Heteroepitaxy of germanium on Si(103) and stable surfaces of germanium

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Despite the Si(103) surface having been reported as having a rough morphology and a thin disordered top layer, the present scanning tunneling microscopy investigation shows that germanium may grow on Si(103) as a heteroepitaxial layer, although with its surface completely faceted. On the surface of the germanium layer eight and only eight different facets can be found: Ge(103), (105), (216), (2 −1 6), (113), (1 −1 3), (15 3 23), and (15 −3 23). These are exactly the eight stable surfaces around (103) that have been reported, thus confirming that all stable germanium surfaces around (103) have already been found. Deposition of a thin layer of indium onto this highly faceted germanium surface followed by annealing may remove all the facets and make the surface consist of only Ge(103) 1×1-In terraces, thus showing that in the In/Ge system the territory of the (103) family extends very far in all directions: to (001), (113), and (15 3 23). [S0163-1829(99)03320-2]

INTRODUCTION

Although the equilibrium thermodynamics of surface morphology has long been a subject of scientific interest[1] and the classical thermodynamic formalism for describing surface morphologies was developed by Herring[2] almost a half a century ago, not much has been done and hence known about the thermodynamics of silicon surfaces until not long ago.[3] Thanks to the invention of scanning tunneling microscopy (STM) and advances in other surface sensitive techniques, such investigations of silicon surfaces have become fruitful and thus hot very recently.[4–16] In these investigations many interesting surface thermodynamic phenomena such as step fluctuations and phase diagrams,[4,5,12,16] the Brownian motion of steps,[10] faceting,[4,6,11] the orientational stability of surfaces,[7] the equilibrium crystal shape and anisotropy of the surface free energy,[8,9,13–15] etc., have been studied. However, so far mainly Si(111), (001), and (113) as well as their vicinal surfaces have been studied, leaving surfaces in the vast area of the unit stereographic triangle of silicon almost untouched, except for a few.[3,7]

In comparison, the thermodynamics of germanium surfaces has received even less attention. In view of this, a systematic investigation of the well-annealed germanium surfaces has recently been carried out.[17–23] In these works the well-annealed Ge(113), (103), (101), (102), (313), (115), (114), (112), (315), (213), (324), (546), (515), (212), and (323) surfaces have been studied, and 14 surfaces (see Fig. 1) have been found or confirmed to be stable. Seven among these, i.e., (001), (111), (113),[17,22] (101),[19] (15 3 23),[20] (313),[21] and (21 9 29) (Ref. 23) are planar, instead of consisting of nanoscale facets, and thus are called the major stable surface (MAJOR). The rest, i.e., (105),[18] (103),[18] (216),[18] (15 1 17),[19] (117),[22] (7 7 13),[22] (10 7 12) (Ref. 23) are called the minor stable surface (MINOR) because they actually consist of nanoscale facets of one or more MAJORs. It has also been shown that each MAJOR has its own family territory,[18,20,22,23] meaning any surface within which after being thoroughly annealed must facet to facets of (only) the MAJOR or to different facets but including those of the MAJOR. The family territories and, in turn, the specific surface free energy of all the seven MAJORs have been approximately determined. Moreover, atomic structural models of these MAJORs and MINORs have been proposed for further investigations.[17–23]

Since the above-mentioned MAJORs and MINORs of germanium were found while we were investigating the faceting of some subjectively selected surfaces, it would be bet-

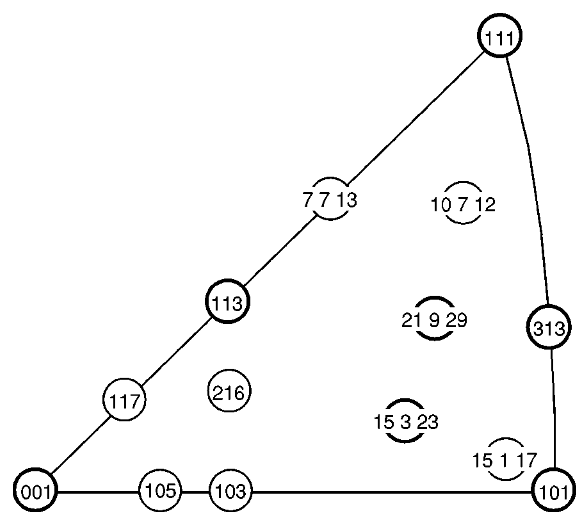

FIG. 1. Unit stereographic triangle, showing the seven major stable (thick circles) and seven minor stable surfaces (thin circles) of germanium determined recently (Refs. 17–23).

ter if they could be confirmed to be not related to the selection of the original surfaces. To achieve this goal, we hope to have a substrate that would not give any orientational preference to germanium islands grown on it. In this regard the well-annealed Si(103) surface seems to be a suitable candidate, because it has been found very recently that not only is the morphology of it very *rough* but also is the top thin layer of it *disordered*, although it is thermodynamically *stable*.[24] It seems to be reasonable to expect that if we deposit at a high rate a thick layer of germanium onto the Si(103) surface at room temperature it would not result in an epitaxial layer, but something like a polycrystal, so that we might be able to find all stable surfaces of germanium on that sample surface. Actually, this idea finds support from two recent papers,[25,26] where the homoepitaxial growth of silicon on the Si(111) surface was studied. The authors of these papers have demonstrated that when the temperature is not very high, the deposition rate is not very low, the deposited silicon layer is thick, and especially the original surface is not very flat, facets and pyramidlike structures may form on the surface.[25,26] In our case, the Si(103) substrate surface not only is rough but also has a thin disordered layer on top and thus the deposited germanium thick layer, in addition to having facets and pyramidlike structures, would not be expected to grow epitaxially. In the present paper we report the interesting result of such an experiment, which is albeit somewhat different from what is expected.

EXPERIMENT

The experiment was carried out in the UHV-STM system that has been used in recent studies[24,27] and has been described in detail elsewhere.[28] Briefly, in addition to the STM, a room-temperature field-ion microscope (FIM) and a low-energy electron diffraction (LEED) are equipped in the UHV system for tip sharpening and surface characterization, respectively. The tip was made out of a W(111) single-crystal wire with electrochemical etching and was cleaned and sharpened *in situ* with the FIM before being used for the first time or whenever necessary afterwards. The bias voltage is applied to the sample and the tip is grounded, so that occupied-state images are obtained when the bias is negative. The STM is capable of imaging the surface with a dual bias, as well as with the dc or ac (that is, the differential or local-contrast enhanced) mode. The Si(103) sample was the same one used in recent works,[24,27] which had a size of $5 \times 25\,\mathrm{mm}^2$ and was cut with a precision of $\pm 0.5°$ from a silicon single-crystal rod (p-doped, 6–8 $\Omega\,\mathrm{cm}$). The clean sample surface was prepared by several cycles of argon-ion bombardment (5×10^{-5} torr, 1000 V, 5 μA, 2 h) and annealing (1000 °C, 5 min). The annealing temperature was monitored with a pyrometer. To ensure that the sample after such treatment was indeed clean, several special measures were taken both in the system arrangement and sample handling.[24] Germanium were deposited onto the clean Si(103) surface at room temperature. The germanium source was a piece of pure germanium put inside the tantalum oven that was heated by dc current. The distance between the source and the sample was about 10 cm, so that during deposition the sample was essentially kept at room temperature. For reasons that will be explained later on, indium was deposited on the surface at some stage. In this case, the indium deposition source was also the same as that used in the recent work,[27] and so was the deposition rate setting: about 0.3 monolayers (MLs) per minute.

OBSERVATION AND DISCUSSION

The clean Si(103) surface is, as disclosed recently and mentioned above, thermally stable while the morphology of a well-annealed clean Si(103) surface is rough and its topmost thin layer is disordered.[24] A thick layer of germanium was then deposited with a very high rate onto the clean and well-annealed Si(103) surface kept at room temperature. Actually what we did was to dump all the germanium of the source in about 3 sec, so that neither the rate nor the coverage was really known, because what we wanted was as high as possible a rate. However, according to the STM images obtained afterwards, the coverage was estimated to be larger than 100 monolayers (ML's), thus corresponding to a rate of about 30 ML/sec. Our consideration of using such high a deposition rate was, apart from those addressed above, to avoid germanium intermixing with silicon and thus to prevent changing of the rough morphology of the original Si(103) surface. We believe that the as-deposited germanium layer was highly disordered or even amorphous, and thus the surface was then annealed at 880 °C for 45 min prior to STM observation, so as to make the deposited layer recrystallized[29,30] and the surface morphology in thermal equilibrium.

To show what the germanium-covered surface looked like, a typical low magnification image acquired from the surface is given in Fig. 2. As one can see, the germanium layer was indeed crystallized rather than amorphous, and the surface morphology was quite complex and indeed consisted of facets and pyramidlike structures, as expected. However, surprisingly, the germanium layer became a *heteroepitaxial* layer on the Si(103) substrate, a result that we neither hoped for nor expected to appear. Nevertheless, it was the fact. To show this fact, typical high-resolution images obtained from all possible facets on the surface are given in Fig. 3. However, to see this fact from these images, one has to go to the details of these images, including (i) what the facets are, (ii) what the orientations of the facets are, and (iii) what the relationships between the orientations of the facets and that of the Si(103) substrate are.

Comparing the high-resolution images given in Fig. 3 with those in published papers,[17,18,20] we have found that there were *eight and only eight* different facets on the surface, i.e., Ge(105) 1×2, (103) 1×4, (216) 1×1, $(2\,\bar{1}\,6)$ 1×1, (113) 3×1 and 3×2, $(1\,\bar{1}\,3)$ 3×1 and 3×2, (15 3 23) 1×1, and $(15\,\bar{3}\,23)$ 1×1. Thus the first two questions are answered. To answer the third question, that is, what are the relationships between the orientations of these facets and that of the Si(103) substrate, or to see if the germanium layer was indeed a heteroepitaxial layer on the substrate, we have to find out the crystalline orientations of the substrate. However, this is impossible on the basis of the images of the clean Si(103) surface (see Fig. 2 in Ref. 24), because the surface is rough and, moreover, its topmost layer is disordered. Of course, in principle the substrate orientations can be deduced from the LEED pattern of the clean

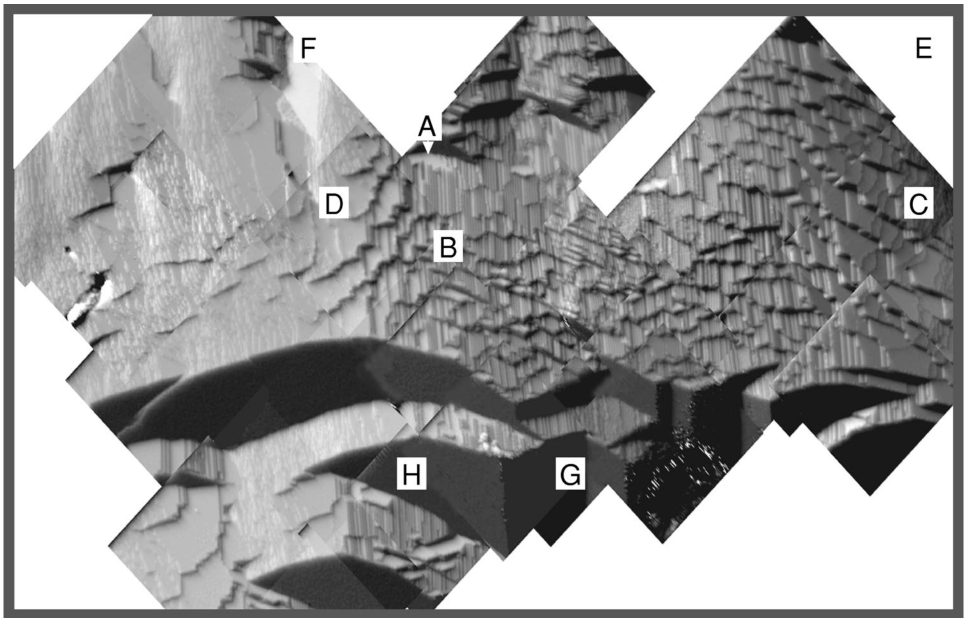

FIG. 2. A large-scale STM image (8000 Å × 5000 Å, 2.0 V, 50 pA, a tiling of many small images) of the heteroepitaxial germanium layer grown on Si(103), showing the hill-and-valley morphology of the completely faceted germanium surface. Facets marked A through H are Ge(105), (103), (216), (2 −1 6), (113), (1 −1 3), (15 3 23), and (15 −3 23), respectively. Note that this figure is rotated clockwise by 45° to save space.

Si(103) surface that we have collected. However, the pattern itself is poor (see Fig. 1 in Ref. 24) because of the same reason. Besides, this is not a direct way and thus would introduce some uncertainty into the result. Taking advantage of that deposition of a thin layer of indium onto the Si(103) surface followed by annealing may change the surface morphology from rough to consisting of large terraces of Si(103) 1×1-In (see Fig. 3 in Ref. 24), we made the surface Si(103)

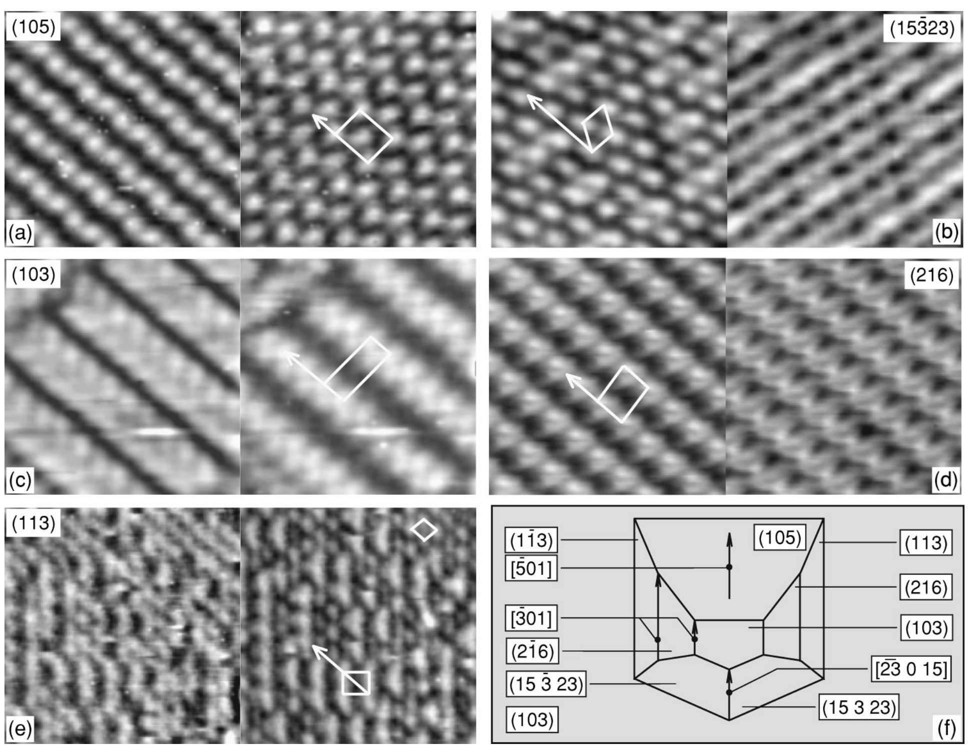

FIG. 3. High-resolution STM images of all different facets in Fig. 2. To save space, only five degenerated facets among all eight different facets are given. (a) Ge(105) 1×2, 80 Å × 80 Å, +2.0 V (left), −2.0 V (right), 100 pA. (b) Ge(15 −3 23) 1×1, 130 Å × 130 Å, +2.0 V (left), −2.0 V (right), 100 pA. (c) Ge(103) 1×4, 88 Å × 88 Å, +1.5 V (left), −1.5 V (right), 100 pA. (d) Ge(216) 1×1, 72 Å × 72 Å, +1.5 V (left), −1.5 V (right), 200 pA. (e) Ge(113) 3×1 and 3×2, 125 Å × 125 Å, +1.8 V (left), −1.8 V (right), 500 pA. (f) Schematic drawing showing the eight different facets and their crystalline orientations. Note that this figure, which is the same as Fig. 2, is rotated clockwise by 45°; otherwise, the orientations shown by the arrows should be parallel to their equivalents shown by the arrows in the images in (a)–(e), respectively.

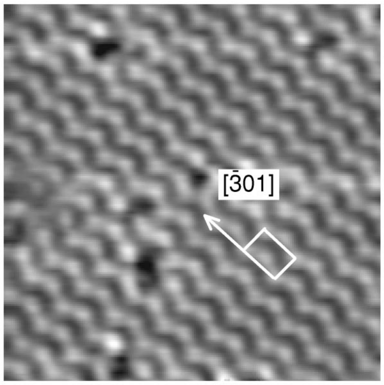

FIG. 4. A high-resolution STM image of the Si(103) 1×1-In surface, 77 Å$\times$77 Å, -1.5 V, 1.5 nA.

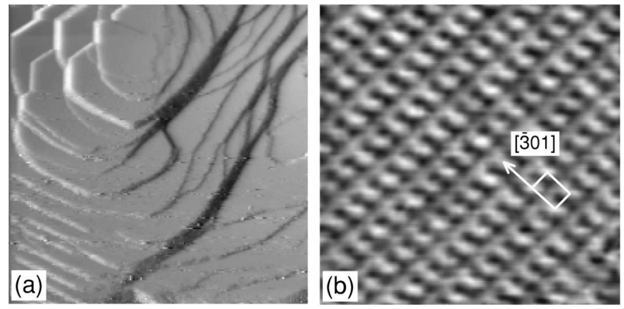

FIG. 5. STM images of the Ge(103) 1×1-In surface structure of the heteroepitaxial germanium layer on Si(103). (a) 2460 Å $\times$2460 Å, 2.5 V, 20 pA. (b) 77 Å$\times$77 Å, -1.2 V, 200 pA.

1×1-In and then found out the crystalline orientation $[-3\,0\,1]$ of the substrate from high-resolution images of the surface (see Fig. 4) without difficulties. Comparing the orientations of the facets imaged in Fig. 3 with $[-3\,0\,1]$ in Fig. 4, we find that the germanium layer was heteroepitaxially grown on the Si(103) surface, although its morphology was quite complicated rather than flat. To our knowledge never has any stable surface of either silicon or germanium been reported to have the strange character like that of Si(103), and hence epitaxial growth on such a silicon or germanium surface must never have been reported either.

At this point we recall that our goal was to find such a substrate and a procedure by which a polycrystallike germanium layer, instead of an epitaxial layer, might grow on the substrate so that all stable surfaces of germanium might appear. As far as this goal is concerned we must admit that the experiment has not been that successful. Nevertheless, the germanium layer does have a hill-and-valley morphology and many different facets have been found on it, so that our goal has been, at least, partly achieved. Remember we have mentioned above that eight and only eight different facets have been found from the germanium layer and that all these facets have been identified as shown in Fig. 3. Comparing these facets with those around (103) found previously (see Fig. 1),[17,18,20] we must conclude that all stable surfaces of germanium around (103) found previously have been confirmed by the present work and that all possible stable surfaces of germanium around (103) have been found.

It is also interesting to see from Fig. 2 that some of the facets such as {15 3 23} are very large while some such as {216} and {113} are quite small. As a result, the surface from (103) to (113) almost becomes rounded rather than consisting of clear-cut facets, and its crossing line with (15 3 23) facets almost becomes a curve. In Fig. 2 there are many such eye-catching curves separating the darker {15 3 23} facets from the brighter areas of the {113} family. This fact implies that steps on {15 3 23} are energetically very costly, while on {103}, {216}, and {113} they are not or even make a *negative* contribution to specific surface free energy, a case that has been suggested to be responsible for nanoscale faceting.[18,22] We believe that these successes have not only confirmed the major results of the recent systematic investigation of high-index germanium surfaces[13–24] but also opened up a new way of investigating the equilibrium shape of germanium and silicon[8,14,15] and, probably, also many other materials.

Finally, taking advantage of having many facets coexisting on the surface, we have made one more observation: after depositing a thin layer of indium on the surface and then annealing it, it turned out that all the facets that existed on the surface of the germanium layer disappeared completely and the entire surface came to consist of larger or smaller terraces of only one kind, Ge(103) 1×1-In (see Fig. 5). Since it has been shown that (103) is a very important plane for group-III/group-IV systems,[31–33,27] this was not completely unexpected. However, as the In/Ge(105), (216), and (15 3 23) systems had not been studied before it is still very interesting to see that their surface also facets to (103). We especially did not expect this to happen to the In/Ge(15 3 23) system, because the plane is really quite far from (103). Combining the present result with those of previous papers,[32,33] we see that in the In/Ge system the territory of the (103) family extends very far in all directions: to (001), (113), and (15 3 23), at least.

SUMMARY

In summary, we deposited with a very high rate (about 30 ML/sec) a thick layer (more than 100 monolayers) of germanium onto the clean and well-annealed Si(103) surface kept at room temperature, which has been shown to be stable and have a rough morphology along with a thin disordered top layer,[24] and then annealed and observed the surface with STM. The major results are the following. (i) The deposited germanium grew into a heteroepitaxial layer, although its surface was completely faceted. We note that epitaxial growth on such a rough and disordered surface as Si(103) had, to our knowledge, never been reported before. (ii) Eight and only eight different facets could be found on the surface, and they are identified as Ge(103), (105), (113), $(1\,-1\,3)$, (216), $(2\,-1\,6)$, (15 3 23), and $(15\,-3\,23)$ facets, which are exactly the eight stable surfaces around (103) that have been reported in recent papers.[17–23] This is an indication that all stable germanium surfaces around (103) have already been found. (iii) Deposition of a thin layer of indium onto the highly faceted germanium surface followed by annealing may remove all eight different facets and make the surface consist of only Ge(103) 1×1-In terraces, thus showing that in the In/Ge system the territory of the (103) family extends very far in all directions: to (001), (113), and (15 3 23), at least.

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