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Published in:
Journal of Vacuum Science & Technology B

DOI:
[10.1116/1.1312262](https://doi.org/10.1116/1.1312262)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2000

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Citation for published version (APA):

Palasantzas, G., & de Hosson, J. T. M. (2000). Fractality aspects during agglomeration of solid-phase-epitaxy Co-silicide thin films. *Journal of Vacuum Science & Technology B*, 18(5), 2472 - 2476. DOI: 10.1116/1.1312262

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Fractality aspects during agglomeration of solid-phase-epitaxy Co–silicide thin films*

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(Received 11 February 2000; accepted 31 July 2000)

Morphology changes of thin CoSi₂ films close to the agglomeration threshold have been investigated by *in situ* scanning tunneling microscopy. Films prior to agglomeration reveal a strong morphology anisotropy where depending on direction the roughness correlation $g(r)$ changes from logarithmic [$g(r) \sim \ln r$] to power law [$g(r) \sim r^{2c}$ with $c \approx 0.78$] at short lateral length scales ($r \leq 30$ nm). Such an anisotropy reflects the complex nature of diffusion process associated with the original anisotropic substrate surface and the formation of pinhole networks. Annealing above the agglomeration threshold (>600 °C), the pinhole network becomes connected breaking the CoSi₂ film into aggregates with a two-dimensional fractal dimension $D \approx 1.66$ which is close to predictions of diffusion limited aggregation within the mean field theory prediction $D = (d^2 + 1)/(d + 1)$ for $d = 2$, and invasion percolation models. © 2000 American Vacuum Society. [S0734-211X(00)04605-9]

I. INTRODUCTION

The fabrication and application of metal silicide thin films has been a great success in the field of microelectronics semiconductor technology. As a result, there is much interest in the fabrication of metal silicide thin films (i.e., CoSi₂, TiSi₂, NiSi₂)¹ because of their application in complementary-metal–oxide–semiconductor processes,² and microelectronics circuits (gates, contacts, interconnects, etc.)³ Moreover, their low resistivity makes them important for the formation of self-aligned silicides⁴ in ultralarge-scale integrated devices. In many cases the application of silicides in microelectronics is limited by stability problems at high temperature processing because of agglomeration of the film into discrete islands.

A variety of film degradation mechanisms which related to grain size, grain-boundary energy, and silicide interface and surface energy have been proposed.⁵ It is suggested that small grain size, small grain-boundary energy, large surface/interface energy, or thicker films may result in better thermal (or more precisely morphological) stability.^{5,6} The surface energy in metals is much larger than grain-boundary and interface energy.⁷ If metal–silicides share the same property,⁶ a large surface energy suggests that thermal grooving would start at the silicide/Si interface rather than at the silicide surface. As a result an increment in the silicide surface energy would not be as efficient as an increment in the silicide/Si interface energy to prevent film agglomeration.^{6,8} Therefore, the interface energy can be the key factor which determines the morphological stability of the films.

Furthermore, a CoSi₂ film of significant thickness (~ 70 nm; CoSi₂ implanted by BF₂⁺) could release its high surface energy through Si precipitation (since Si surface has lower

energy than the CoSi₂ surface) and silicide/Si interface roughness.⁶ Silicide/Si interface roughness (e.g., in CoSi₂ formed via the nucleation control process associated in some cases with a native oxide on the original Si surface^{6,9}) contributes positively to the interfacial energy, and thus to the resistance against agglomeration to a degree that depends on the specific roughness characteristics.¹⁰ In addition, the growth of larger area epitaxial silicides possibly eliminates thermal grooving paths possibly promoting silicide morphological stability.^{6,11} On the other hand, in polycrystalline films the agglomeration mechanism can be thermal grooving at grain boundaries. The maximum grain size L_c for which agglomeration cannot occur via this mechanism is given by $L_c \approx 10\tau$ (with τ the film thickness).⁵ This is estimated assuming comparable grain boundary and interface energies of about 1/3 of the surface free energy (e.g., pure metals).^{5,7,12}

In the present work we will investigate the morphology characteristics of ultrathin CoSi₂ films grown by solid-phase epitaxy (SPE) close to the agglomeration threshold using topology information obtained by scanning tunneling microscopy (STM) and scanning electron microscopy (SEM). The SPE technique involves metal deposition on clean Si which is followed by annealing at elevated temperatures to form epitaxial silicide.¹ Morphology quantification will be performed in terms of a height–height correlation function measurement prior to agglomeration, and two-dimensional fractal analysis by means of the box counting technique after agglomeration has occurred.

II. EXPERIMENTAL SAMPLE PREPARATION

The Si(111) wafers used in this study were n doped with resistivity of ~ 100 Ω cm, and nominally flat (miscut angle $< 0.1^\circ$). The sample preparation was performed in an ultra-high vacuum chamber of base pressure $P_b \approx 1 \times 10^{-10}$ mbar. Clean Si(111) 7×7 reconstructed surfaces were formed by resistive heating at a temperature ~ 500 °C

*No proof corrections received from author prior to publication.

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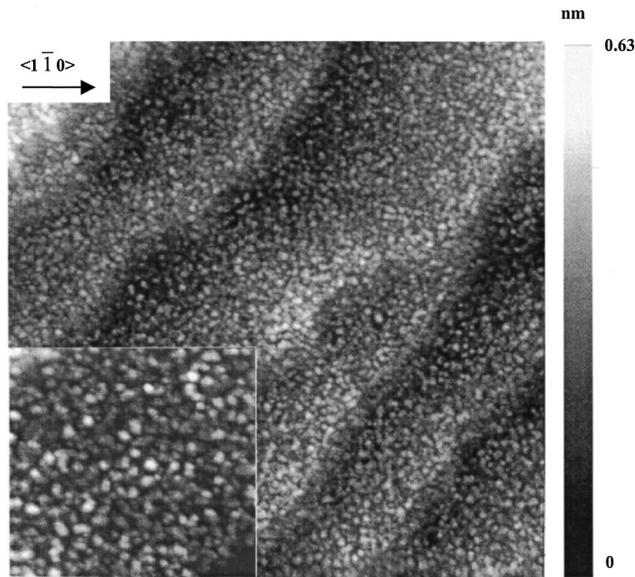


FIG. 1. Co film of 0.5 nm deposited on clean Si(111)7 \times 7 surface held at RT. STM filled state image acquired at 1.55 V bias voltage and 0.16 nA tunnel current. Scan size 200 \times 200 nm. The inset at the right bottom of 50 \times 50 nm scan size depicts the short length scale granular Co morphology.

and at a pressure of $\sim 5 \times 10^{-10}$ mbar for gas desorption followed by a flash to ~ 1200 °C for ~ 1 min. The specimen temperature was determined by infrared pyrometry to better than ± 10 °C above 400 °C. Co films of 0.5 nm in thickness were deposited *in situ* by means of e-beam evaporation at a rate 0.1 nm/min on Si(111) samples held at room temperature (RT). The evaporation rate was calibrated by a quartz crystal microbalance to within $\sim 10\%$. During evaporation the chamber pressure did not exceed $\sim 5 \times 10^{-9}$ mbar. In all stages the samples were imaged *in situ* into an STM (OMICRON) chamber held at a base pressure $\sim 1.5 \times 10^{-10}$ mbar. Mechanically cut Pt/Ir STM tips were used for imaging purposes.¹³

III. MORPHOLOGY ANALYSIS PRIOR TO FILM AGGLOMERATION

Figure 1 shows the topology of the Co/Si films just evaporated on a clean Si(111)7 \times 7 surface. As seen in the STM images the grain size is about ~ 3 nm. Co atoms react with Si atoms even at room temperature for the first few monolayers of deposited metal.^{14,15} Complete surface coverage is possible because of the high surface diffusivity of unreacted Co migrating to regions of unexposed Si surface. The granular structure indicates that the film is not fully reacted to form an epitaxial CoSi₂ (the RT Co–Si reaction only takes place locally while no long-range order transport occur by either species, namely, Co and Si).^{13,15}

Drastic changes in the surface morphology of the Co/Si film occurs during further annealing at elevated temperature to form CoSi₂ as Fig. 2 indicates. Indeed, annealing at 500 °C for 3 min (Fig. 2) leads to the formation of pinholes which are surrounded by stepped epitaxial terraces.¹³ The surface morphology is quantified by measurement of the

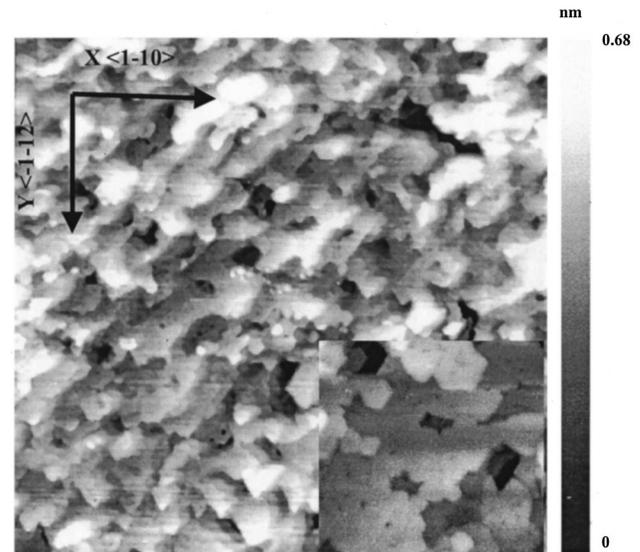


FIG. 2. Annealing of the film in Fig. 1 at 500 °C for 3 min. Large scale image of 500 \times 500 nm scan size where the roughness measurements took place. The inset is a small scan size image of 100 \times 100 nm to show in more detail the film granular. STM empty state images acquired at 1.62 V bias voltage and tunnel current 1.56 nA.

height–height correlation function $g(r) = \langle [h(r) - h(0)]^2 \rangle \times (r=x, y)$ along the x and y axis as shown in the STM image of Fig. 2.¹⁴ In each direction (x and y), six one-dimensional height profiles $h(r)$ vs r were acquired (at different locations) over a lateral scan size of 500 nm (which is about ten times larger than the average terrace size ~ 60 nm), followed by computation of $g(r)$ vs r for each profile separately, and finally the average of all six $g(r)$ vs r curves.

The anisotropy of the initial Si(111)7 \times 7 stepped surface will impose anisotropy in the growth of CoSi₂ (as Fig. 2 shows in comparison with Fig. 1) along directions running at about 45° from the x and y directions (Fig. 2). Along the x axis ($\langle 1, -1, 0 \rangle$ direction), a logarithmic behavior of $g(x) \propto \ln x$ is revealed at short length scales 3–30 nm [Fig. 3(a)]. Saturation appears to commence at larger length scales $x \geq 70$ nm, which compare to lateral sizes of epitaxial domains formed in between the network of pinholes. In fact, logarithmic behavior corresponds to roughness exponents $c = 0$.¹⁶ The saturated root mean square (rms) roughness amplitude is $\sigma_x \approx 0.18$ nm. On the other hand, $g(y)$ along the y axis ($\langle -1, -1, 2 \rangle$ direction) shows a power law behavior $g(y) \propto y^{2c}$ with $c = 0.78 \pm 0.05$ for lateral length scales $y < 20$ nm [Fig. 3(b)], and a saturated rms roughness amplitude $\sigma_y \approx 0.13$ nm at lateral length scales $y \geq 30$ nm. The structural change from logarithmic to power law behavior of the correlation functions in the x and y directions indicates, qualitatively, the complex anisotropic character of the CoSi₂ growth at short length scales smaller than the terraces (which have a period of 70–100 nm; Fig. 1) of the initial Si(111)7 \times 7 surface. Large roughness exponents close to $c \approx 0.7$ –1 indicate a surface diffusive process with a mountain-valley structure developing, while a logarithmic behavior (or alternatively roughness exponent $c \approx 0$) indicates the absence of any surface diffusion.¹⁷

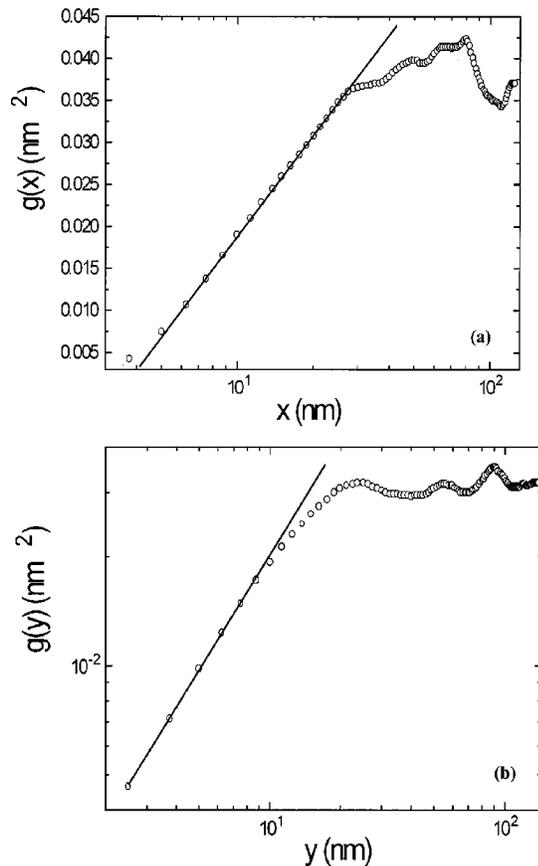


FIG. 3. Schematics of the correlation function $g(r)$ vs r (a) along the x axis. (b) along the y axis. The line indicates the linear fit to measure the roughness exponent $c = 0.78 \pm 0.05$.

The occurrence of pinholes has been related to the transformation of the Co-rich to the Si-rich silicide surface (which has a lower surface energy and possibly drives the process).^{15,18} The necessary amount of Si is provided from the Si substrate by bulk outward diffusion to the surface and the subsequent reaction with Co.¹³ Our measurements indicate that the associated diffusion process on the silicide surface are rather highly anisotropic resulting in strong directional dependence of the film growth front. In any case, the growth mode of such a system is too complicated to be accounted for solely in terms of simple nonreactive growth models.^{17,19} Further studies are necessary in this direction.

IV. MORPHOLOGY ANALYSIS AFTER FILM AGGLOMERATION

During further annealing of the film at 700 °C for 3 min (Fig. 4), the pinhole network is getting connected breaking up the film into complicated still shape CoSi_2 precipitates.¹³ The height of these precipitates can be as high as ~ 10 nm. Further annealing leads to more polygonal shapes (crystallographically oriented) of the CoSi_2 precipitates (Fig. 5). Despite the variety of shapes, the polygonal precipitate sides are formed mainly along two preferential orientations: along the substrate Si(111) terraces or $\langle 1\bar{1}0 \rangle$ direction and other two at $\sim 60^\circ$ and $\sim 120^\circ$ (threefold symmetry). The dominant sur-

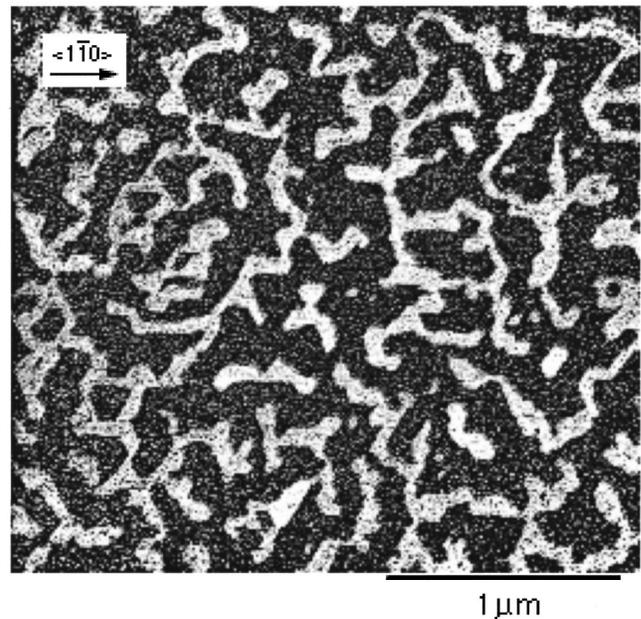


FIG. 4. SEM image of the CoSi_2 precipitate network formed upon agglomeration by heating the film up to 700 °C for 3 min. The arrow shows the direction of the Si(111) 7×7 terraces exposed upon film agglomeration.

face orientation of the CoSi_2 precipitates is the $\{111\}$ crystallographic plane, which is energetically favorable independently of the matrix orientation.¹⁸

The dewetting process of the Si surface from the silicide film during high temperature annealing shows a rather complex aggregate structure which implies the possibility of two-dimensional fractal analysis. A simple way to measure the fractal dimension of a two-dimensional object is the box counting technique.¹⁹ The image in Fig. 4 is digitized and

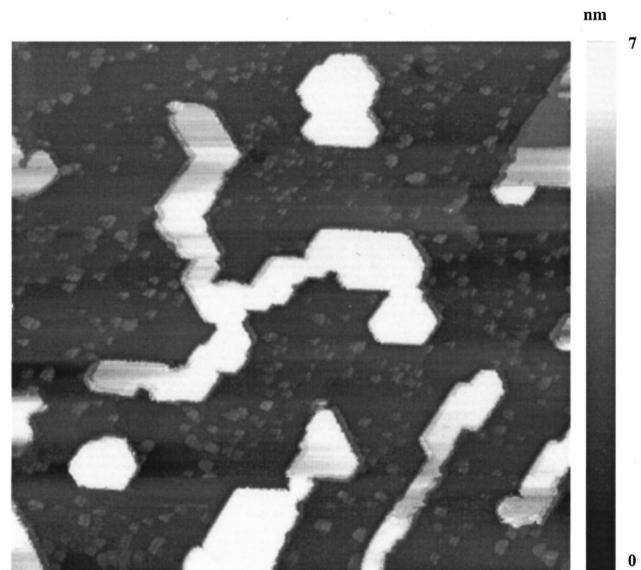


FIG. 5. Development of polygonal CoSi_2 precipitates with further annealing at 900 °C for 1 min (scan size 800 \times 800 nm). STM empty state images of bias voltage 2.07 V and tunnel current 0.54 nA taken at different places on the sample.

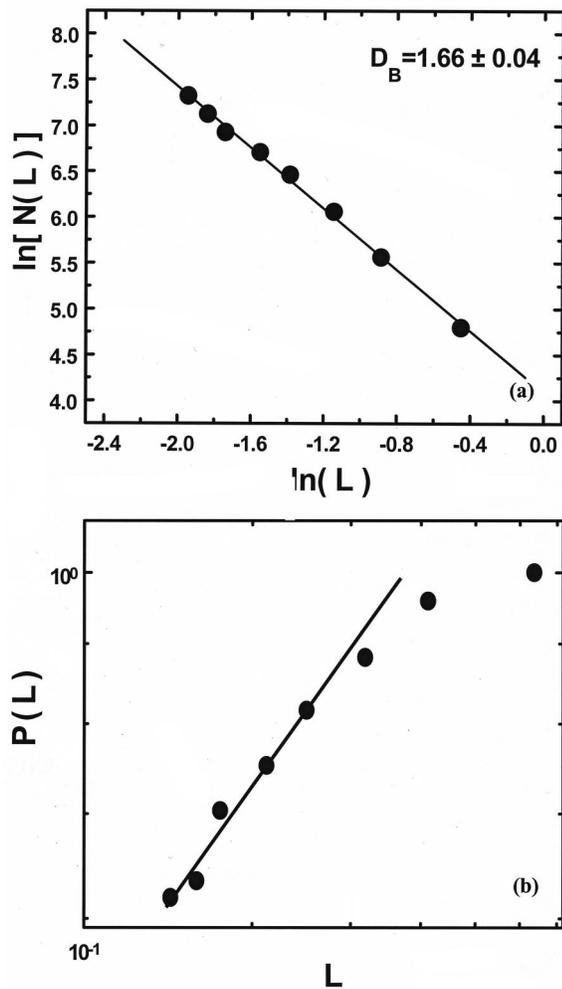


FIG. 6. (a) Measurement of the box counting fractal dimension as obtained from the line slope in the log-log of occupied boxes vs box size L . (b) Probability distribution of box occupation $P(L)$ vs the box length of size L . The line fit gives the slope 0.5 ± 0.05 which is the power law of $P(L)$.

covered with grids of varying box size of length L . If part of the CoSi_2 precipitates intersects a box from the grid, then the box is considered occupied by the aggregate complex. Plotting the number of occupied boxes $N(L)$ vs L we obtain a power law behavior of the form¹⁹

$$N(L) \propto L^{-D_B}, \quad (1)$$

with D_B the box counting fractal dimension. The linear fit in Fig. 6(a) yields $D_B = 1.66 \pm 0.04$. If we denote by A the image area, then the total number of grid boxes of size L covering the image is $N^* = A/L^2$. Thus, the probability $P(L)$ of a box of size L to be occupied by the aggregate is $P(L) = N(L)/N^* \propto L^{2-D_B}$. As is shown in Fig. 6(b), at small box sizes $P(L)$ shows a power law behavior $P(L) \propto L^{0.5 \pm 0.05}$ which is close (within the experimental uncertainty in the exponents) to the scaling relation $P(L) \propto L^{2-D_B}$. $P(L)$ at large box sizes saturates to the value 1.²⁰

The dewetting behavior of the Si surface from the CoSi_2 face shows qualitatively features observed within the framework of the invasion percolation model. Indeed, such models

were developed originally to study the slow displacement of a wetting fluid by a nonwetting fluid in porous media.¹⁹ Computer simulations²¹ gave for invasion percolation with trapping sites a fractal dimension $D_{>} = 1.81$ above the percolation threshold and $D_{\text{per}} = 1.37$ at the percolation threshold. In addition, simulations of diffusion limited aggregation (DLA) in two-dimensional networks gave fractal dimensions of $D_{\text{DLA}} = 1.6 - 1.7$.²² Indeed, the measured fractal dimension coincides with the mean field theory (in the sense that the strongly fluctuating but strongly correlated cluster density in a random fractal is replaced by a radial average) prediction for DLA growth,^{19,22} namely,

$$D = (d^2 + 1)/(d + 1), \quad (2)$$

which for a two-dimensional aggregation (or $d = 2$) yields $D = 1.66$. Despite the uncertainties concerning the asymptotic scaling structure for $d = 2$, the value predicted by Eq. (2) may eventually be shown to be correct for DLA growth.¹⁹ Note that the mean field theory prediction for DLA [Eq. (2)] gives the correct result for $d = 1$, and satisfies the limit $D \geq d - 1$ for $d \rightarrow \infty$.¹⁹

V. CONCLUSIONS

We have investigated morphology changes of thin solid-phase-epitaxy $\text{CoSi}_2/\text{Si}(111)7 \times 7$ films close to agglomeration. The annealed films below the agglomeration threshold ($\sim 600^\circ\text{C}$) reveal a strong morphology anisotropy, where depending on direction, the roughness correlation alternates from logarithmic ($\sim \ln r$) to power law ($\sim r^{2c}$ with $c \approx 0.78$) at short lateral length scales ($r < 30$ nm). Such a morphological anisotropy reflects to a significant degree the anisotropic nature of the diffusion process, because of the original anisotropic Si surface, that lead to formation of a pinhole network, and result in the more energetically stable Si-rich CoSi_2 surface. Annealing above the agglomeration threshold ($> 600^\circ\text{C}$), the pinhole network becomes connected breaking the Co-silicide film into aggregates with a two-dimension fractal dimension $D_B = 1.66$. Such a value resembles fractal characteristics close to those of invasion percolation and diffusion limited aggregation models. Indeed, $D_B \approx 1.66$ lie between the invasion percolation model prediction $D_{\text{per}} < D_B < D_{>}$, as well as is very close to DLA model predictions $D_B (\approx D_{\text{DLA}}; \text{ especially within the framework of the mean field theory DLA approach})$. The later indicates a scenario that might describe such a complex agglomeration process. Further studies are required in this direction.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the hospitality of the NEXT Laboratory at the Department of Applied Physics of Delft University of Technology, and fruitful correspondence with B. Ilge and L. J. Geerligs.

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