Gas-source growth of group IV semiconductors: II. Growth regimes and the effect of hydrogen


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Abstract

The crucial difference between gas-source molecular beam epitaxy (MBE) and conventional MBE is the presence of hydrogen on the growth surface. The amount and behaviour of the hydrogen are controlled by a combination of temperature and disilane flux. In situ observations under growth conditions are essential for an accurate understanding of non-equilibrium growth phenomena such as nucleation and coarsening, because once the flux has been cut off the surface material will redistribute itself. We have found that not only does surface hydrogen block silicon diffusion, but also hydrogen saturation of the substrate step edges blocks step-flow growth so that island growth predominates below 700 K, even at low fluxes. The denuded zones seen in MBE are not observed. Above 700 K, the adsorption barrier at step edges is overcome, and a transition from island growth to step-flow growth is observed as the flux is varied. © 1997 Elsevier Science B.V.

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1. Introduction

The growth of silicon on Si(001) is a good model system to study epitaxial growth, and is also important for the growth of Si–Ge alloys. SiGe alloys are used for HBTs, FETs, and MOS devices, and there is much interest in the use of Si/Si–Ge heterostructures for quantum devices, using existing group IV technology. For many of these devices, the roughness and the chemical abruptness of the interface is extremely important. It is therefore invaluable to be able to observe roughness at an atomic level, and learn how the user-controllable parameters, temperature and flux, affect the surface morphology. Before discussing the effects of germanium on this system, it is essential to understand homoepitaxial growth. The growing surface, far from equilibrium, must be observed in situ. This has traditionally been done using indirect techniques such as RHEED. In order to study local effects, however, a real-space technique is needed; we have used an elevated-temperature scanning tunnelling microscope (STM), and imaged continuously under a disilane flux, to do this at the atomic level. Details of reactions, such as barriers, which cannot be measured using the STM, have been studied using computational modelling. Building on the detailed atomistic viewpoint of our previous paper [1], we will concentrate here on the larger-scale growth phenomena.
At a substrate temperature above 450 K, disilane breaks down on impact into clean dimers and atomic hydrogen; higher hydrides and unpaired hydrogen are rarely seen [1,2]. Hydrogen resulting from the break-up of the disilane is adsorbed onto the substrate, where the atoms pair up to form saturated monohydride dimers. The details of the chemical reaction described previously [1] can, therefore, be simplified into the interaction of the substrate with a surface silicon dimer population and a corresponding surface hydrogen concentration. The silicon dimer population will ultimately condense onto the surface, whereas the hydrogen concentration will desorb slowly, even at 650 K, well below the peak desorption temperature from this surface (790 K) [3]. Both are constantly renewed by the incoming disilane in the proportions of H:Si = 2:1.

In molecular beam epitaxy (MBE) studies of silicon growth, it has been observed that the silicon will adsorb preferentially at the B-type step edges [4], as well as nucleate islands. At low temperatures, the area far from a step edge is covered in long, narrow, dimer strings [5], whereas close to the step edge, where the diffusion time to the step is less than the nucleation time of an island, there are so-called “denuded zones” [6]. The transition from island growth to step-flow growth has been observed using an elevated-temperature STM under an atomic silicon beam [7]. At low temperatures, islands nucleate on both A- and B-type terraces, and the ratio of the two remains roughly constant. At higher temperatures, the B-type steps grow out faster than the A-type steps, forming double-height steps; islands can then nucleate on the A-type terraces; as these merge into the step edges, they are quickly overgrown by the B-type step. At high temperatures, in the pure step-flow growth mode, the denuded zones around the A-type steps are sufficiently large that no islands are nucleated.

A hierarchy of growth phenomena may, therefore, be drawn up. The transition from island growth to step-flow growth is controlled by the denuded zone width. This is in turn controlled by the terrace diffusion rate, the sticking coefficient and the diffusion barrier at the step edge, and the nucleation barrier. These processes are illustrated schematically in Fig. 1. All of these underlying mechanisms may be affected by the presence of hydrogen on the surface. Although we would like to be able to isolate each effect in our experiments, we can only observe the effect of hydrogen on gross phenomena, such as the size and shape of islands, which will result from a combination of the underlying mechanisms. In this paper, we shall present our observations of growth, and then, using these data, we shall untangle this web of interdependent processes, and come to a deep understanding of the effect of hydrogen on growth.

1.1. Hydrogen

The presence of hydrogen on the surface is the root cause of the difference between MBE and gas-source (GS) MBE. The hydrogen desorption flux is comparable with our range of disilane fluxes at around 650 K, and so we have been able to observe the effect of a range of dynamic hydrogen coverages. However, the majority of our work was carried out in a relatively low hydrogen-coverage regime, and growth with a high hydrogen coverage, where the reaction mechanisms and kinetics are likely to be significantly different, has not been studied. This is because STM observations of a hydrogen-saturated surface become difficult above 700 K, as the hydrogen begins to desorb and sticks
to the tip. Even at a low concentration, however, we shall see that hydrogen is having an effect on all the parameters that control growth: the terrace diffusion rate, the sticking coefficient and diffusion barrier at step edges, and the nucleation barrier.

1.2. Diffusion blocking

The effect of hydrogen on diffusion has previously been studied by looking at the island size distribution during MBE at different temperatures and hydrogen coverages [8]. It was found that the largest effect was below 550 K, which would be where the hydrogen is immobile [9]. At this temperature, even a very small coverage, around 0.04 ML, doubled the effective diffusion barrier, from 0.67 eV to 1.35 eV. The presence of hydrogen was found to have a small effect on the silicon diffusion coefficient even above 550 K. The hydrogen at the small coverages reported will be mostly singly adsorbed [10]. In our experiments, however, we have higher coverages, and have observed that the hydrogen is mostly adsorbed pairwise onto the substrate dimers. These paired hydrogen atoms are more stable than singly adsorbed hydrogen atoms by about 0.2 eV, and do not become mobile until at least 600 K [11]. Thus, they are likely to have an even greater effect than reported previously.

1.3. Step-edge adsorption

The adsorption of hydrogen at steps will have two effects; it is likely to reduce the adsorption probability of dimers at the step edge, and it may block silicon diffusion across the step edges: a Schwoebel barrier [12]. Experimental evidence that there is a favourable site for hydrogen to take up at step edges is given by the observation of step-edge desorption from vicinal Si(001) [13]. If step-edge diffusion is blocked completely, material which adsorbs onto epitaxial islands will be forced to nucleate there, and multilayer growth will result. Some large, unidentified clusters, which move slowly across the terraces, appear to be unable to cross step edges [14], thus supporting the idea of some kind of a barrier present there. In general the effect of a barrier can be asymmetric in its effect on denuded zones, giving rise to different widths above and below a step.

1.4. Nucleation barrier

Aside from the increase in nucleation rate as a result of reduced diffusivity and the lack of step-edge adsorption, the hydrogen may stabilise different metastable intermediate structures, and lead to a lower nucleation barrier. The square structure which we have observed in our experiments [1,15] is not seen in MBE experiments, and may provide a lower-energy pathway. In our modelling, this structure appears to be clean, however. On a larger scale, hydrogen adsorbed at step edges may reduce the perimeter energy, and thus reduce the energy cost of forming a nucleus. Once the first layer of islands has grown, the subsequent layers will have additional preferential nucleation sites in the form of the antiphase boundaries (APBs) between the merging islands. Preferential nucleation of islands on top of these APBs has been observed [16].

2. Experimental

Experimental and theoretical details have been discussed in a previous paper [1]. Two types of experiment were used in this work. Firstly, the surface was allowed to settle at a temperature and then exposed to a finite dose of disilane in the STM chamber. The pressure was allowed to pass its peak, and fall back towards base pressure before STM imaging began. This has produced the "static" data, where the flux of disilane during imaging is effectively zero, and only the aftermath of the adsorption can be seen. In these images, the amount of disilane will be measured as an exposure in langmuirs (L). Secondly, scanning of the clean surface was begun, and once a stable tip had been achieved and thermal drift had become small, the surface was exposed to a continuous pressure of disilane while scanning. In these images, therefore, the amount of disilane will be measured as a pressure (pascals). There was a delay of about 3 min between the beginning of the exposure and the observation of disilane on the surface by the
STM. It is likely, therefore, that the pressure of disilane at the surface is somewhat less than the pressure of disilane measured elsewhere. Series of STM images can be recorded automatically, without stopping the scan, using a specially written program. These series of images may then be played back as a movie. Under stable conditions, the surface can be imaged for several hours, long enough to observe the growth of several monolayers. In this paper, we shall present sets of stills from movies. However, the observations are best appreciated when animated; several animated growth movies can be viewed at our Web site pages.\footnote{http://squid.ucsb.edu/~jhgwen/silicon/silicon.html}

3. STM observations

A typical image of the mature growth surface, shown in Fig. 2, illustrates the main features of this system. The two images are separated by about 13 min, at either end of a movie. The first monolayer has grown rapidly from the B-type steps, such that the steps are mostly double-height. This has occurred not only by step growth but also by island growth. This situation is equivalent to the transient growth mode seen in MBE [7]. The gaps between islands are still being filled in (A). The second layer has begun to nucleate homogeneously on the terraces, with the long axis (A-type step) running parallel to the step edges. As we shall see, the shape and size of these islands depend upon the growth conditions. Between the islands, the surface is covered with smudges caused by fast-moving dimers, and slow-moving, unidentified clusters [14]. Growth of the double-height steps is controlled by the slow growth of the A-type step; they have a low sticking coefficient, and so growth is mostly by island incorporation. As the A-type step advances, rapid overgrowth of the B-type step maintains the double-height step. During the movie, several islands have merged
into the step edge (B). Others are prevented from doing so by their phase; instead APBs form (C), some of which become decorated by a dimer string (D). These APBs provide an alternative nucleation site for the islands [16]. The nucleation of islands at B-type APBs has been observed many times in our STM images. When two islands merge, their dimerisation may either be in phase, in which case they merge, or else they may be out of phase, in which case an APB forms between them. An APB can form in two directions, parallel to either an A-type step, or to a B-type step. A diagram of the two different types is seen in Fig. 3 and an STM picture of both types of APB is seen in Fig. 4.

Previous work [5] has named these two types APB1 and APB2 respectively. APB1s have two A-type steps facing each other, whereas APB2s have two B-type steps facing each other; in this work, they will therefore be referred to as A-type and B-type APBs. The dimers that make up the boundary can easily shift their positions from one phase to the other. This may be seen in Fig. 5, which is an enlargement of the boxed area in Fig. 2. However, the boundary can be removed only by growth of one island and the consumption of another island.

3.1. Growth of the first monolayer

At 650 K, the shape and size of the islands depends strongly upon the disilane flux. In static experiments at 650 K (Fig. 6), where the peak pressure during adsorption was around $1 \times 10^{-7}$ Pa, the islands formed after a dose of 2 L were initially widely spaced, and more than one dimer wide (Fig. 6a). After six such doses (Fig. 6b), when nearly 1 ML has been grown and the second layer is beginning to nucleate, the islands were still equiaxed. The clean appearance of the islands indicates that the hydrogen is able to desorb readily at this temperature during the interval between cutting off the flux and obtaining the STM image, so that there is plenty of time for significant diffusion to take place, and coarsening can occur. Similar behaviour is observed in our in situ growth experiments (Fig. 2) (with a slightly higher flux and temperature), where the islands are again fairly equiaxed. As the flux increases, the islands become longer and thinner. At 650 K under a flux of $5 \times 10^{-7}$ Pa, the islands initially appeared as dimer strings; an example is shown in Fig. 7. During the growth of the first monolayer the strings became much longer, sometimes up to 10–20 dimers. Some of these thicken, but not beyond two dimers wide. At this combination of flux and temperature the hydrogen is able to desorb fast enough so that there is no build-up of hydrogen, and growth of a whole monolayer can proceed. However, a higher flux, $3 \times 10^{-6}$ Pa pro-
duces an increasing surface coverage of hydrogen (the increase in apparent defects between Figs. 8a and 8b), and so although the silicon is able to diffuse rapidly to begin with (the long, white smudges in Fig. 8a), after further deposition, a high density of small strings is produced, but further adsorption is blocked by adsorbed H, so growth is choked off. There is, therefore, a transition as the flux is decreased from short dimer strings to longer strings and narrow islands, and then to broad islands with an aspect ratio around 3:1.

3.2. Beyond the first monolayer

At 650 K we were unable to observe the transition from island growth to step-flow growth, even at very low fluxes, islands nucleated on the terraces and there were no denuded zones. After the first monolayer is complete, a new nucleation site becomes available, the APBs between the first-layer islands. This site became the predominant nucleation site in our higher-temperature experiments. The first event in the nucleation process is the formation of a small string of dimers across the B-type APB. This string will fluctuate in length, as dimers adsorb and desorb from the surface dimer population (Fig. 9). Modelling of different arrangements of dimers on top of the APB [17] has found that a string of epitaxial dimers is 0.1 eV/dimer more stable on top of the APB rather than elsewhere on the terrace. This lowest-energy structure may be seen in Fig. 10. The dimers at the end of the string are less stable, as there are large local strains, but these edge effects are outweighed as the dimer string lengthens. When the dimer string reaches the end of the APB, it will be unable to add any more dimers (Fig. 9a). Further dimer adsorption must, therefore, be by the nucleation of a second row. This nucleation event seems to be the transition from a subcritical, unstable nucleus into a small island, which will no longer fluctuate in length (Fig. 9b). The island will now continue to grow; however, it is still vulnerable so long as it is below the critical nucleus size for homogeneous nucleation. Without the APB the island is no longer stable and will vanish. This has occurred in Fig. 11, where a small island sur-
rounded by three islands with the same phase (Fig. 11a) is consumed, forming a complete section of new terrace (Fig. 11b).

At 750 K, we were able to observe the transition from island growth to step-flow growth, as a function of flux. At high fluxes, growth was as a combination of island growth and step-flow growth (Fig. 12). During the course of the movie, two islands nucleate on an APB, grow and finally merge. At the same time, step growth occurs at a B-type step edge on a higher terrace. Unlike the situation at 650 K, where even at low fluxes
Fig. 8. 70 nm wide, $-1.5$ V, 650 K under a flux of $3 \times 10^{-6}$ Pa. The surface hydrogen coverage is too high to allow diffusion of silicon: many small islands form, which are unable to grow more than a few dimers long. Under these conditions, stable two-dimensional growth does not occur.

(Fig. 6) the islands were still stable, at 750 K the islands are stabilised by the high flux. In another experiment, the flux which previously had been sustaining island growth was abruptly cut off (Fig. 13). Over the course of the experiment (a few minutes) the islands shrank and disappeared. First the small ones disappeared and the larger ones merged or grew, but ultimately all the material from the islands migrated to steps to cause local step-flow growth. The original line of the step edge is marked by a white line. This type of reaction is known as coarsening, and is driven by the excess perimeter energy of the islands compared with the step edges.

Fig. 9. 64 nm wide STM images taken at 670 K. The motion of the APBs can be seen from image to image. Nucleation of an island on an APB is occurring. The initial island, only one dimer wide, fluctuates in length (A,B), until it is able to widen (A). This wider island, no longer fluctuates, and begins to grow.
Fig. 10. A schematic diagram of the lowest-energy arrangement for dimers on top of an APB. Unlike a homogeneous nucleus, there is no alternation from row to trench dimer as the string grows. The major strain is at the ends of the dimer string, and so the string lowers its average energy per dimer as it grows longer.

4. Discussion

4.1. Island nucleation

Getting away from the detailed chemical mechanisms of our previous paper (Figs. 6 and 8 in Ref. [1]), there is, in general, a barrier to nucleation of a new island, since at very small island sizes the extra perimeter energy of the island is higher than the gain in free energy from the formation of the island. Thus, until this critical size is reached, a small island is liable to dissolve back into its constituent dimers. Nucleation is therefore likely to occur at those sites where the additional perimeter energy is smaller, such as at a step edge or else at a high-energy surface site, which may be reduced by the presence of an ad-dimer, and thus the excess free energy of a small nucleus is lowered. In the case of the Si(001) surface, the B-type step edge is the preferential adsorption site for dimers [4], whereas a suitable high-energy site is an APB between two previous-layer islands [16]. If diffusion is the only limiting factor, at low fluxes/high temperatures, where diffusion is fast, step-edge adsorption will be favoured (Fig. 13). At higher fluxes/low temperatures, where diffusion is slower, island nucleation will be favoured, and will preferentially occur at APBs (Figs. 9 and 12). However, at sufficiently high fluxes these nucleation sites will saturate, and diffusion to them will not be possible; then, homogeneous nucleation will become the dominant route (Fig. 2). The majority of nucleation is on the substrate, even under a relatively high hydrogen coverage (Fig. 7); there is little nucleation of the second layer on top of the first layer, until

Fig. 11. 52 nm wide STM images taken at 670 K. A small island (A) is surrounded by three islands all of the opposite phase. These islands consume the out-of-phase island. Note that the island which has decorated one of the APBs has also disappeared when this happens.
the first layer is virtually complete. This would seem to indicate that there is no significant Schwoebel barrier to dimer diffusion across the step edges. The major role that the hydrogen is playing here is as a diffusion blocker, although the square structure discussed elsewhere [1,15] may be a new lower-energy pathway, which would increase nucleation.

4.2. Coarsening

Silicon dimers adsorb preferentially onto the B-type end of an island [4], and so the starting shape of the silicon islands is kinetically controlled: a long dimer string, one dimer wide. Although the length of these strings in our GSMBE experiments appears to be somewhat shorter than in MBE (strings of up to 60 dimers have been observed [5]), they nevertheless have a high perimeter energy associated with them which can be reduced if the island develops a more equiaxed shape, albeit with anisotropy reflecting the different A- and B-type step energies. This may occur within an island. Further reductions in perimeter energy can be achieved by interactions between islands; either
static coalescence during growth or by the Ostwald ripening mechanism after growth. Coarsening occurs because of the dynamic equilibrium between mobile dimers on a terrace joining an island and those leaving it. This is analogous to the dynamic equilibrium between the surface of a liquid and its vapour, with the equilibrium vapour pressure being described by the Gibbs–Thomson effect as a function of both the temperature and the curvature of the surface. The concept of ripening was first applied to solid surfaces by Chakraverty [18]. The temperature at which coarsening begins in our experiments is around 600 K, which agrees well with the measured activation barrier of 1.7 eV for dimers to break away from a step edge [19], and island size measurements from MBE [20]. This temperature is unrelated to the hydrogen coverage. However, as we saw in our 650 K experiments (Figs. 2 and 6–8) the size and shape, and therefore the amount of coarsening which has occurred, depend strongly upon the disilane flux. This is partly due to the fact that there is less time for
coarsening to take place at higher silicon fluxes, but also due to the effect of hydrogen on diffusion. Stable growth is possible only so long as the hydrogen desorption rate is faster than the deposition rate. At higher fluxes the surface hydrogen coverage will increase with time, and as it approaches 1 ML will completely block the surface diffusion of silicon and prevent coarsening. The surface becomes covered in small nuclei and hydrogen, and thus growth is blocked. Again, the major role of hydrogen in coarsening is as a diffusion blocker, although step-edge and island-edge adsorption is also reducing the amount of coarsening.

4.3. Island growth and step growth

The local density of surface dimers is reduced near a step edge or other adsorption site, in the region where the diffusion time is less than the nucleation time. If the reduced dimer concentration drops below that necessary to form a nucleus, then the nucleation rate in this region will drop to zero, and a denuded zone will be formed. The range of the flux depletion, and hence the effective width of the denuded zone near a step edge, will be proportional to the diffusion coefficient, which will increase with temperature and decrease with disilane flux. Ultimately, the denuded zone width will be greater than the terrace width, and no island nucleation will occur. The growth mode will have then changed to step-flow growth. Experimentally, large denuded zones are observed in MBE studies, around 1000 Å at 593 K [6]. In our images, by contrast, the denuded zone width at 650 K is effectively zero, even at low fluxes (Fig. 6). Small islands are growing close to the B-type step edges. The low apparent hydrogen coverage and the equiaxed shape of the islands in Fig. 6, and the fast motion of silicon dimers across the terrace (Fig. 8a) indicate that low diffusion is not the cause of the absence of large denuded zones at this temperature. It is much more likely that the absence is caused by a reduction in the adsorption probability for dimers at the step edge, probably by hydrogen adsorption. Computational modelling of hydrogen-saturated steps has found that hydrogen favourably adsorbs at B-type edges.

So long as the flux is sufficient to maintain saturation of the step-edge sites, step-edge growth will be prevented. Some step growth is taking place at 670 K (Fig. 2), but even so, the denuded zones are extremely small at this temperature, less than 100 Å. At 750 K, however, this saturation must have been reduced, or else the barrier to adsorption has been overcome at this temperature, since step-edge growth (Fig. 12) and coarsening from islands to step edges (Fig. 13) has been observed. Islands seem to be less affected by the presence of the hydrogen than the step edges. In Fig. 6a, for example, equiaxed islands, rather than dimer strings, are observed close to the step edges, indicating that island-edge adsorption, necessary for coarsening, can still occur at the same time that step-edge adsorption cannot. This may be explained from the fact that the hydrogen initially adsorbs onto the substrate. The step edges become saturated by hydrogen atoms from the terrace above, while the islands are forming. These islands are clean, and so no hydrogen can move onto the island edges. Disilane will tend to dissociate on the substrate until the islands are of a substantial size, at which point they can also be saturated with hydrogen. This accounts for the shorter dimer strings in GS growth, compared with MBE. All the different effects of hydrogen, diffusion blocking, step-edge poisoning, and nucleation enhancement are interacting here.

5. Conclusions

All the phenomena involved in the growth of Si(001) from disilane are affected by hydrogen on the surface. Hydrogen's major role is as a diffusion blocker, but it also has a strong effect at step edges, and may decrease the nucleation barrier. The dynamic hydrogen coverage is controlled during growth by a combination of flux and temperature. This non-equilibrium situation makes the use of in situ observation essential. The different regions of the phase space which we have studied are shown in Fig. 14.

Away from steps, high hydrogen coverage on the terraces inhibits movement of the growing material. As either the flux or the temperature
changes, there is a transition from a few, equiaxed islands towards longer, thinner islands, as the hydrogen coverage increases. Ultimately, a high hydrogen coverage blocks two-dimensional growth completely. This effect is larger than had been expected from previous work [8]. The difference probably lies in the distribution of hydrogen on the surface. In the previous study the adsorbed hydrogen was unpaired, whereas in our work the majority is paired up and is, therefore, much less mobile.

The effect of hydrogen at steps depends crucially on the temperature. Below 700 K the steps are generally saturated with hydrogen. The hydrogen prevents dimers from sticking to step edges, and there is an increased barrier to flow of material down a step. Step-flow growth cannot happen, and island growth occurs across the full width of each terrace. Above 700 K the step edges are no longer saturated with hydrogen and step-flow growth is observed, with associated denuded zones whose width is determined by the factors controlling the diffusion length of dimers on the terraces. There does not appear to be a large Schwoebel barrier at the step edges since, in most cases, the first layer is nearly complete before the next layer nucleates.

No doubt there are still gaps to be filled in our understanding of the growth processes involved in GSMBE of silicon on silicon, but there are also many challenges in understanding the growth of germanium and germanium–silicon alloys on silicon. We trust that some of the principles learnt from the study of GSMBE growth of silicon will also prove fruitful in these more complicated systems.

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