between $CoSi_2$ and Si than the mismatch between $NiSi_2$ and Si should be the cause why epitaxially aligned $CoSi_2$ cannot grow with the same initial metal thickness as Ni. The peak at $2\theta \approx 33°$ originates from the (200) reflection of Si. It occurs when the Si substrate is distorted.[16] CoSi is indicated by the Raman band at 204 cm$^{-1}$, which has been reported previously.[17] The $CoSi_2$ is Raman-inactive, owing to its high symmetry with the face-centred cubic (fcc) structure.[18] Within the detection limit of XRD, we failed to detect any silicide peaks in the samples with $t_{Co} < 4$ nm. Further analyses of phase formation in these samples with $t_{Co} < 4$ nm are carried out with the results from MRS and TEM shown below.

It is noticed in the MRS results in Fig. 3(a) that only Si signals are detectable by MRS and no CoSi is detected for samples with $t_{Co} = 1$ nm at all annealing temperatures. But for samples with $t_{Co} = 2$ nm, CoSi signals in Fig. 3(b) appear at 450 °C and 500 °C, and then disappear from 550 °C. The MRS results reveal that CoSi forms at 450 °C for the 2-nm thick Co layer, and then the usual formation sequence will proceed with the increase of $T_{RTP}$. All CoSi is completely transformed into $CoSi_2$ at 550 °C. In contrast, $CoSi_2$ could grow directly for samples with $t_{Co} = 1$ nm at low $T_{RTP}$ without the usual phase sequences from CoSi to $CoSi_2$.

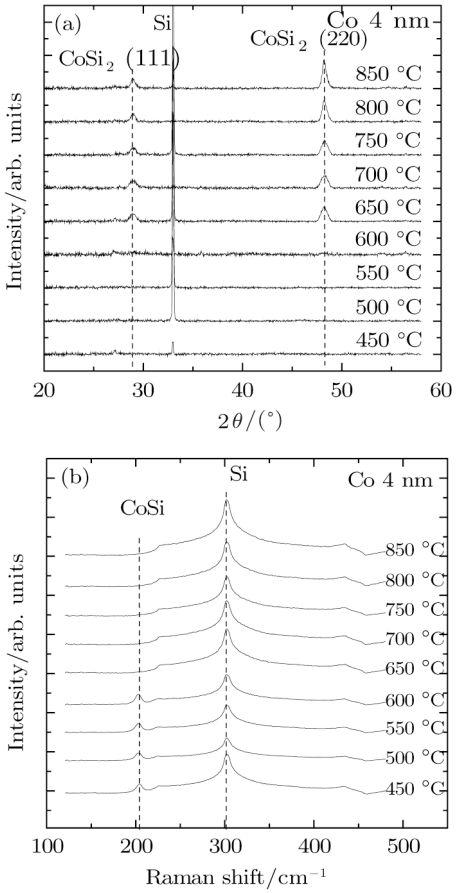



**Fig. 2.** (a) XRD and (b) MRS results for silicidation at different annealing temperatures with $t_{Co} = 4$ nm.

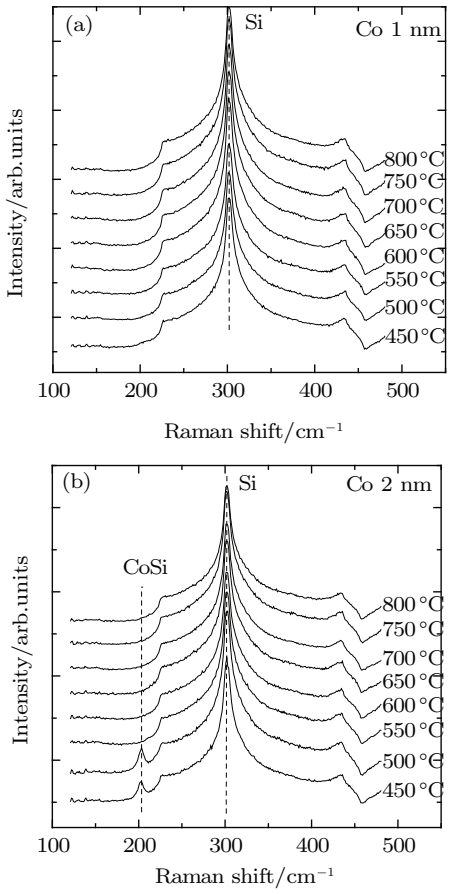



**Fig. 3.** MRS results for Co-silicide films with (a) $t_{Co} = 1$ nm and (b) $t_{Co} = 2$ nm formed at different annealing temperatures.

The HR-TEM images in Fig. 4 reveal the epitaxial aligned $CoSi_2$ in the samples with $t_{Co} = 1$ nm annealed at (a) 450 °C showing defects such as stacking faults and twins, and (b) 550 °C showing the better epitaxial quality, (c) a poly CoSi film in the sample with $t_{Co} = 2$ nm annealed at 450 °C, (d) a poly $CoSi_2$ film in the sample with $t_{Co} = 2$ nm annealed at 550 °C. The thicknesses of the $CoSi_2$ films, 2.5 nm–2.8 nm formed with $t_{Co} = 1$ nm are 20% to 28% thinner than the expected thickness of 3.49 nm of a stoichiometric $CoSi_2$. The thickness deviation could be due to nonstoichiometry of the epitaxial Co-silicide films, which could be expressed as $CoSi_{2-y}$ with $y = 0.4 \sim 0.6$. In Ref. [13], a significant stoichiometric deviation of $NiSi_2$ from the Si:Ni composition ratio of 2:l has been ascribed to Si vacancies and antisite defects (Ni atoms on Si sites), but it is still unclear in the case of $CoSi_2$. In detail, figures 4(a) and 4(b) each show the coherent Co-silicide structure on Si substrate, which means that an epitaxial aligned $CoSi_2$ film already forms at 450 °C when the initial Co layer is 1-nm thick, and higher temperature will treat the film and reduce the defects. The improved crystallographic arrangement in Fig. 4(b) as compared with that in Fig. 4(a) is concluded to be responsible for the continual decrease of $R_s \times t_{Co}$. In Fig. 4(d), the $CoSi_2$ layer transformed from CoSi with $t_{Co} = 2$ nm apparently shows the noncoherent structure on the Si substrate, and the thickness of the $CoSi_2$ film is around 4.8 nm–5.2 nm. Despite the fact that the $CoSi_2$ film thickness formed with $t_{Co} = 2$ nm is almost twice as much as the film thickness formed with $t_{Co} = 1$ nm, the $R_s \times t_{Co}$ of the former begins to increase above 550 °C. The latter has better thermal stability than the former because of the epitaxially aligned structure. To summarize, epitaxially aligned $CoSi_2$ films directly grow below 500 °C for $t_{Co} = 1$ nm, and exhibit better morphological stabilities than $CoSi_2$ films formed with $t_{Co} = 2$ nm. Above 1 nm, CoSi films form at a low $T_{RTP}$, and then transform into poly $CoSi_2$ with the increase of $T_{RTP}$. A critical thickness with $t_{Co} = 1$ nm exists for $CoSi_2$ epitaxy on Si(100), with an excellent correlation between the HR-TEM results and the $R_s$ data as well as further support from the MRS analysis. The Ni disilicide film formed with $t_{Ni} = 1$ nm exhibits good morphological stability up to 700 °C. The worse morphological stability of the $CoSi_2$ film formed with $t_{Co} = 1$ nm could also be ascribed to the larger lattice mismatch between $CoSi_2$ film and silicon substrate.

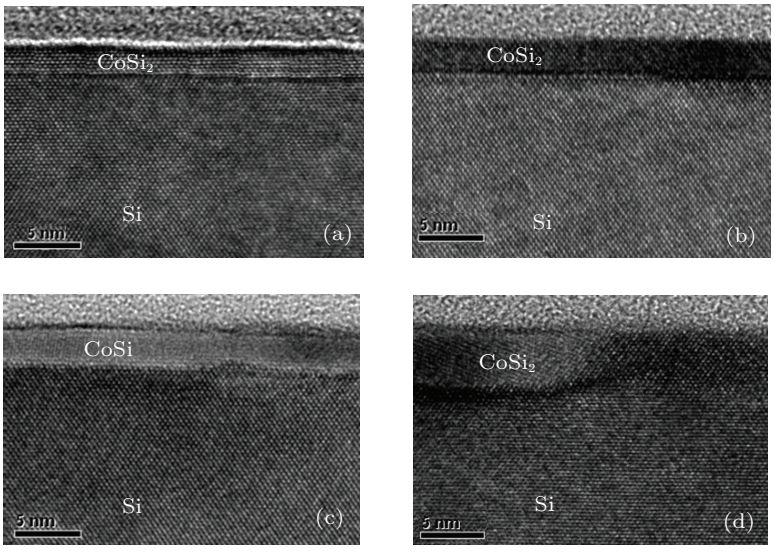



**Fig. 4.** (colour online) Cross-sectional HR-TEM images for epitaxially aligned $CoSi_2$ with $t_{Co} = 1$ nm formed at (a) 450 °C and (b) 550 °C; poly CoSi films with $t_{Co} = 2$ nm formed at (c) 450 °C; poly $CoSi_2$ films with $t_{Co} = 2$ nm formed at (d) 550 °C.

A reasonable explanation for the observed thickness dependence of phase formation and morphology stability is discussed as follows. For the initial Co film 2–4 nm thick, the formation of CoSi continues to be preceded by that of $Co_2Si$ as is the case with relatively thick Co films. Based on purely thermodynamic data, the values of heat of formation of $Co_2Si$ (–38 kJ/gram-atom), CoSi (–48 kJ/gram-atom) are greater (i.e., more negative) than that of $CoSi_2$ (–33 kJ/gram-atom),[19] supporting the selection of

$Co_2Si$ or CoSi. CoSi would be the first phase to form according to these data without considering its dynamic behaviours. However the Marker experiment has shown that $Co_2Si$ forms and becomes the first phase through the motion of the Co atoms.[5,20] The discussion on phase selection and competition can thus be focused on $Co_2Si$ and $CoSi_2$, and we assume that once $Co_2Si$ is favored the CoSi forms subsequently. Surface energy will play an increasingly important role when film thickness decreases. The nucleus of a new silicide phase has a free energy given by[21]

$$(\text{at T1})\Delta G \sim BS\Delta\sigma + AV\Delta G_v, \tag{1}$$

where $A$ and $B$ are geometrical factors; $V$ and $S$ are volume and surface area of the silicide film, respectively; $V = St_{\text{sil}}$, with $t_{\text{sil}}$ being the film thickness of silicide; $\Delta\sigma$ and $\Delta G_v$ denote, respectively, surface energy change and Gibbs' free energy change associated with the formation of the nucleus of a new phase; $\Delta G_v$ also varies with $T$ through $\Delta G_v = \Delta H - T\Delta S$ consisting of the enthalpy and entropy terms $\Delta H$ and $T\Delta S$. Since the determination of $A$ and $B$ needs many assumptions, and the other thermo-chemical data also have large uncertainties, the exact calculation of $\Delta G$ will be very hard. However a qualitative analysis is still very helpful for the understanding of phase change. Assuming that all the samples have the same surface area $S_0$, and $A = B = 1$, equation (1) becomes

$$\frac{\Delta G}{S_0} \sim \Delta\sigma + t_{\text{sil}}\Delta G_v. \tag{2}$$

In the solid state, interface energies are likely to vary between the value approaching zero for epitaxial interface and the maximal value in the order of $2 \times 10^{-4}$ J/cm$^2$ for a noncoherent interface.[21] In the present study, we choose $2 \times 10^{-4}$ J/cm$^2$ for all noncoherent interfaces.

At 500 °C, the values of $\Delta G_v$ are $-4.12$ kJ/cm$^3$ and $-5.96$ kJ/cm$^3$ for $CoSi_2$ and $Co_2Si$, respectively.[19] From Fig. 5, the surface energy changes of $Co_2Si$ and $CoSi_2$ will be $\Delta\sigma_{21} = \sigma_2 - \sigma_1$, and $\Delta\sigma_{31} = \sigma_3 - \sigma_1$. Since all structures for initial and final phase are poly structures, $\Delta\sigma_{21} = \Delta\sigma_{31} \approx 0$. The surface energy change would have little influence on the final free energy change. For silicide films with $t_{\text{sil}} = 50$ nm, the values of $t_{\text{sil}}\Delta G_v$ will be $-2.06 \times 10^{-2}$ kJ/cm$^2$ and $-2.98 \times 10^{-2}$ kJ/cm$^2$ for $CoSi_2$ and $Co_2Si$. Even if the $CoSi_2$ film is an epitaxial film, $\Delta\sigma_{31} = -\sigma_1 = -2 \times 10^{-4}$ J/cm$^2$, and it still has little influence on the final $\Delta G$ because it is 100 times lower than the values of $t_{\text{sil}}\Delta G_v$ of $CoSi_2$ and $Co_2Si$. $Co_2Si$ is favored and consequently CoSi forms. With the decrease of thickness of the ultrathin silicide film, $t_{\text{sil}}\Delta G_v$ decreases and $\Delta\sigma_{31}$ would be closer to $t_{\text{sil}}\Delta G_v$ if $CoSi_2$ is an epitaxial film, but $\Delta\sigma_{21}$ is still close to 0 at this time. The total $\Delta G$ of $CoSi_2$ could be higher (i.e., more negative) than that of $Co_2Si$, and $CoSi_2$ is thus favored. Gallego and Miranda,[9] and Hwang *et al.*[11] reported that one Co ML would be transformed into $CoSi_2$ even at room temperature, which is consistent with the above discussion. To summarize, when $t_{\text{Co}}$ is smaller than the critical thickness, the lower interfacial energy from the epitaxially aligned film would cause $CoSi_2$ to have more negative free energy change than $Co_2Si$, and then the formation of epitaxially aligned $CoSi_2$ is thus energetically favourable.

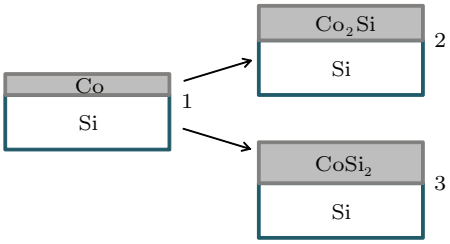



**Fig. 5.** Sketch showing the formation of a new silicide phase accompanied by a change in surface energy.

## 4. Conclusion

In this paper, thickness dependence of Co-silicide is studied in detail. A critical thickness with $t_{\text{Co}} = 1$ nm exists for $CoSi_2$ epitaxy on Si(100). Epitaxially aligned $CoSi_2$ films readily grow for $t_{\text{Co}} = 1$ nm at $T_{\text{RTP}}$, and each exhibit a good morphological stability up to 600 °C. Above 1 nm, CoSi films form at low $T_{\text{RTP}}$, and then transform into poly $CoSi_2$ with an increase of $T_{\text{RTP}}$. The surface energy is identified as the root cause for epitaxially aligned $CoSi_2$. It will play a critical role in the formation of a silicide phase for an ultrathin deposited Co layer.

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