Topography of the Si(111) Surface during Silicon Molecular-Beam Epitaxy

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(Received 18 May 1989)

A one-to-one correspondence of silicide interface dislocations to Si(111) surface steps has been discovered for epitaxial silicide layers grown at room temperature. This has allowed the examination, by transmission electron microscopy, of the topography of large areas of the Si surface after various treatments. Growth modes of molecular-beam epitaxy (MBE) at different temperatures and growth rates are clearly displayed and explained. A change of step character from $\langle 11\bar{2}\rangle$ to $\langle \bar{1}\bar{1}2\rangle$ at the initial stage of MBE is observed and is attributed to the stabilities of the two types of steps in relationship to the 7×7 structure.

PACS numbers: 68.35.Bs, 61.16.Di, 68.55.Bd

Structures of clean semiconductor surfaces have interested scientists for decades. Earlier studies concentrated on the nature of various reconstructions and relaxations. Recently, considerable efforts have been devoted to understanding various dynamical effects on semiconductor surfaces.[1] The topography of a clean surface is usually considered in terms of equilibrium thermodynamics.[2] Notably, the arrangement of reconstruction has been shown to have an important effect on the shape of the surface steps.[2-5] During many important surface processes, such as reaction, evaporation, and epitaxial growth, steps play an active role. Under these nonequilibrium conditions, steps and other surface features not only affect but are also affected by surface kinetics. An examination of the surface topography often sheds light on the nature of the surface dynamics. In this paper, various aspects of molecular-beam epitaxy (MBE) are studied through an examination of the surface topography. Growth by MBE is a topic of much current scientific and technological interest. Presently, novel quantum-mechanical phenomena have been observed in various artificial semiconductor structures fabricated by MBE.[6] The ability to control the surface topography during MBE is of paramount importance to fabricating atomically abrupt interfaces to further these studies.

The topography of clean semiconductor surfaces has been studied through *in situ* surface-sensitive techniques. Oxidation and other contaminants have prevented *ex situ* examination, with one noted exception.[7] The Si(111) surface has thus far been studied by diffraction techniques[2,8-12] and imaged in the real space by surface-sensitive electron microscopies including reflection electron microscopy (REM),[4] scanning electron microscopy (SEM),[13] microprobe reflection high-energy electron diffraction (RHEED),[14] low-energy electron microscopy (LEEM),[3] transmission electron microscopy (TEM),[15] and scanning tunneling microscopy (STM).[5,16,17] Each of these techniques has its advantages and weaknesses. For instance, STM has very high resolution but is limited in the size of its viewing area. Almost all electron microscopy instruments mentioned above are tight in space around the specimen which severely hampers the achievable vacuum and control over deposition. As a result, studies concerning MBE growth have thus far been limited to surfaces prepared under low deposition rates, typically a few monolayers (ML) per minute, and nonideal vacuum conditions, $p > 10^{-9}$ Torr.

Recently, the growth of epitaxial $CoSi_2$ (Ref. 18) and $NiSi_2$ (Ref. 19) at room temperature has been realized. High-quality silicide thin films have been grown on Si(111) by (pre-)deposition of 2–3 ML of metal and codeposition of disilicide at room temperature. Because of the absence of long-range diffusion at room temperature, surface imperfections on the original Si(111) surface, such as steps, are preserved at the interface between silicide and silicon. The type-*B* orientation of these silicide thin films requires a phase difference of $\frac{1}{3}[111]$, with possible addition of any lattice translation vector, across a step with single height (3.14 Å). Strain fields associated with these partial defects are easily detected and analyzed in TEM. Both the direction and the sense (up or down) of the steps may be obtained. This exact correspondence of defects seen at the silicide interface to features on the original Si surface provides a convenient means of investigating large-area (> 1000 μm^2) surface topography with an atomic resolution along the surface normal and the high lateral resolution usually found in TEM. Furthermore, since there is no constraint on sample preparation, growth under usual MBE conditions (e.g., a growth rate ~ 1 Å/s, and $p < 1\times10^{-10}$ Torr) may be studied.

The density of steps on annealed Si surfaces is determined by the misorientation angle between the surface normal and the exact [111] direction.[18] Selected, precisely oriented (within 0.1°), wafers are employed for the present study. Wafers are chemically cleaned and a protective oxide layer grown at the final step.[20] Substrates are introduced into a MBE chamber (base pressure $< 4\times10^{-11}$ Torr) through a load lock. After thorough degassing of the substrates, the oxide layer is removed by Si beam cleaning.[21] A thick Si "buffer" lay-

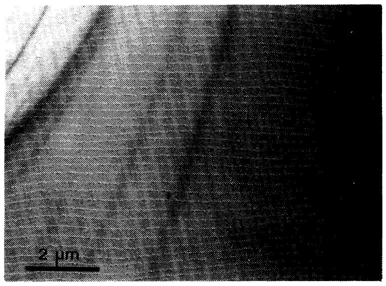

FIG. 1. A dark-field TEM image of a $CoSi_2$ layer grown on a Si(111) surface prepared by Si beam cleaning and buffer growth.

er, ~100–200 Å, is then grown at ~700–750 °C and a brief anneal to ~950 °C follows. On substrate surfaces so prepared, Si MBE growths under various conditions are carried out. Finally, a ~50–70-Å-thick layer of $CoSi_2$ is grown (0.5 Å/s) at room temperature[18] to "preserve" the surface topography. The pressure in the growth chamber remains below 1×10^{-10} Torr during all depositions. TEM samples are ultrasonically cut and thinned from the backside. A Phillips EM420 microscope is employed with an operating voltage of 120 kV.

A substrate prepared by the present procedures is shown in Fig. 1. Evenly distributed, approximately parallel steps of single atomic height (3.14 Å) are always observed. On some surfaces, small carbide particles were observed after oxide removal,[18] which were subsequently "buried" through the growth of the Si buffer layer.[22] After Si buffer growth, no observable carbon or oxygen was detected by Auger analysis (sensitivity ~0.2% ML). The topography of the starting surface is always examined along with the part of the sample where additional MBE growth has taken place. This is possible through the use of a movable shadow mask during MBE depositions. Shown in Fig. 2 are step arrangements on Si surfaces after MBE growth of ~32-ML Si at temperatures of 750, 650, and 550 °C. The deposition rate is 2.5×10^{14} cm^{-2}/s (0.5 Å/s). Note that 1 ML is 7.8×10^{14} atoms cm^{-2} and it takes 2 ML to complete the growth of one layer, 3.14 Å in height, on Si(111). This substrate has a small unintentional misorientation of ~0.05° made up by $[11\bar{2}]$ steps. (A "$[11\bar{2}]$ step" is one which runs parallel to the $[1\bar{1}0]$ direction with its outward direction pointing toward $[11\bar{2}]$.[2,11] The $\langle 11\bar{2}\rangle$ and the $\langle \bar{1}\bar{1}2\rangle$ steps are inequivalent.) In Fig. 2, all micrographs are mounted the same way, with the bottom parts of the picture showing regions of higher surface elevation. Figures 2(a)–2(d) are imaged with the same diffracted $\mathbf{g}=[\bar{2}20]$, as marked by an arrow in Fig. 2(a). The orientation and the sense of the steps have been uniquely determined by the use of surfaces with measurable misorientations.[23] Under the weak diffracting condition used ($s_{\mathbf{g}}>0$), it is discovered that the majority of steps whose outward

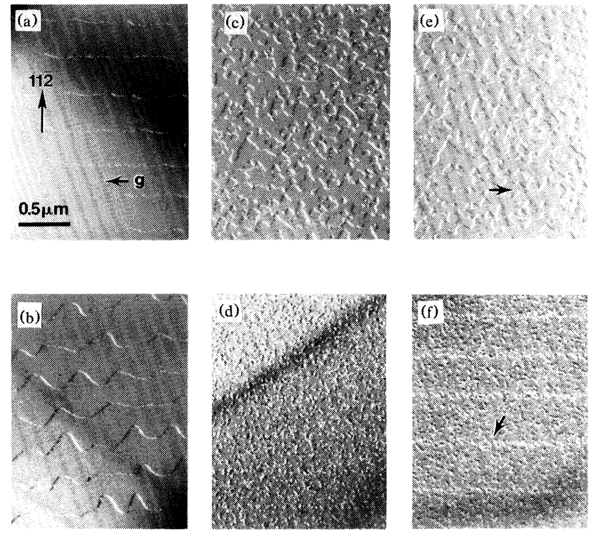

FIG. 2. Dark-field TEM images of $CoSi_2$ layers grown on Si surfaces after Si MBE growth. (a) Substrate surface, and (b)–(f) surfaces after the growth of 50-Å Si at a rate of 0.5 Å/s. Deposition temperature was (b) 750 °C, (c) 650 °C, and (d) 550 °C. (a)–(d) were imaged with $\mathbf{g}=[\bar{2}20]$. (e) shows the same area as (c), imaged with $[2\bar{2}0]$. (f) shows approximately the same area as (d), imaged with $[\bar{2}02]$.

direction makes a sharp angle with $\mathbf{g}$ appear darker than the background. Those making an obtuse angle with $\mathbf{g}$ will appear lighter than the background. One may get a sense of the surface contour by simply looking down on Figs. 2(a)–2(d) and imagine as if the surface is being illuminated along the $\mathbf{g}$ direction, i.e., by a light source placed on the right-hand side. When the direction of $\mathbf{g}$ is reversed, as in Fig. 2(e), the surface appears under illumination from the opposite (left) side. Short sections of different characteristics are also observed, but these occupy a small fraction of the total defect length and do not interfere with the determination of topography.

Step-flow type of growth has obviously taken place at 750 °C, as shown in Fig. 2(b).[24] However, the steps have taken up a sawtooth shape consisting largely of sections with approximately $\langle \bar{1}\bar{1}2\rangle$ character. No RHEED oscillation is expected in this growth mode. It is clear that growth at 550 °C, shown in Fig 2(d), occurred principally through two-dimensional nucleation and growth (2D NG) of islands on the terraces.,[1,10] Despite the presence of many islands and holes, the approximate locations of the straight steps on the original surface are still visible after 50-Å Si grown at 550 °C. This is more clearly demonstrated in Fig. 2(f), using a different $\mathbf{g}$ direction. Although not demonstrated here, it is likely that the total density of steps fluctuates during growth giving rise to RHEED oscillation. The growth at 650 °C has proceeded through both misorientation-step movement and 2D NG. Isolated islands are found on the terraces and the steps have changed to an irregular shape.

It is noted that both steps and islands show a preference of $\langle\bar{1}\bar{1}2\rangle$ edges. The density of islands on the terraces, in the 2D NG mode, is higher near the up steps than the down steps. This slanted distribution of steps is discernible in Figs. 2(c) and 3(c), and is in agreement with calculated asymmetric distribution of adatoms on a sequence of parallel steps under high supersaturation.[24] The presently observed change of MBE growth mode from step flow to 2D NG with increasing supersaturation (decreasing temperature) has been discussed,[8–10,25] although the nucleation of islands from adatoms has not been adequately modeled.

The initial stages of homoepitaxial growth are very conveniently studied by the present technique. Two examples are shown in Fig. 3. Figures 3(a), 3(b), and 3(c) are a deposition series with 0-, 1-, and 2-ML Si, respectively, deposited at 650 °C on a surface with a small misorientation (0.05°) toward approximately $[11\bar{2}]$. Figures 3(d), 3(e), and 3(f) are a series carried out under identical conditions, except that the substrate has a small orientation (~0.1°) roughly toward $[2\bar{1}\bar{1}]$. The imaging condition for all micrographs in Fig. 3 is the same as that used in Figs. 2(a)–2(d). A slow deposition rate of 1×10^{13} cm^{-2}/s was used. In the first series, deposition first leads to the nucleation and growth of large islands on the terraces. Subsequently, these islands are absorbed by the ledges and thus change the dominant-step character from $\langle11\bar{2}\rangle$ to $\langle\bar{1}\bar{1}2\rangle$. Deposition of more than 2-ML Si does not lead to a surface topography significantly different from Fig. 3(c). The observed initial change of the character of steps from $[11\bar{2}]$ to $[\bar{1}\bar{1}2]$ may be related to the observed delay of the onset of RHEED oscillation.[9,10]

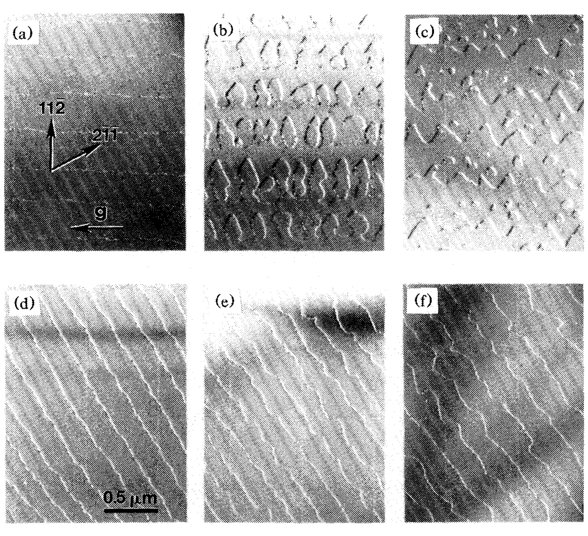

FIG. 3. Plan-view TEM micrographs illustrating the initial stages of Si homoepitaxial growth at 650 °C. (a) A substrate with a small misorientation toward $[11\bar{2}]$. (b),(c) Surfaces after the deposition of 1- and 2-ML Si, respectively, on this substrate. (d) A substrate with a small $[2\bar{1}\bar{1}]$ misorientation; (e),(f) the topographies after the deposition of 1- and 2-ML Si, respectively.

In the second series, Figs. 3(d)–3(f), the surface starts with the more stable $\langle\bar{1}\bar{1}2\rangle$ steps. After depositions, no isolated islands are found. Steps become less straight but still appear to largely maintain the original $[2\bar{1}\bar{1}]$ character. So it seems that, regardless of the direction of steps on the original Si surface, steps with $[\bar{1}\bar{1}2]$ character become more prevalent during MBE growth at < 750 °C. Therefore, even though precisely oriented wafers are used, the azimuth direction of the small unintentional misorientation still plays an important role in the determination of surface topography during epitaxial growth. The presence of islands in Fig. 3(c) and the absence of such in Fig. 3(f) is likely related to a small difference in the terrace widths between the two surfaces. With the same MBE temperature (650 °C) but a higher deposition rate of 0.5 Å/s, the surface adopts a topography similar to Figs. 2(c) and 2(e) after > 1 ML.

The present study demonstrates that $\langle\bar{1}\bar{1}2\rangle$ steps may be favored over $\langle11\bar{2}\rangle$-type steps during epitaxial growth, in good agreement with a recent STM study.[17] At the growth temperatures used, 7×7 reconstruction exists on the surface. The risers of these two types of steps consist of very similar atomic structures,[5] both based on the dimer–adatom–stacking-fault model of the 7×7 reconstruction.[12] The difference in the stabilities of these two types of steps is presently not well understood. Upon heating to above the 7×7→1×1 transition temperature this preference for $\langle\bar{1}\bar{1}2\rangle$-type steps is lost.[2–4] The overall direction of the steps is dictated by wafer misorientation. An example of this is already implicitly shown in Fig. 2: The surface shown in Fig. 2(a) is itself the result of annealing a surface similar to Fig. 2(b) to ~950 °C. Therefore, Si MBE on a 1×1 surface, at ≳870 °C, is expected to occur via movement of parallel steps. On surfaces with large misorientation angles (> 4°), it has been shown that single steps of $\langle11\bar{2}\rangle$ character are unstable against the formation of microfacets.[2] $\langle\bar{1}\bar{1}2\rangle$-type steps do not cluster, but form steps with triple atomic height.[2,11] Preliminary experiments have confirmed these findings and, in addition, showed that single $\langle\bar{1}\bar{1}2\rangle$-type steps are stable at low temperature, at least up to a misorientation angle of ~1.3°.[23]

The successful application of the present technique to the study of Si surface topography is based on a faithful one-to-one correspondence of silicide interface dislocations to Si surface steps. Two conditions are vital to this relationship. First, limited diffusion at room temperature in the silicide growth process preserves original surface steps into steps at the epitaxial interface. From the large amount of data thus far obtained, the absence of long-range movement of the surface steps during silicide growth seems self-evident. For instance, the interface topographies as shown by silicide growth on MBE-grown Si surfaces agree well with deductions from diffraction experiments.[8-10,14] Also, topographies of misoriented surfaces, as revealed by the silicide technique,[23] are identical to those deduced from other studies.[2,11] Since the silicide growth process consists of an initial deposition of < 3-ML Co, the lateral movement of steps is expected to be no more than the vertical interfacial movement, ~11 Å. Second, a change in the crystal symmetry at the interface leads to a phase difference across a step and, therefore, a dislocation. The nature of the interfacial defects seen at the silicide-silicon interfaces has not been fully determined.[26] There is also an observable variation of dislocation character upon slight intentional contamination of the Si surface or a change of the silicide growth condition.[23] However, it is noted that a Burgers vector of $\frac{1}{3}[111]$ may give rise to contrasts similar to those presented in these figures. One notes that capping a surface by an amorphous layer or a regular heteroepitaxial layer, such as GeSi or type-*A* silicide, also leads to interface steps. But no dislocation is formed at these steps and therefore no diffraction contrast to allow their observation by TEM. This symmetry requirement is also satisfied for other overlayer/substrate combinations. For instance, epitaxial $CoSi_2$, CaF_2, or GaAs layers may show a $\frac{1}{4}\langle 111\rangle$-type phase difference across a single step on Si(100). However, study of surface topography using these material systems has not been possible because the epitaxial quality is low (dislocations not resulting from steps are also present) and also because at the growth temperature of these epitaxial layers, one expects changes in the Si surface topography.

In this Letter, we demonstrated that clean Si(111) surface topography may be imaged by TEM through epitaxial silicide formation. The observed overall surface topographies at different MBE temperatures and rates demonstrate the importance of incorporating nucleation in the existing theories. Furthermore, steps on 7×7 reconstructed surface during MBE growth show strong preference for a $\langle\bar{1}\bar{1}2\rangle$ character, presumably for energetic reasons. Therefore, on this surface, the azimuthal direction of the surface misorientation, as well as the magnitude of the misorientation, is an important parameter for epitaxial growth.

We are indebted to D. Loretto, D. J. Eaglesham, R. Becker, and H.-J. Gossmann for discussions.

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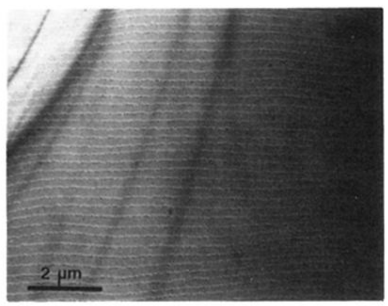
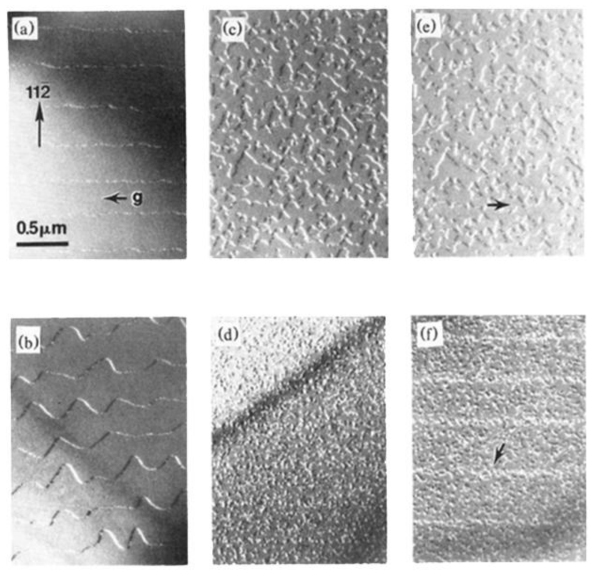


FIG. 1. A dark-field TEM image of a $CoSi_2$ layer grown on a Si(111) surface prepared by Si beam cleaning and buffer growth.



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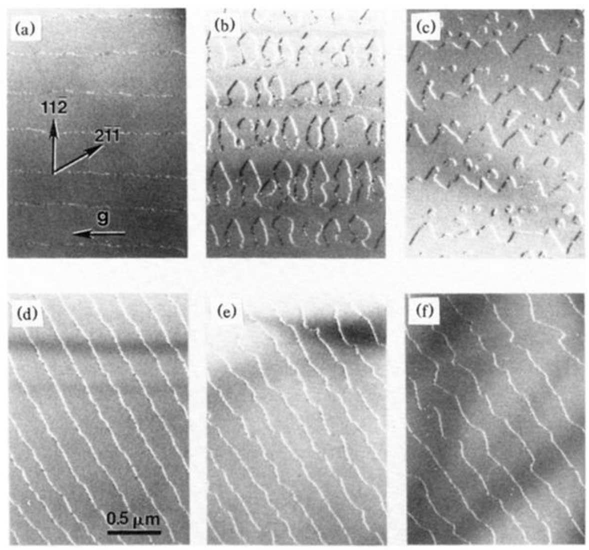

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