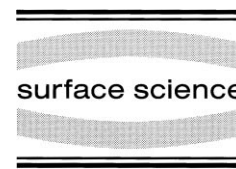




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A kinetic scanning tunneling microscopy study of iron silicide growth on Si(113)

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Abstract

High-temperature kinetic scanning tunneling microscopy (STM) studies are used to investigate the surface morphology and growth mode of iron silicide on Si(113) formed by gas-source reactive iron deposition with $\text{Fe}(\text{CO})_5$ as precursor. The first monolayer of silicide on Si(113) forms a $(4 \times n)$ reconstruction that covers the surface completely before growth proceeds via the formation of strongly anisotropic, three-dimensional silicide islands. After the first monolayer is closed, growth is slowed down by a blocked interdiffusion with the silicon substrate and a reduced sticking probability for the precursor. Lateral spreading of the islands is achieved by a stoichiometric codeposition of iron and silicon using $\text{Fe}(\text{CO})_5$ and Si_2H_6 . In this way, nearly closed layers of silicide can be grown. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Low energy electron diffraction (LEED); Metal–semiconductor nonmagnetic thin film structures; Scanning tunneling microscopy; Silicides; Single crystal epitaxy

1. Introduction

Despite the interesting physical properties of iron silicide, there is still a lack of technological applications. Problems regarding wetting of the silicon substrates, rough interfaces and the presence of different competing silicide modifications diminish the quality of the layers. Especially on Si(111), three-dimensional (3D) silicide islands form already in the submonolayer range [1,2]. Higher-index or vicinal silicon surfaces may offer one way to overcome part of these problems. When the orientation is varied continuously from

(111) to (001) a number of stable faces have been found [3]. In particular, Si(113), being the most stable of these faces, has attracted considerable interest in past years. Whereas the atomic arrangement of the Si(113)- (3×2) reconstruction seems to be resolved by a model containing a subsurface interstitial [4], little is known about the growth behavior on this surface. In homoepitaxial growth on Si(113), a strong anisotropy in the island shape was found [5] that led to nearly one-dimensional structures along the $[1\bar{1}0]$ direction. Another possible application of Si(113) is given by the faceting behavior when the surface is annealed [6]. The resulting periodic groove arrangement may serve as a template during heteroepitaxial growth to produce nanostructured layers. This paper presents an overview on the nucleation and initial growth behavior of iron silicide on the Si(113) surface.

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2. Experimental

All experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with optics for low-energy electron diffraction (LEED) and a high-temperature scanning tunneling microscope (STM) that was specially designed for in situ measurements directly during growth. The temperature of the substrate could be adjusted between room temperature (RT) and 850°C, while sequences of scanning tunneling microscopy (STM) images of a selected location on the surface were taken to study the kinetics of epitaxial growth. The gas-phase precursors $\text{Fe}(\text{CO})_5$ and Si_2H_6 were supplied through a standard UHV leak valve controlled by an ion gauge and a quadrupole mass analyzer (QMA). The Si(113) substrate samples were prepared by outgassing the samples at 600°C for 8 h, followed by slow oxide removal at 800°C and several short flashes up to 1250°C. To exclude any influence of the STM scanning process on the deposition from the gas phase, bias voltages below 2.5 V were used. A comparison of ex situ (not in the STM) and in situ grown silicides shows exactly the same structure of the layers. All STM images shown in this paper were taken in the constant-current mode with a tunneling current of 0.5 nA and a sample bias of -2 V.

3. Results

Fig. 1 shows the morphology of the Si(113) surface after an $\text{Fe}(\text{CO})_5$ exposure of 5 min at $p=1 \times 10^{-7}$ mbar at 400°C. Whereas on Si(111) iron deposition at elevated temperatures leads immediately to the formation of 3D islands of iron silicide, which cover only a fraction of the surface [1,2], on Si(113) a two-dimensional (2D) iron-induced reconstruction is formed. Fig. 1a displays details of this structure. On the left the clean Si(113) surface is visible and, on the right, an iron-induced chain structure along the $[1\bar{1}0]$ direction. The protrusions in the chains have a separation of 15 Å along $[1\bar{1}0]$ which, by comparison with the (3×2) reconstruction of the silicon substrate, can be identified as a four-fold periodicity. In the $[33\bar{2}]$ direction a six-fold periodicity is visible. If the same sticking coefficient of ≈ 0.03 for the $\text{Fe}(\text{CO})_5$ precursor is assumed on Si(113) as on the Si(111) surface, each (4×6) unit cell contains 10–15 iron atoms. If these iron atoms are located in the outermost surface layer, the iron-induced chain reconstruction can be considered as a silicide structure. Because of the complex structure of the reconstruction that contains chain structures also in lower levels in between the main chains (see Fig. 1a), it is impossible to make an atomic model on the basis of the present data set.

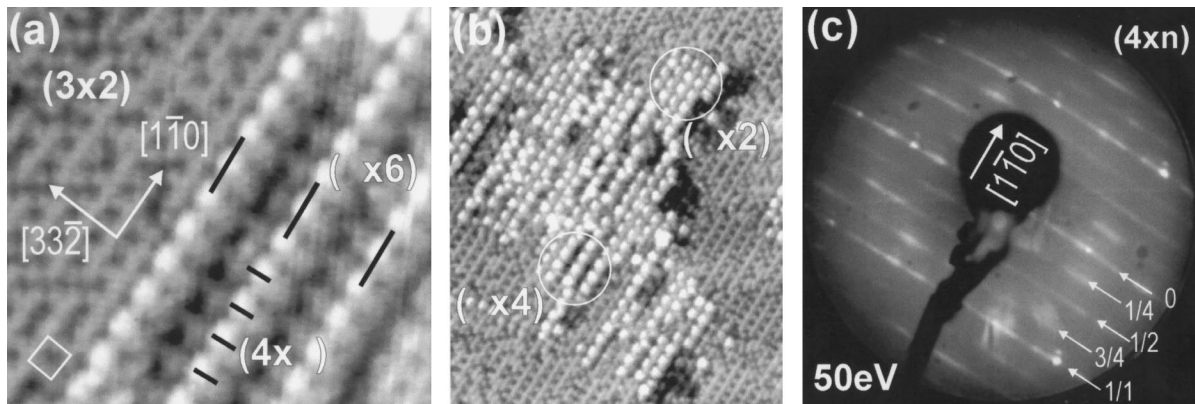


Fig. 1. Structure of the submonolayer iron silicide on Si(113) grown at 400°C and scanned at RT. (a) STM image ($165 \text{ Å} \times 150 \text{ Å}$): chains of protrusions along $[1\bar{1}0]$ show a four-fold periodicity. (b) Larger area ($370 \text{ Å} \times 440 \text{ Å}$): in the $[33\bar{2}]$ direction, two-fold, four-fold and [as seen in (a)] six-fold periodicities are found. (c) LEED pattern of a surface completely covered by the chain structure. The mixture of periodicities along $[33\bar{2}]$ results in the formation of streaks.

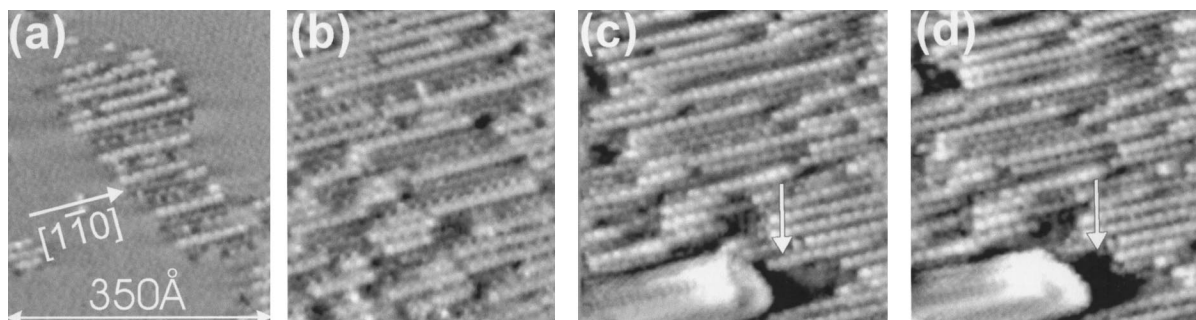


Fig. 2. Sequence of STM images (derivative image) showing details of the completion of the first monolayer of silicide (a and b) before 3D islands are formed (c and d).

Fig. 1b shows a larger arrangement of chains. The distance between the chains along $[3\bar{3}2]$ varies between 2 and 6 silicon unit cells. The chain structure is therefore referred to as a $(4 \times n)$. Whereas in the $[1\bar{1}0]$ direction the four-fold periodicity is typically maintained in domains of five to 15 protrusions, in the $[3\bar{3}2]$ direction an average domain size of only two or three chains is present. This low degree of order leads to the formation of streaks in the LEED pattern (Fig. 1c) perpendicular to $[1\bar{1}0]$. Along $[1\bar{1}0]$, on the other hand, narrow diffraction features are visible with a four-fold periodicity.

Upon further iron deposition the surface is completely covered by the $(4 \times n)$ structure. Fig. 2 shows the completion of the 2D silicide structure at 485°C and the subsequent growth of 3D silicide islands (Fig. 2c and d). Obviously, iron silicide grows on the Si(113) surface in the Stranski–Krastanov mode. The 3D islands are strongly elongated in the $[1\bar{1}0]$ direction, displaying an aspect ratio of more than 8 (see also Fig. 3). A similar anisotropy in growth has also been found for homoepitaxial growth on Si(113) [5].

Rarely, holes in the 2D silicide layer can be found in the neighborhood of 3D islands (see arrows in Figs. 2 and 3) where the first monolayer of silicide is removed. During further growth these holes (see Fig. 2d) deepen and the silicon of the substrate is consumed to proceed in silicide formation. Fig. 3 shows the temporal evolution of 3D silicide islands during growth at 470°C . Only a minority of the islands are connected to holes in the substrate where silicon out-diffusion takes

place. The growth is slowed down dramatically when the first monolayer is closed. The 3D islands grow slowly in height but lateral spreading is largely suppressed. The presence of the completely closed 2D silicide layer seems to block silicon out-diffusion in contrast to iron silicide formation on Si(111), where the substrate is removed layer-by-layer to provide silicon for the formation of iron silicide islands [2]. Besides the blocked silicon diffusion, the slowing down of the silicide growth after completion of the 2D layers has also to be connected to a dramatically decreased sticking probability for the $\text{Fe}(\text{CO})_5$ precursor, since no piling up of bare iron is found on the surface. Further experiments are in progress to quantify this behavior.

This blocked silicon diffusion, on the other hand, should result in a sharp interface between the substrate and the silicide layers when both iron and silicon are supplied. Fig. 4 shows the resulting growth at 485°C when iron is supplied by $p = 2.1 \times 10^{-7}$ mbar of $\text{Fe}(\text{CO})_5$ and silicon by $p = 1.9 \times 10^{-7}$ mbar of Si_2H_6 .

In contrast to pure iron deposition, the codeposition of iron and silicon leads to a lateral spreading of the 3D islands. Additionally, island coalescence can be found (see Fig. 4b and c). Eventually an interconnected net of islands results with only small gaps in between (Fig. 4e). The surface of the islands is flat and presents an arrangement as shown in Fig. 4f, with a periodicity of $\approx 12.5 \text{ \AA}$ in the $[1\bar{1}0]$ direction. In the perpendicular direction two different periodicities are found as marked in Fig. 4f. The step height on the islands is 2 \AA . The

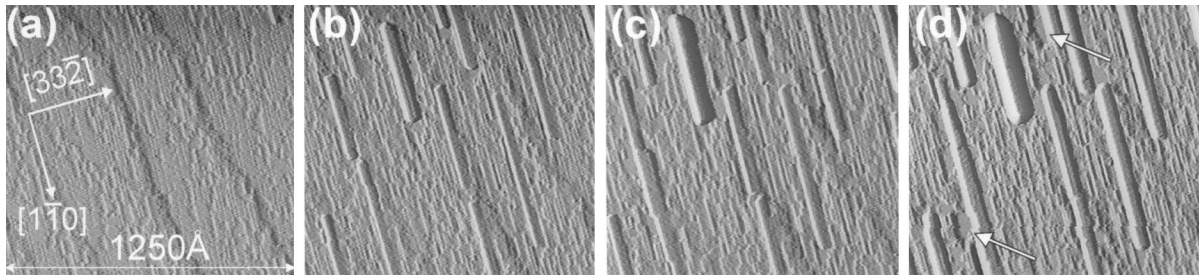


Fig. 3. Sequence of STM images (derivative image) giving an overview of the growth of the highly anisotropic 3D islands after the submonolayer chain structure completely covers the surface. In only a few locations (see arrows), out-diffusion of silicon leads to the formation of holes in the first silicide layer. Growth is slowed down dramatically after the first monolayer is closed.

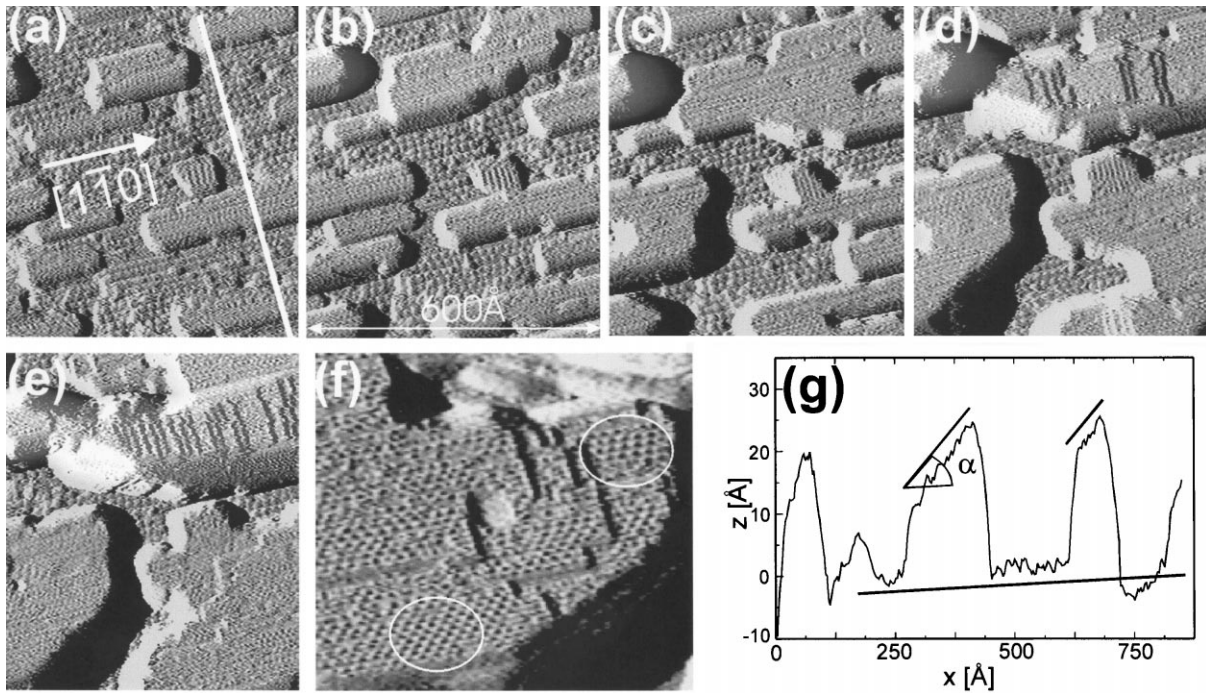


Fig. 4. Sequence of STM images (derivative image) showing the codeposition of silicon and iron with (Si_2H_6) and $\text{Fe}(\text{CO})_5$. In contrast to pure iron deposition (see Fig. 3), the 3D islands spread out laterally. (f) shows a zoom-in on one of the islands. (g) shows a height profile along the line marked in (a).

height profile, Fig. 4g, along the line in Fig. 4a, shows that the surface of the 3D silicide islands is inclined by 5° in the $[33\bar{2}]$ direction with respect to the substrate. Assuming the same epitaxial relationship between silicon and iron silicide as found on Si(111) and the same temperature-dependent phase behavior [1,2], a CsCl defect structure (composition FeSi_{1+x} , $x \approx 0.7$) exposing a (225)

surface is roughly consistent with the present set of data. Further studies are needed to determine the crystalline structure of the iron silicide on Si(113) unambiguously.

The present study has shown that the use of higher-index silicon surfaces may provide a means to improve the interface quality between substrate and silicide layer by blocking the interdiffusion

using an intrinsic 2D silicide layer. In contrast to low-index silicon surfaces, a complete 2D wetting layer is formed on Si(113) before the formation of 3D islands starts. Further studies on Si(114) and Si(5 5 12) are currently in progress.

Acknowledgement

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References

- [1] F. Thibaudau, L. Masson, A. Chemam, J.R. Roche, F. Salvan, *J. Vac. Sci. Technol. A* 16 (1998) 2967.
- [2] U. Köhler, P. Kohstall, V. Dorna, in preparation.
- [3] A.A. Baski, S.C. Erwin, L.J. Whitman, *Surf. Sci.* 392 (1997) 69.
- [4] J. Dabrowski, H.J. Müssig, G. Wolff, *Phys. Rev. Lett.* 73 (1994) 1660.
- [5] V. Dorna, Z. Wang, U. Köhler, *Surf. Sci. Lett.* 401 (1998) L375.
- [6] S. Song, M. Jong, S.G.J. Mochrie, G.B. Stephenson, S.T. Milner, *Surf. Sci.* 372 (1996) 37.