Direct Observation of Subcritical Fluctuations during the Formation of Strained Semiconductor Islands

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We have directly imaged subcritical fluctuations during the nucleation phase of three-dimensional islands in strained layer epitaxy. The fluctuations are defect mediated and are found to be large even at low growth temperatures. We attribute the existence of large fluctuations to the time dependence of the supersaturation. This indicates classical nucleation concepts are relevant, even at low growth temperatures.

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Mechanisms of strained semiconductor island formation and growth are receiving considerable attention because of their relevance to the fabrication of quantum dot arrays for novel device applications [1]. Substantial progress has been made in identifying the important energetic [2] and kinetic [3,4] factors which potentially govern island size distributions. However, the important initial stages of island formation are still relatively poorly understood. Identifying such mechanisms is directly relevant to controlling the nucleation phase of quantum dots during the self-assembly of uniform island arrays.

Key questions concerning the mechanisms of strained island formation include the relevance of thermal fluctuations, the nature of subcritical nuclei (embryos), and the size of the critical nucleus [5,6]. In standard nucleation theory, three-dimensional island embryos are formed as thermal fluctuations [7]. This is a dynamic process in which subcritical fluctuations, once formed, will on average decay with time. However, there is little experimental evidence to identify subcritical nuclei, or the time scales and growth conditions during which they form and decay.

It is customary to assume that classical nucleation theory is valid when the supersaturation is low and the critical nucleus size is relatively large [7]. Such near equilibrium conditions are approached for Si homoepitaxy at growth temperatures greater than 650 °C, whereas the critical nucleus size is reduced to a single dimer below 500 °C [8]. This raises important questions regarding the nature of 3D island nucleation during low temperature strained layer heteroepitaxy and, in particular, the relevance of classical nucleation theory.

In this Letter, we use molecular beam scanning tunneling microscopy (STM) [9] to image and quantitatively measure the size and shape of subcritical 3D island fluctuations during Ge deposition on Si(001) at 300 °C. Surprisingly, even at these low growth temperatures, the fluctutations consist of hundreds of atoms indicating a relatively large critical nucleus size. We attribute large fluctuations to the time dependence of the adatom chemical potential during the growth phase of quantum dots.

To investigate subcritical 3D island fluctuations, we utilize high temperature STM in which a Ge evaporator is directed towards the Si sample under ultrahigh vacuum (base pressure 3×10^{-11} mbar). The open beetle-type design allows continuous imaging of the growing film during deposition [9]. Measurements were performed with a sample bias voltage of +2 V and a tunneling current of 300 pA.

Ge was deposited at 0.01 monolayer/min (ML/min) on a clean Si(001) substrate at 300 °C to form a three monolayer thick wetting layer. The surface of this layer is associated with a $M \times N$ surface reconstruction [10] as shown in Fig. 1(a). A two monolayer deep pit, indicated by the arrow, appears as a dark region in this image. After 3.3 min, an embryo, containing 270 atoms, forms adjacent to the pit [panel 1(b)]. However, this structure vanishes before the next STM image is obtained at 6.6 min. After 23.0 min, a second fluctuation consisting of 120 atoms appears adjacent to a different side of the same pit [panel 1(c)]. However, again this embryo completely decays before the next image is obtained at 26.3 min [panel 1(d)]. Another fluctuation involving 140 atoms occurs at 29.6 min [panel 1(e)] and decays before the next image [panel 1(f)].

The sequence of images in Fig. 1 reveals several interesting properties of subcritical fluctuations in strained layer epitaxy. Embryos are typically two monolayers high and the largest observed fluctuation size is 270 atoms. It is interesting that such large embryos can form and decay, even during low temperature strained layer epitaxy. In addition, surface pits are providing likely sites for 3D island fluctuations. Indeed, a successful nucleation event occurs adjacent to the larger pit located towards the left of Fig. 1(c).

To explain these observations, we first of all consider the role of surface defects in island formation. Steps or pits in the surface are associated with elastic strain

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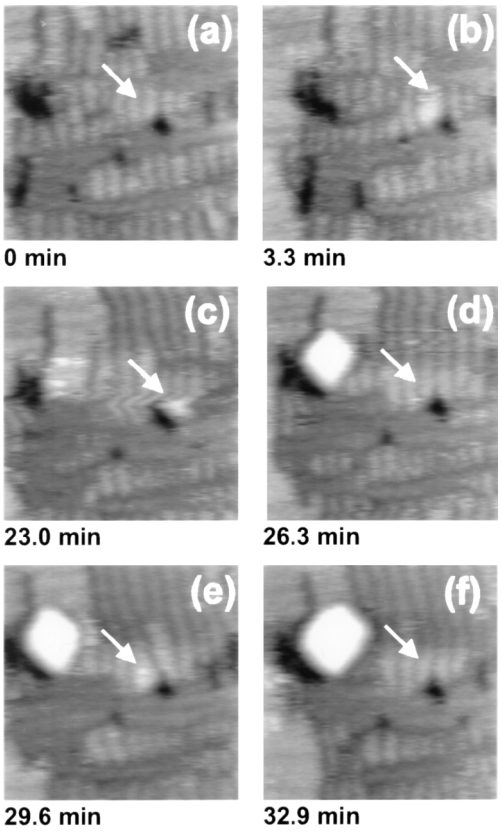

FIG. 1. STM images taken from a movie of Ge deposition on Si(001) at 300 °C. The scanned area in all images is 50×50 nm^2. Two monolayer high fluctuations containing 270, 120, and 140 atoms occur at the arrowed pit after 3.3, 23.0, and 29.6 min, respectively. Embryo sizes were measured to an accuracy of $\pm 15\%$.

fields which, in principle, can mediate fluctuations [11]. Consider, for example, a two monolayer high fluctuation of closest step spacing s forming adjacent to a two monolayer deep pit of step spacing d as shown in Figs. 2(a) and 2(b). The discontinuity in the height of the surface at a particular step produces a force monopole in the projected two-dimensional stress. The elastic relaxation energy can be obtained from the interaction of these monopoles, so that for two steps a distance L apart the interaction energy per unit length of step is $C\sigma^2 h^2 \ln(L/a)$ [12]. Here, h is the step height, σ is the misfit stress, and $C = (1 - \upsilon)/\pi\mu$, where μ is the shear modulus and υ is Poisson's ratio. The microscopic cutoff length a is usually taken as a lattice constant. The interaction is positive (attractive) if the steps are the same sense (e.g., both down steps) or negative (repulsive) for opposite sense steps (e.g., up and down steps).

The elastic relaxation energy ΔG_r associated with the formation of an embryo adjacent to the pit is equal to the total relaxation energy of the island and pit, including the interaction energy, minus the self-relaxation energy of the pit. We approximate this by summing appropriate interactions between steps and weighting the

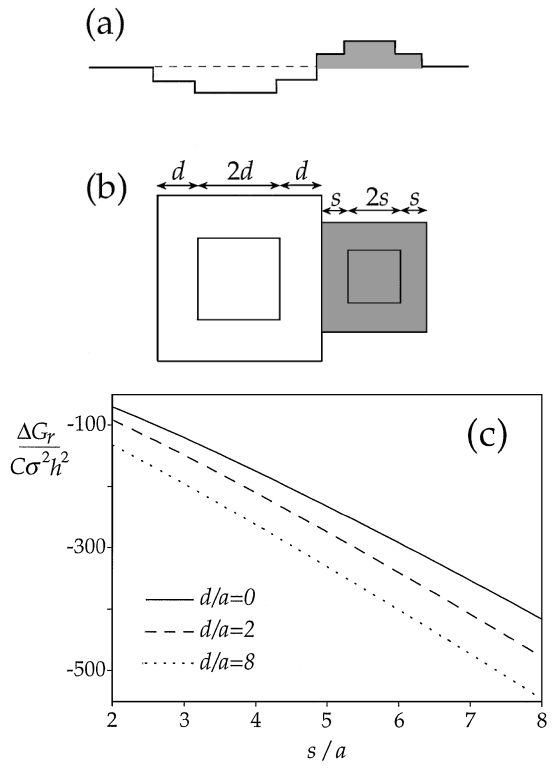

FIG. 2. (a) Cross-sectional and (b) plan-view schematic representation of a two monolayer high fluctuation (shaded) of closest step spacing s forming adjacent to a two monolayer deep pit of step spacing d. (c) Embryo relaxation energy ΔG_r including the elastic interaction with the pit as a function of step spacing s for different pit sizes.

logarithmic terms by the mean terrace width involved in the interaction. The value of ΔG_r evaluated in this way is displayed in Fig. 2(c) as a function of embryo size for several pit geometries. ΔG_r is negative and increases in magnitude with increasing pit size reflecting the elastic attraction between islands and pits. Since the probability of forming a fluctuation of step spacing s is proportional to $\exp[-\Delta G_r(s)/kT]$, this explains why pits are likely sites to observe subcritical fluctuations. The larger the pit, the greater the relaxation energy for a given embryo size which is consistent with a reduced energy barrier for nucleation at the larger pit of Fig. 1(c).

Having explained how fluctuations can be mediated by the elastic field of defects, we now consider the size of subcritical and critical fluctuations during low temperature strained layer epitaxy. As observed in Fig. 1, subcritical fluctuations which decay with time can consist of 270 atoms. Furthermore, we can estimate an upper limit to the critical nucleus size of 1500 atoms from the smallest island which is observed to grow in this sequence [Fig. 1(d)]. It is interesting that, in all cases, islands which are observed to grow are always bounded by {105} facets. This applies, for example, to the large hut shaped island with a square base in panels 1(d)–1(f). These observations are consistent with a faceted critical nucleus and subcritical embryos composed of individual steps.

The fact that large fluctuations consisting of hundreds of atoms occur during growth at 300 °C is surprising given that the critical nucleus size for 2D cluster formation is only a few atoms [8]. We propose that large fluctuations are associated with the time variation of the adatom chemical potential during the sequence of events comprising the 2D to 3D transition. These events are detailed in the following mean-field description which summarizes the essential physics leading to large fluctuations.

After completion of the wetting layer in Stranski-Krastanow growth [13], further deposition will result in the formation of 2D islands or platelets [14]. The formation energy of a square 2D island of side ℓ is

$$\Delta G_{2D} = A\ell - Ch^2\sigma^2\ell \ln\left(\frac{\ell\eta}{a}\right) - \frac{\Delta\mu h\ell^2}{\Omega_V}, \quad (1)$$

where $A = 4\gamma_s$, γ_s is the step energy per unit length, and Ω_V is the atomic volume. The supersaturation $\Delta\mu$ is equal to the mean-field adatom chemical potential and $\eta = \exp(-0.0809)/2$ [15]. In the high supersaturation regime (low growth temperature) where the critical nuclei are very small, elastic relaxation makes a negligible contribution to the 2D island formation energy [Eq. (1)]. A significant nucleation rate J_0 will occur above a critical supersaturation $\Delta\mu_c^{2D} = 4\Omega_V\gamma_s^2/hkT\ln(\alpha_{2D}/J_0)$, where the preexponential factor α_{2D} varies slowly with $\Delta\mu$. In principle, if the wetting layer is sufficiently thick to appreciably reduce the wetting layer/substrate interaction, large 3D fluctuations are possible. However, if the surface step density is relatively low, $\Delta\mu > \Delta\mu_c^{2D}$ and 2D island formation will occur rapidly before large fluctuations can form. Following this rapid nucleation phase, $\Delta\mu$ will fall below $\Delta\mu_c^{2D}$ as the increased step density due to 2D island growth provides efficient sinks for adatoms. At this stage, when the surface step density is sufficiently high to reduce $\Delta\mu$ below the threshold for 2D island nucleation, it becomes possible to form 3D islands through large fluctuations.

Consider the formation energy of an isolated 3D pyramidal island of volume V given by

$$\Delta G_{3D} = BV^{2/3} - 3\sigma^2 CV\tan\theta - \frac{\Delta\mu V}{\Omega_V}, \quad (2)$$

where $B = 4\Gamma\tan^{1/3}\theta$ and $\Gamma = \gamma_f\csc\theta - \gamma_w\cot\theta$ [4]. The pyramid facets are inclined at an angle θ to the surface, and γ_f and γ_w are the respective facet and wetting layer surface free energies per unit area. For simplicity, we assume that the wetting layer is sufficiently thick so that the substrate/wetting layer interaction can be neglected. The condition for isolated 3D island nucleation, at a rate J_0, is then given by $\Delta\mu > \Delta\mu_c^{3D} = 16\Omega_V[\Gamma^3\tan\theta/27kT\ln(\alpha_{3D}/J_0)]^{1/2} - 3\sigma^2 C\Omega_V\tan\theta$. However, defect mediated nucleation, involving elastic interactions with pits or preferential nucleation at steps, will allow island formation at supersaturations significantly below $\Delta\mu_c^{3D}$. The change in number density of 3D island nuclei N^{3D} with time is then given by [16]

$$N^{3D} = \int_0^{\Delta\mu(t)} N_d(\Delta\mu_c)\{1 - \exp[-J(\Delta\mu_c)t]\}\, d\Delta\mu_c, \quad (3)$$

where $N_d(\Delta\mu_c)$ is the density of defect sites which operate at critical supersaturations $\Delta\mu_c$, and $J(\Delta\mu_c)$ is the nucleation frequency per active site.

Equation (3) implies that a sudden onset of 3D island formation will occur over a range of defect sites when the wetting layer is sufficiently thick to suppress the wetting layer/substrate interaction and $\Delta\mu$ is also smaller than $\Delta\mu_c^{2D}$. This is consistent with the abrupt increase in 3D island density observed experimentally after 3.16 monolayers in Fig. 3. It is also possible to determine the growth rate of individual islands using molecular beam STM [17]. Immediately following 3D island nucleation, the island volume increases rapidly (see Fig. 2 of Ref. [17]). To accommodate this rapid initial growth phase, the mean-field $\Delta\mu$ must again fall, implicating defect sites in Eq. (3) which operate at lower $\Delta\mu_c$. In this low $\Delta\mu$ regime, especially large subcritical fluctuations, such as those present in Fig. 1, will occur at specific defects for which $\Delta\mu \sim \Delta\mu_c$.

It is important to point out the intriguing possibility of enhanced secondary nucleation of 3D islands. Following the rapid initial growth phase, the 3D island growth rate eventually slows with time [17]. Assuming that this self-limiting behavior is intrinsically liked to the growth kinetics of coherent islands [17–19], this will cause $\Delta\mu$ to increase. Enhanced secondary nucleation will then occur by reactivating unsaturated defect sites in Eq. (3), which operate at higher $\Delta\mu_c$. This is consistent with experimental observations of continuous island nucleation occurring throughout the self-limiting growth phase [17]. Note that the formation of dislocated islands can also reduce the growth rate of coherent islands by acting as

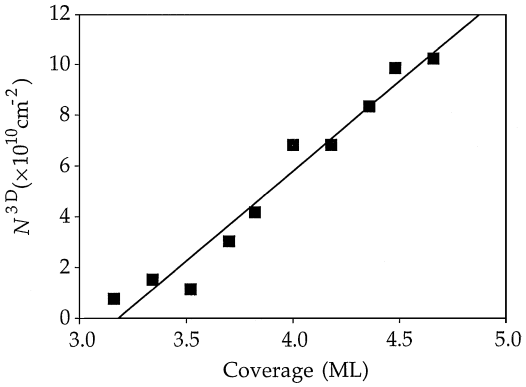

FIG. 3. 3D island number density N^{3D} as a function of coverage for Ge deposition on Si(001) at 300 °C and 0.06 ML/min. An abrupt increase in island density occurs at a coverage of 3.16 ML.

efficient adatom sinks and lowering $\Delta\mu$ [20]. This will, however, result in an appreciable decrease in, or complete prevention of, 3D island nucleation which is not apparent up to a coverage of five monolayers (Fig. 3).

In conclusion, we have demonstrated experimentally that large subcritical fluctuations consisting of several hundred atoms can occur during the strain induced 2D to 3D transition, even at relatively low growth temperatures where the supersaturation is high and critical nuclei are anticipated to be small. In a qualitative mean-field description, we attribute this to the time dependence of $\Delta\mu$. Our observations and interpretation suggest that classical nucleation concepts are relevant to strain induced islanding, even at low growth temperatures.

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