Effect of Strain on the Appearance of Subcritical Nuclei of Ge Nanohuts on Si(001)

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(Received 10 March 2005; published 7 July 2005)

Real-time scanning tunneling microscopy observations of nucleation and heteroepitaxial growth of Ge nanocrystals (from germane) on Si(001) indicate that in the absence of Si-Ge intermixing the formation of full hut cluster islands is preceded by the nucleation of “subcritical” nuclei consisting of two adjacent truncated tetrahedral pyramids, which, upon unification, form a tiny square-based pyramidal “critical nucleus.” It is suggested that such a precursor aids in surpassing the nucleation barrier and that the recently reported gradual faceting of prepyramids is characteristic of only Ge(Si) alloys.

DOI: 10.1103/PhysRevLett.95.025501

Although the Ge/Si system has been intensely studied for at least two decades, it keeps attracting ever-growing interest and research efforts because of its technical importance and the perception of it as a model heteroepitaxial system. Perhaps paradoxically, scores of new details, revealed by modern state-of-the-art methods almost on a regular basis, unfold the immense complexity of this seemingly simple system. Mentions only a few, the wealth of discoveries includes the mere fact of three-dimensional nanocrystal formation in a Stranski-Krastanow mechanism (preceded by two types of ordered line defects in the wetting layer [1–3]), either in the shape of elongated huts [4], symmetrical pyramids [5], or rounded domes [5,6], shape transitions [5,7], undulating ripples [8], formation of pyramidal pits [1], growth instabilities [9], etc. Only recently, new findings related to the nanocrystal nucleation stage have been reported. Vailionis et al. [10] have observed the gradual formation of three-dimensional (3D) Ge pyramids on Si(001) via unfaceted “prepyramids.” These observations have been later supported and explained by another group [11,12]. It is shown in this work that (a) such a mechanism is strain dependent and, in fact, takes place only with intermixing-induced Ge(Si) alloy nanocrystals, and (b) that in case of maximally strained pure Ge nanocrystals no unfaceted “prepyramids” exist. Instead, a faceted and split subcritical nucleus, consisting of two adjacent truncated tetrahedral pyramids, precedes the formation of full {105}-bound hut cluster islands. Alloying of these pyramids causes the {105} facets to be replaced by shallower ones, resulting in a nippelike appearance.

The scanning tunneling microscopy (STM) micrographs shown here were obtained by scanning the growing Ge/Si(001) epilayer under the GeH₄ flux (as described in the previous publications [1–3]) and at the growth temperatures of 350, 420, and 480 °C, using electroetched W tips and routine tunneling conditions of $I_T = 0.1$ nA and $-3 < V_T < +3$ V. A high-precision exposure valve made sure of an arbitrarily low deposition rate (0.01–0.1 ML/min, calculated by subtracting successive images from one another at submonolayer coverage), necessary to impose evolution times on a scale comparable to that of a typical single scan (∼18 seconds at those experiments). At this deposition rate 9–10 Ge monolayers (ML’s) were deposited at each temperature. This truly real-time observation (as opposed to a growth-interruption-cooling observation) mode minimizes the possibility of overlooking one of the principal evolution stages. Figure 1 shows three discrete nucleation events [1(a)–1(u)] from a larger scan area, during a 350 °C growth experiment. Three statements should be made at this point: (i) although nucleation of only three hut nanocrystals is shown in Fig. 1, all the huts on this surface demonstrated the same behavioral pattern, (ii) the flat impression was caused by a deliberate saturation of the STM contrast for a better focus on the wetting layer—the split subcritical nuclei in Figs. 1(e), 1(f), 1(g), and 1(s), and the full huts [e.g., Figs. 1(f), 1(g), 1(m), 1(n), and 1(u)] were, in fact, {105} faceted (e.g., as in Fig. 2), and (iii) at no time, prior to the formation of the first 3D features, were ill-defined unfaceted agglomerates observed. Furthermore, the same nucleation stages were repeated during 420 °C growth. A typical example is shown in Fig. 2. This time the contrast was adjusted for the nanocrystal height, and so its 3D nature is apparent. Again, the split subcritical nucleus is formed already {105} faceted the moment it appears, as can be judged from the characteristic {105} fringes in Fig. 2(a); however, it is strongly truncated. The truncation gradually disappears as the area of the bounding {105} facets increases [Fig. 2(b)] until, finally, the two tetrahedrons coalesce and form a full pointy pyramid in Fig. 2(c), with its crest formed by the intersection of the four {105} facets. In this sense, there is a certain resemblance to the “T pyramids” in Refs. [11,12]. The foot of such a facet must be aligned along one of the ⟨100⟩ directions, and, as evident from Figs. 2 and 3, the in-plane base orientation is, indeed, parallel to the ⟨100⟩ directions [at 45° to the ⟨110⟩-oriented dimer rows, dimer-vacancy lines (DVL’s),
and dimer-row vacancies (DRV’s) [1–3], and is maintained at all times.

In the case of unfaceted precursors to 3D nucleation, there is no true activation barrier, since the nanocrystal energy is a monotonically decreasing function of size [11]. While there exists a barrier to a first-order transformation to a faceted shape (faceting transition), this barrier shrinks to zero when the nanocrystal reaches a certain size, and hence can transform with practically no activation. This is not the case for the nucleation of a 3D faceted nanocrystal, where the nucleation barrier and the critical volume scale with the fourth ($\sim e^{-4}$) and the sixth ($\sim e^{-6}$) power of the mismatch, respectively [13]. It is therefore conceivable that the observed splitting at the subcritical stage aids to surpass the faceting barrier, since a higher height/base area aspect ratio provides better relaxation [14–17]. It follows from Figs. 1(r), 1(s), 2(a), 2(b), 3(a), and 3(b), as, indeed, from all the observed nucleation events, that the two subcritical tetrahedrons are separated either by a DRV trench [2,3] or in the nearest vicinity of it [Figs. 1(e) and 1(l)]. This makes sense since, because Ge growth on the (M × N) surface is limited to the patches located between DVL’s and DRV’s, its lateral growth is limited, and at a critical thickness Ge begins to pile up [3]. That could, in principle, lead to 3D Ge piles separated by both DVL’s and DRV’s; however, the periodicity of the former is too small. Thus, eventually, the 3D Ge piles get to be separated by DRV’s, and serve as subcritical nuclei. Such a formation of 3D patches with the subsequent formation of adjacent 3D tetrahedrons can be seen in Figs. 1(a)–1(e).

The combined volume of the two tetrahedrons is identical to that of a single pyramid, and the addition of the surface area is rather small ($\sim 0.144w^2$ assuming $\sim11.5^\circ$ inclination, where “w” is the pyramid base width). Yet,
whatever the couple of the new internal facets on both sides of the diagonal gap separating the two neighboring members of a tetrahedron pair may be, e.g., \{110\}, they cannot be lower in energy than \{105\}-type facets [18,19], which may even be considered as cusps in the effective equilibrium strained nanocrystal shape Wulf plot [11]. Therefore, at the first stages of the hut cluster nucleation, the high aspect ratio of the tetrahedrons may aid with surpassing the nucleation (faceting) barrier. However, eventually, when the combined tetrahedron volume reaches the critical value, unification (i.e., elimination of these two facets) and formation of a full \{105\} pyramid follows.

The results of Vailionis et al. can be explained by the reduction of mismatch strain due to Si-Ge intermixing, as they themselves suspect [10]. It is well known from temperature-dependent studies that, while no interdiffusion has ever been detected below 550 °C [20–23], Si readily diffuses into Ge islands above this threshold temperature, e.g., up to 35% Si have been found in Ge islands of various shapes at 560–600 °C [20–25], let alone at 650 °C [22,26] used by Vailionis and co-workers. One indirect support of such a claim comes from the experiments of Rastelli and co-workers, who observed very similar nonfaceted prepyramids and huts, only with even shallower slopes of \(0.0024\) at 600 °C [11,12]. In the present work no such intermixing effects were observed even during 480 °C Ge/Si(001) growth, since no other than pyramidal shapes were observed to be present on this surface at all times [see Fig. 3(a)]. The top-left inset in Fig. 3(a) shows the gradient image of the same couple of huts, where the darker areas represent steeper inclinations. The four slopes are presented graphically in the bottom-right inset in Fig. 3(a), and their value of 11.5° is consistent with \{105\} facets. However, an overnight anneal at 550 °C has completely changed that pyramidal appearance into a nipplelike one, as shown in Fig. 3(b), strongly resembling the micrographs in the work of Vailionis et al. [10] and providing an additional indication that the effects observed by them have been, in fact, caused by Si-Ge intermixing. Yet, even in this case, the mounds are not entirely nonfaceted: while their slope diagram, displayed in the inset in Fig. 3(c), does not show well-developed facets, it does show immature facets inclined by about 8.5° to the (001) surface. These immature facets do show well (darker) in the gradient image in Fig. 3(d). In fact, Fig. 3(d) shows pyramidal islands with their sides parallel to the \langle100\rangle directions, just like the \{105\}-faceted pyramids and huts, only with even shallower (by about 3°) facets. Lower vertical aspect ratios are expected for lower strains [17], e.g., because of alloying and/or misfit dislocations. Hence the gradual transformation of completely nonfaceted mounds into \(T\) pyramids and finally into mature \{105\}-faceted pyramids, observed by Vailionis et al. [10] and Rastelli et al. [12], and the explanation provided by Tersoff et al. [11,12] seem to be more valid for alloyed \(\text{Ge}_x\text{Si}_{1-x}\)/Si(001) nanocrystals and accordingly lower than 4.2% mismatch, rather than for fully strained pure Ge/Si(001) ones.

In summary, in this work nucleation details of Ge hut cluster islands on Si(001) were observed by real-time scanning tunneling microscopy. Growth at temperatures below 500 °C results in negligible (if any) Si-Ge intermixing, and the nucleation and evolution of Ge hut nanocrystals and formation of a gradient image, and the bottom-right inset shows the respective gradient diagram with the four lobes corresponding to 11.5°. In the present work no such intermixing effects were observed even during 480 °C Ge/Si(001) growth, since no other than pyramidal shapes were observed to be present on this surface at all times [see Fig. 3(a)]. The top-left inset in Fig. 3(a) shows the gradient image of the same couple of huts, where the darker areas represent steeper inclinations. The four slopes are presented graphically in the bottom-right inset in Fig. 3(a), and their value of 11.5° is consistent with \{105\} facets. However, an overnight anneal at 550 °C has completely changed that pyramidal appearance into a nipplelike one, as shown in Fig. 3(b), strongly resembling the micrographs in the work of Vailionis et al. [10] and providing an additional indication that the effects observed by them have been, in fact, caused by Si-Ge intermixing. Yet, even in this case, the mounds are not entirely nonfaceted: while their slope diagram, displayed in the inset in Fig. 3(c), does not show well-developed facets, it does show immature facets inclined by about 8.5° to the (001) surface. These immature facets do show well (darker) in the gradient image in Fig. 3(d). In fact, Fig. 3(d) shows pyramidal islands with their sides parallel to the \langle100\rangle directions, just like the \{105\}-faceted pyramids and huts, only with even shallower (by about 3°) facets. Lower vertical aspect ratios are expected for lower strains [17], e.g., because of alloying and/or misfit dislocations. Hence the gradual transformation of completely nonfaceted mounds into \(T\) pyramids and finally into mature \{105\}-faceted pyramids, observed by Vailionis et al. [10] and Rastelli et al. [12], and the explanation provided by Tersoff et al. [11,12] seem to be more valid for alloyed \(\text{Ge}_x\text{Si}_{1-x}\)/Si(001) nanocrystals and accord-
tals do not follow the Vailionis-Rastelli-Tersoff pathway of “prepyramids → T pyramids → \{105\} pyramids.” It is shown that \{105\} facets nucleate instantaneously (on the scale of a single-scan time), however, forming a split pyramid made of two truncated tetrahedrons, rather than a full square-based pyramid. It is speculated that the observed pyramid splitting aids the nucleation process by helping to surpass the energy barrier, because of increased relaxation in higher aspect-ratio tetrahedron pairs. If these pairs do not grow to reach some critical volume they dissolve; however, if they do, they first form a sort of split, truncated \(T\) pyramid, then unite to eliminate the two high-energy facets and increase the area of the \{105\} facets to form a full square-based pyramid bound by these facets only. A prolonged anneal at 550 \(^\circ\)C (and hence the expected Si-Ge intermixing [21,23]) causes shape transition from well-defined pyramids and huts to nipplelike mounds with ill-defined and shallow (\(~8.5^\circ\) ) facets. It thus appears that the gradual steepening model adequately describes alloyed \(\text{Ge}_{1-x}\text{Si}_{x}/\text{Si}(001)\) nanocrystals with reduced mismatch, rather than pure and fully strained \(\text{Ge}/\text{Si}(001)\).