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Antiphase boundaries as nucleation centers in low-temperature silicon epitaxial growth

Michael J. Bronikowski, Yajun Wang, and Robert J. Hamers*

Department of Chemistry, University of Wisconsin, 1101 University Ave., Madison, Wisconsin 53706

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The epitaxial growth of silicon on Si(001) from disilane at 720 K has been investigated using scanning tunneling microscopy. Epitaxy occurs by island nucleation and growth, with islands nucleating preferentially at antiphase boundaries between different regions on the substrate terraces. These islands begin as a single dimer string which grows to cover the entire antiphase boundary before lateral growth begins. The islands increase in size until they meet on the surface, forming new antiphase boundaries (50% of the time) for nucleation of the next layer. We find that islands nucleated at such boundaries account for approximately 94% of the area of a growing layer, indicating that essentially all epitaxial growth at this temperature occurs by this mechanism.

Epitaxial growth of silicon on Si(001) is a technologically important process which has also received wide attention as a model system for understanding the nucleation and growth of thin films.[1–10] The desire to reduce semiconductor processing temperatures has motivated increased attention to the low-temperature growth regime, in which epitaxy occurs by nucleation and growth of islands, instead of the step-flow mechanism that is operative at higher temperatures.[10–15] While scanning tunneling microscopy (STM) investigations of silicon islands[3–7,14,15] have identified many important aspects of low-temperature epitaxial growth, the nucleation process has remained virtually unexplored. STM investigations of submonolayer growth[3,4] and of sputter-annealed samples[16] have pointed to antiphase boundaries (APB's) as potentially important nucleation sites for epitaxial growth. Yet, the importance of anitphase boundaries in *multilayer* growth has not yet been established. In this paper, we report on STM investigations of silicon growth by chemical-vapor deposition (CVD) at low temperatures in the multilayer regime. Our results show a striking preference for island nucleation at antiphase boundaries, provide an atomic-level picture of the nucleation process, and indicate that APB's play a dominant role in the growth of multilayer epitaxial films at low temperatures.

Our STM consists of a single tube scanner mounted on a Burleigh "Inchworm," vibrationally isolated inside an ultrahigh vacuum system (pressure $<1\times10^{-10}$ torr). Samples of n-type Si(001) wafers (on axis within 0.25°) are cleaned by thermal annealing at 1500 K to produce a well-ordered (2×1) surface with no antiphase boundaries. The silicon is then heated to 720 K while dosing with disilane (Voltaix, Inc.). Typical growth rates are approximately 0.5 monolayer per minute. After the desired total dose, the disilane is turned off before cooling the sample for STM imaging. All STM images shown here utilize a combination of height and curvature mapping in order to show the surface structure on several different terraces simultaneously.

As shown in Fig. 1, epitaxial growth on the Si(001)-(2×1) surface results in islands with two possible phases, differing by a translation of 3.85 Å perpendicular to the dimer rows. As noted in previous STM studies,[3–5] Si islands are anisotropic and grow longer parallel to the dimer-row direction. When islands intersect, there is a 50% probability that they will have opposite phases, thereby producing two kinds of antiphase (AP) boundaries. The antiphase boundaries running parallel to and perpendicular to the dimer rows are denoted AP1 and AP2, respectively. Because of the anisotropy of the island shapes, the AP1 boundaries are longer than the AP2 boundaries. In STM images, AP1 boundaries appears as a narrow row of vacancies running parallel to the dimer rows, such that dimer rows immediately adjacent to the boundary are separated by $3a_0$, instead of $2a_0$, where a_0 is the 3.85-Å lattice constant of the (001) surface. Type AP2 boundaries appear as a sudden shift by 3.85 Å in the row position, such that the dimer rows on one side of the boundary are aligned with the troughs between the dimer rows on the other side. STM images of bare AP2 boundaries show them to have a width of several dimers and a structure similar to that depicted in Fig. 1; their structure has been discussed in our previous work[3,4] and will not be discussed here. It is important to note that neither AP1 nor AP2 boundaries can occur in isolation, but must always terminate at other AP boundaries or at a step edge.

Figure 2(a) shows a large-scale image of a Si(001) surface on which about ten layers of silicon have been grown

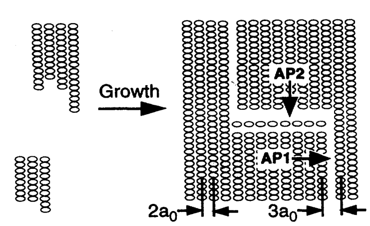

FIG. 1. Schematic illustration of silicon islands on the Si(001)-(2×1) surface and the formation of antiphase domain boundaries when these islands intersect.

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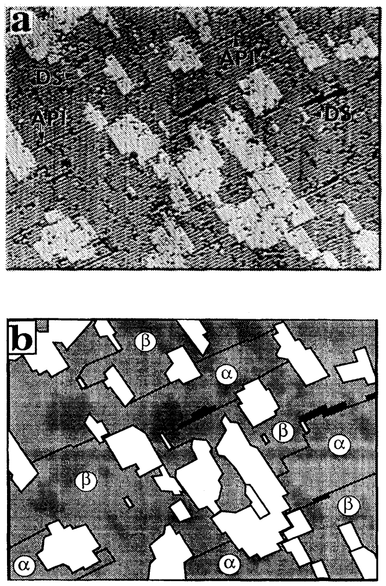

FIG. 2. (a) STM images of an Si(001) surface after growth of about ten layers of silicon. Several AP1 boundaries (AP1) and some regions where islands have nucleated at AP2 boundaries by forming dimer strings (DS) are indicated. Imaging conditions: −2.0 V sample voltage, 0.3 nA tunneling current; 1000 Å×750 Å. (b) Schematic indicating phases of the various regions. α and β denote different (2×1) phases differing by a translation of 3.85 Å perpendicular to the dimer rows, and dark lines indicate antiphase boundaries and step edges.

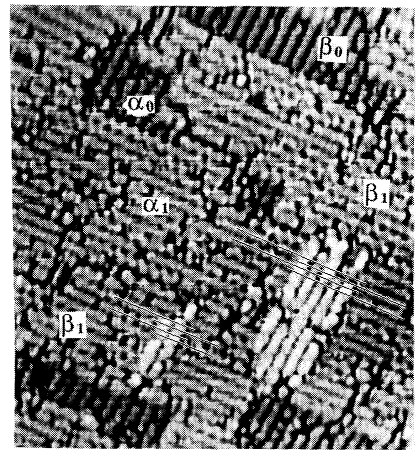

FIG. 3. STM image showing lateral shift of rows across islands, demonstrating that nucleation occurs atop AP2 antiphase domain boundaries. Lines are drawn atop dimer rows on each side of islands. Phases of each terrace are indicated by α and β. Imaging conditions as in Fig. 2, 250 Å×325 Å.

at 720 K; the topmost layer is 25% completed. While the islands stand out as the most prominent feature of the surface, closer inspection of the images reveals a complicated network of antiphase boundaries resulting from the nucleation of islands in the growing surface. To show more clearly the phase relationships of the various regions, Fig. 2(b) depicts the phases (represented by α and β) of the reconstructions on each of the terraces: solid lines represent either antiphase boundaries or step edges. In Fig. 2(a), type AP1 antiphase boundaries appear as narrow strings of vacancies, several of which are indicated in the image. More importantly, Fig. 2 also shows a striking *absence* of any visible type AP2 boundaries. Instead, the image shows that any time an AP1 boundary has shifted or terminated, an island of next-layer growth has formed upon the AP2 boundary which is necessarily present. Some of these islands are only a single dimer wide; two such "dimer strings" (DS) are indicated in Fig. 2(a). It is important to recognize that even though the AP2 boundaries are not observed, their presence can be unambiguously inferred from the fact that if an AP1 boundary extends under an island but does not reappear directly across on the other side of the island, there must have been an AP2 boundary underneath that island connecting the AP1 boundary to another AP1 boundary or to a step edge.

To show more clearly the manner in which the presence of an APB can be established, Fig. 3 shows a higher-resolution image at an antiphase boundary, in which three atomic layers are visible. The two highest islands each extend between a step edge and an AP1 boundary, which terminates at the islands. That an AP2 boundary lies underneath these islands can be inferred from the termination of the AP1 boundary, or by directly noting that the dimer rows on opposite sides of islands are shifted by 3.85 Å, equal to one-half the normal row spacing. Likewise, studying the row structure in the upper part of the image shows that an AP2 boundary lies underneath the main terrace between the regions labeled α_0 and β_0.

Upon closer examination of images like Fig. 2(a) at various stages of growth, we find three important facts: (1) very few "bare" AP2 boundaries are observed, (2) almost all islands have AP1 boundaries which either terminate or shift by one or more rows under them, necessitating the presence of an AP2 boundary under the island, and (3) island nucleation on straight type AP1 boundaries is never observed, although larger islands can cross AP1 boundaries. These observations indicate that virtually all islands on this surface nucleate at AP2 boundaries. To quantify these statements, we have analyzed the distribution of islands and antiphase boundaries on a number of large-area STM images such as that shown in Fig. 2. The analysis shows that under multilayer growth conditions at 720 K, 94% of the growth layer (by area) consists of islands atop AP2 phase boundaries, and only 6% of the growth has nucleated elsewhere. These results lead us to conclude that AP2 antiphase boundaries represent the *principal* nucleation center for low-temperature epitaxial growth of Si on the Si(001) surface.

The initial nucleation step can be understood better by studying images in which the growth has been stopped just at completion of one layer, as in Fig. 4. Here the overall miscut of 0.5° leads to three large terraces separated by monatomic steps, with seven very small islands (labeled $I1-I7$) nucleated on the terraces. Again, a complicated network of antiphase boundaries exists on the large

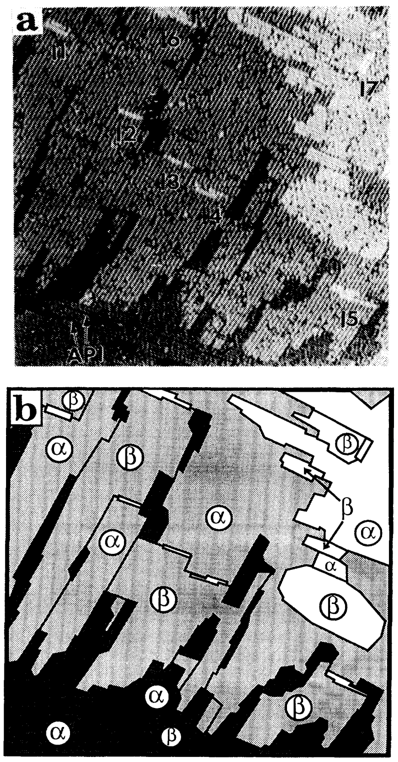

FIG. 4. (a) STM image acquired after one layer of growth, in which the next (second) growth layer is only a few percent complete. The seven islands indicated in the figure are all nucleated atop AP2 domain boundaries. Image dimensions are 800 Å×800 Å. (b) Schematic illustration of (2×1) phases corresponding to the topograph shown in (a).

terraces, as depicted in Fig. 4(b). Two long AP1 boundaries extending nearly 200 Å are indicated at lower left, and numerous AP1 boundaries can be observed on the other terraces as well. As before, locations where AP1 boundaries shift or terminate are almost always covered by island growth, even though these boundaries constitute less than 1% of the total surface area. Of the seven islands visible in this figure, all seven have nucleated at AP2 boundaries. Two of these islands (*I*2 and *I*3) are one-dimer-row-wide "dimer strings," while the rest are two or three dimer rows wide.

Analysis of a large number of images such as those shown in Figs. 2–4 reveals some general trends. While in Fig. 4 all the AP2 boundaries are covered, we do occasionally find AP2 boundaries which are not yet completely covered by island growth. In such cases, growth on the AP boundary usually extends to a kink site where AP2 and AP1 boundaries intersect, suggesting that such kink sites initiate the nucleation of the dimer strings. Islands nucleated at AP2 boundaries remain as dimer strings until the AP2 boundary is completely covered, and only at higher coverages do the islands grow wider. The unusual stability of dimer strings atop AP2 boundaries is further supported by recent work of Bedrossian and Kaxiras,[16] who found that these same structures are produced when Si(001) surfaces are sputter-etched with Xe atoms and then annealed. Both their results and ours demonstrate that a dimer string atop an AP2 boundary represents a particularly stable surface structure which apparently plays a key role in the epitaxy process.

A comparison of Figs. 4 and 2 shows that when the topmost layer is just beginning to grow (Fig. 4), the AP boundaries are often seen threading away from the ends of the nucleated islands, whereas when this top layer is more complete (Fig. 2), the AP boundaries are observed threading away from the islands *near,* but not necessarily *at,* the ends of the islands. This demonstrates that once an island has nucleated and completely covered the AP2 boundary, its spatial extent is not restricted by the presence of an AP1 boundary. As a result, once the AP2 boundary is covered, further growth and the ultimate size and shape of the islands are not strongly affected by the structure of the AP boundary at which nucleation occurred, permitting the continuous growth of the islands into a complete monolayer and the concurrent formation of a new set of antiphase boundaries from their intersection.

We have also conducted experiments to determine whether the APB's nucleate islands by preferential adsorption or dissociation of disilane at these sites, or by acting as stable binding sites for silicon atoms or dimers left behind as products of the disilane decomposition (our experiments are conducted just above the hydrogen desorption temperature). Si(001) surfaces with many APB's of both types were prepared by growth at submonolayer total coverage; this produces many small islands, including many which show small AP1 and AP2 boundaries. Exposing these surfaces to disilane at 300 K and imaging showed that the disilane molecular fragments are randomly distributed and exhibit no preference for adsorption at AP2 boundaries. The preferential island nucleation at AP2 boundaries therefore does not occur in the initial disilane dissociative adsorption, but rather in a later step, and likely arises from preferential occupation of AP2 sites by silicon monomers or dimers which diffuse onto these sites. If this is the case, then observations reported here under CVD conditions should also be applicable to epitaxial growth via solid-phase (molecular beam) epitaxy from a pure silicon source.

The STM images at various stages of growth provide the following picture of nucleation and growth at low temperatures: silicon atoms or dimers diffuse on the surface and stick at the AP2 domain boundaries (preferentially at the intersection of AP1 and AP2 boundaries) forming one-dimensional dimer strings. Once the dimer string has extended the length of the AP2 boundary and encounters a step edge or AP1 boundary, growth occurs through the formation of parallel dimer rows. Once the islands are sufficiently large, they are able to extend across AP1 boundaries. Growth continues until islands intersect, generating (with 50% probability) new AP2 antiphase boundaries which in turn nucleate the next growth layer. Our results do not support an alternative growth model suggested by Rockett, in which ad-dimers pin the locations of mobile AP boundaries. Using Rockett's estimated activation barrier for APB motion

(2.0 eV) and prefactor (10^{12} sec^{-1}), that model predicts hop times at 720 K greater than the time required to grow one monolayer in our experiment. Therefore, we attribute the observed features to nucleation on top of stationary AP boundaries.

These results have important implications for understanding the growth of silicon at low temperatures. Whereas modeling studies usually assume either step-flow growth or random nucleation of islands,[1,2,8,9] our results clearly demonstrate that nucleation of islands on Si(001) is not random, but is intimately associated with the network of antiphase boundaries on the surface. STM images of surfaces prepared by high-temperature annealing[3–7] invariably show that each terrace contains a single uniform phase, and there are no antiphase boundaries. The growth of the *first* epitaxial layer, therefore, must involve homegeneous nucleation or else nucleation at some other type of defect. Once these first-layer islands intersect, a network of APB's will be established which will serve as nucleation sites for the second layer. Our results show that once APB's are created in any significant concentration, they dominate the nucleation process. The nucleation of the first epitaxial layer plays a special role in the growth process by establishing the initial island density, and hence the initial density of antiphase boundaries, in the epitaxial film.

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* Author to whom correspondence should be addressed.

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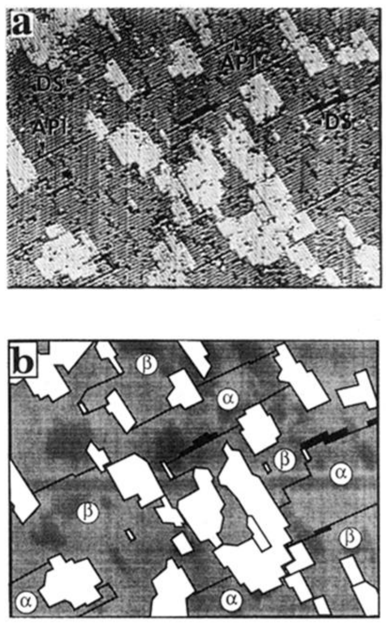

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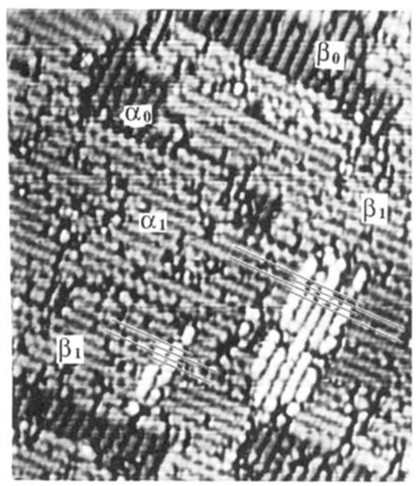

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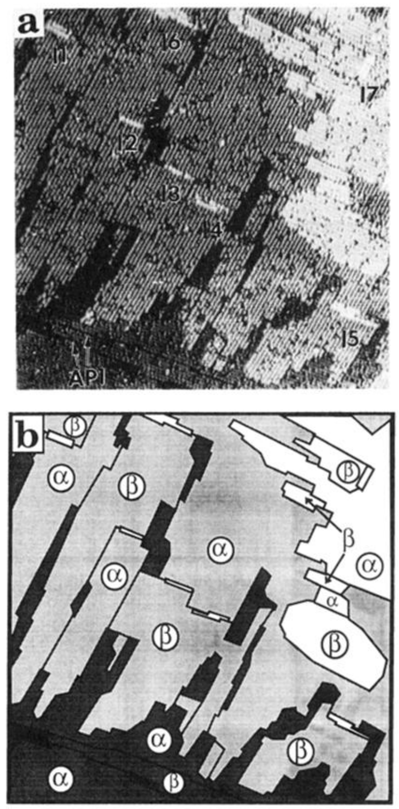

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