

Nucleation in Si(001) Homoepitaxial Growth

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From low energy electron microscopy observations of the surface topography of Si(001) during homoepitaxial growth at 650 °C, we have determined the nucleation density profile on top of a "base" island, and the distribution of the base island radius at the time of nucleation. Comparison with homogeneous nucleation theory yields a typical critical nucleus size of ~ 650 dimers, and allows nucleation on Si(001) to be understood in a common framework with equilibrium step-edge fluctuations and 2D island ripening.

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In homoepitaxial growth, one often distinguishes step-flow growth from layer-by-layer growth. Step-flow growth is characterized by the absence of nucleation: All impinging atoms diffuse and adhere to step edges. However, if the temperature is reduced, the incoming flux increased, or the distance between steps increased, not all incoming atoms may reach the step edge, and new islands may nucleate on the terraces. In general, a transition is seen from nucleation and growth to step-flow growth with increasing temperature. Thus, a complete understanding of growth requires an understanding of nucleation.

In this Letter we present a study of 2D island nucleation on Si(001), at a (technologically) realistic growth temperature of 650 °C. In particular, we demonstrate the need for a theoretical approach for treating nucleation in homoepitaxial growth at elevated temperatures that goes beyond the widely held notion of a constant (small) critical nucleus size. We introduce a theory for homogeneous nucleation based on step-terrace exchange kinetics, demonstrating that nucleation on Si(001) can be understood in a common framework with equilibrium step edge fluctuations [1] and ripening [2].

The experiment was performed by growing Si from silane or disilane gas on a Si(001) surface held at 650 °C (i.e., above the H desorption temperature) at growth rates ranging from 0.1 to 2 monolayers (ML) per minute. At a given growth rate no significant differences were found between silane and disilane. The change of surface topography during growth was imaged by low energy electron microscopy (LEEM) [3] and recorded on video tape. Figure 1(a) shows a LEEM image depicting a nucleation event on top of an elliptical island. The images were recorded in dark field imaging mode using a half-order diffraction beam corresponding to one of the two orientations of the (2×1) dimer reconstruction. The dimer orientation alternates with every additional atomic layer, causing subsequent layers to appear alternately bright and dark in the image. From the LEEM images the location of the nucleation event with respect to the center of the underlying ("base") island and the dimensions of the base island were determined. As one of the points

of interest is the spread of the underlying island size due to the statistical nature of the nucleation event, great care was taken to exclude additional causes for such a spread by recording only nucleations on top of islands of similar shape and in similar surroundings. This was accomplished by observing subsequent nucleations on top of a single hill of islands as shown in Fig. 1(a). After some time of growth the configuration of the hill attains a steady state cycle resulting in highly similar initial conditions for subsequent nucleations. Such measurements of the dimension of the base island at the time of nucleation, as well as the nucleation site, were inspired by a recent paper by Tersoff, Denier van der Gon, and Tromp [4] which introduced the notion of a critical radius of the base island for nucleation. We will extract quantitative information

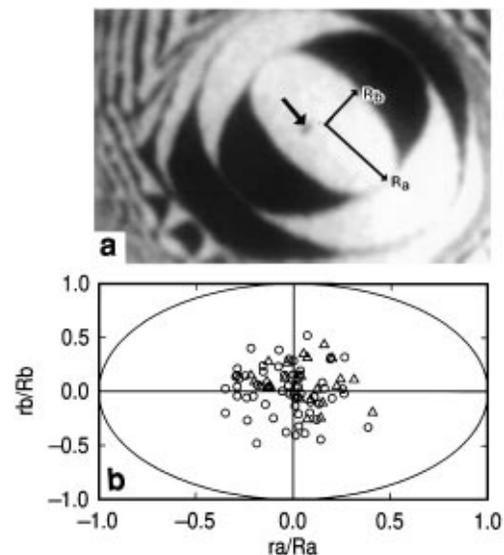


FIG. 1. (a) LEEM image of the nucleation of a new (black) 2D Si island (large arrow) on a (white) base island with major radius R_a and minor radius R_b . The base island forms the top of a hill. Field of view $\sim 1 \mu\text{m}$. (b) Relative locations of a large number of nucleation events. Each data point represents a single nucleation event on a newly grown base island, as shown in (a). (Circles obtained with silane, triangles with disilane.)

on nucleation by analyzing a relatively large number of such nucleation events.

In Fig. 1(b) we show the locations of the nucleation events on the base island, where the size of the base islands in individual nucleation events has been normalized. Although the base island is elliptical, we will further reduce these data to conform to a circular geometry; i.e., we will define a normalized radius of nucleation $r/R = [(r_a/R_a)^2 + (r_b/R_b)^2]^{1/2}$, with $R^2 = R_a R_b$. Figure 2(a) plots the probability that a nucleation event occurs within a radius r on a base island with radius R . Since most nucleation events appear near the center of the base island, this probability rises sharply for small r/R . Similarly, we can plot the probability that a nucleation event has occurred on a base island with radius R . Since there is a critical radius (which depends on temperature and growth rate) at which this probability rises sharply, Fig. 2(b) shows this probability as a function of R/R_c . For small R/R_c no nucleation occurs at all. The curve rises sharply at $R/R_c \sim 0.9$, and saturates at $R/R_c \sim 1.05$.

In the following we will present a theory of nucleation to obtain the fits in Figs. 2(a) and 2(b) (solid lines). First, we determine the spatial distribution of adatoms on the base island and the associated adatom chemical potential. Next, using homogeneous nucleation theory, we obtain a first estimate of the critical nucleus size.

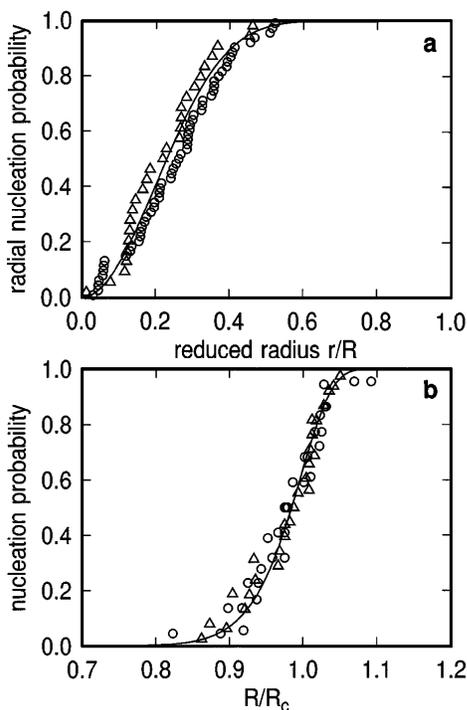


FIG. 2. (a) Normalized probability that a nucleation event will occur within a radius r , on a base island with radius R . (b) Probability that a nucleation event has occurred on a base island with radius R . (Circles obtained with silane, triangles with disilane.) Solid lines in (a) and (b) are fits obtained using homogeneous nucleation theory as explained in the text.

Further elaboration yields the spatial dependence of the nucleation rate, from which we derive expressions that can be compared with the data. To simplify matters we will formulate a theory for a circular base island.

It has been shown earlier [4] that the equilibrium concentration of adatoms on an island of radius R , with a constant incoming flux F is given by $c_1(r) = c_0 + (F/4D)(R^2 - r^2) + c_{\text{edge}}$. D is the adatom diffusion coefficient. The term c_0 (usually neglected) is the equilibrium concentration of adatoms in the absence of an external flux. The second term gives the parabolic adatom concentration due to diffusion of the incoming adatom flux to the edge of the island. The final term c_{edge} is zero if we neglect the curvature of the island edge, and if there is no barrier to incorporation of an adatom at the island edge. Following Ref. [4], assuming $c_0 = c_{\text{edge}} = 0$, and an island nucleation rate ω proportional to c_1 to the power ν , where ν is the (fixed) critical nucleus size, we obtain a good fit for $\nu = 14$ for the data shown in Figs. 2(a) and 2(b). If c_{edge} is not zero, then a larger critical nucleus size is needed to fit the data. However, the assumption that $c_0 = 0$ is unjustified. To first order, let us assume that $c_{\text{edge}} = 0$. It is then easy to see that for $r = 0$ (i.e., on the center of the base island) $(c_1 - c_0)/c_0 = FR^2/4Dc_0$. For experimentally determined values of $F = 0.036/(\text{s}/\text{nm}^2)$, $R = 420$ nm, and $a^2 D c_0 = 25\,000$ nm³/s (Ref. [5]) ($a = 0.543$ nm), we find that the added adatom concentration due to the impinging flux is only 1.75% of the equilibrium adatom concentration; i.e., the surface is close to thermodynamic equilibrium, and the external flux adds only little to the equilibrium adatom concentration. Clearly, the simple theory that considers only the adatoms deriving from the external flux is inadequate, and the equilibrium concentration of adatoms must be taken into account explicitly. Including c_0 into the theory presented in Ref. [1], we can fit the data again, leading to $\nu = 800$. However, this form of the theory would allow for nucleation even in the absence of an external flux, which is unphysical. The situation of a slightly supersaturated adatom gas is very similar to that of a slightly supersaturated vapor, for which the nucleation of droplets is described by classical homogeneous nucleation theory. In the following we will show how this theory may be applied to our experiments.

The adatom chemical potential is given by $\mu_{\text{adatom}} = kT \ln(c_1/c_0) = kT(c_1 - c_0)/c_0$. To find the c_{edge} contribution to c_1/c_0 we consider the growth rate of the base island. The rate of change of its radius depends on the incoming flux F as well as on the surrounding topography (i.e., how this flux is distributed between the base island and the steps surrounding it). As the topography scales with R_c , so does this rate of change. From the experiments, we determine that $dR/dt = 0.9Fa^2R_c$, corresponding to a flux per step-edge site $j = 0.8FaR_c$ (taking into account a factor of 1.1 for the elliptical shape of the island). From our studies of thermal step-edge

fluctuations [1] as well as 2D island ripening [2] in this temperature range we know that the flux per edge site is given by $j = (\Gamma/a^3kT)(\mu_{\text{edge}} - \mu_{\text{adatom}})$, with a the lattice constant, $\mu_{\text{edge}} = a^2\beta/R$ the chemical potential of an edge with curvature $1/R$, and step free energy β . Γ is the step edge mobility, which has been shown to be approximately equal to a^3/τ_a , where τ_a is the average time between step-terrace exchange events [6]. Substituting $j = 0.8FaR_c$ into this expression, we obtain the offset in the chemical potential due the attachment barrier at the step edge (i.e., the c_{edge}/c_0 term), and we can write down the full expression for the chemical potential:

$$\mu_{\text{adatom}}(r) = kT \frac{FR^2}{4Dc_0} \left[1 - \left(\frac{r}{R}\right)^2 + \left(\frac{L_1}{R}\right)^2 + \left(\frac{L_2}{R}\right)^3 \right], \quad (1)$$

with $L_1^2 = 3.2a^4Dc_0R_c/\Gamma$ and $L_2^3 = 4a^2\beta Dc_0/kTF$.

We now turn to classical homogeneous nucleation theory to obtain the size of the critical nucleus and the nucleation rate on top of the base island [7]. The free energy cost of creating an island with radius ρ is $\Delta G = \beta 2\pi\rho - \mu_{\text{adatom}}\pi\rho^2/a^2$. The critical nucleus size is defined by $d\Delta G/d\rho = 0$, leading to $\mu_{\text{adatom}} = a^2\beta/\rho_c$; i.e., the chemical potential of the critical nucleus is equal to the chemical potential of the surrounding adatom sea. Taking the ‘‘adatom’’ (i.e., the diffusing entity) to be a dimer occupying an area a^2 (i.e., $a^2N = \pi\rho^2$), we find that the number of N dimers in the critical nucleus is given by

$$\sqrt{N} = \frac{a\beta\sqrt{\pi}}{\mu_{\text{adatom}}}. \quad (2)$$

Since μ_{adatom} depends on r (i.e., the location on the base island), the critical nucleus size is also dependent on r . Experimentally determined values of $T = 650^\circ\text{C}$, $a^2\beta = 18 \text{ meV nm}$ (Ref. [1]) and $\Gamma = 100 \text{ nm}^3/\text{s}$ (Ref. [8]) yield a size of the critical nucleus on the order of 650 dimers at the center of the base island and 4000 dimers close to the edge. The critical nucleus is large and depends on location. In the following we will obtain expressions for the rate of nucleation that can be compared directly with the experimental results shown in Fig. 2.

The ratio of the concentration of critical nuclei over dimers is given by homogeneous nucleation theory [7]: $c_N/c_1 = \exp(-\beta a\sqrt{\pi N}/kT)$, where $\beta a\sqrt{\pi N}$ is the free energy cost of the critical nucleus. The nucleation rate of supercritical nuclei $\omega(r)$ is given by the rate at which single dimers attach to the critical nucleus (i.e., the number of attachment sites at the nucleus circumference, $2\sqrt{\pi N}$, times the attachment rate per site, $1/\tau_a = \Gamma/a^3$, times the abundance of critical nuclei, c_N :

$$\omega(r) = 2\sqrt{\pi N} \frac{\Gamma}{a^3} c_1 e^{-\beta a\sqrt{\pi N}/kT}. \quad (3)$$

The integrated nucleation rate $\Omega(r, R)$ within a radius r on top of an island with radius R is $\Omega(r, R) = \int_0^r 2\pi x \omega(x) dx$. While an exact analytical expression cannot be obtained for this integral, the normalized probability for a nucleation event to occur within a radius r on an island of radius R is accurately approximated by

$$\frac{\Omega(r, R)}{\Omega(R, R)} = \frac{1 - e^{-(\alpha+1)x^2/(b-x^2)}}{1 - e^{-(\alpha+1)/(b-1)}}, \quad (4)$$

with $x = r/R$, $b = 1 + (L_1/R)^2 + (L_2/R)^3$, and $\alpha = 4\pi\beta^2 a^2 Dc_0 / (kTR)^2 Fb$.

We will now discuss the distribution of radii of the base island for which nucleation occurs. Let $f(R)$ be the fraction of islands of radius R which have had an island nucleate on top of them. Then

$$\frac{df}{dR} = \Omega(R, R) \left(\frac{dR}{dt}\right)^{-1} (1 - f), \quad (5)$$

where we may substitute $dR/dt = 0.8Fa^2R_c$. Again, an exact analytical integration to obtain an expression for $f(R/R_c)$ (with R_c defined by $\ln[1 - f(R_c)] = -1$) is not possible, but a very good approximation is given by

$$f(R/R_c) = 1 - \exp(-R/R_c)^\gamma, \quad (6)$$

where $\gamma = (2\alpha + 2)/b - 1$. We can use Eqs. (4) and (6) to fit the data in Fig. 2. (We have verified that there are no significant differences between the approximate expressions given here and a numerical integration of the exact expressions.) The solid lines are the results of a fitting procedure. The values for the step free energy β , the step mobility Γ , and the surface diffusion coefficient a^2Dc_0 are as given above, in agreement with previous experimental results. The resulting critical nucleus size at the center of the island is ~ 650 dimers. To estimate the accuracy of this determination we define a new quantity $g = 2\alpha/b$, which is equal to γ to better than 5%. The value of γ is constrained to better than 20% by the fit in Fig. 2(b). The expression for the critical nucleus size [Eq. (2)] can be rewritten as

$$N = \frac{2gDc_0}{FR^2}. \quad (7)$$

The uncertainty in the critical nucleus size is dominated by the uncertainty in the diffusion coefficient a^2Dc_0 , about a factor of 2.

In addition to the data presented here, we have performed measurements of R_c , as a function of temperature, showing that R_c increases with temperature as a thermally activated quantity with an activation energy of $\sim 0.6 \text{ eV}$. From these data, and from the known temperature dependences of β , Γ , and a^2Dc_0 , we can estimate the size of

the critical nucleus at lower temperatures. From this extrapolation we find that (for growth rates on the order of 1 ML/min) the critical nucleus reaches the size of a single dimer at a temperature of about 500 °C. Thus, our results do not conflict with scanning tunneling microscopy studies in which much smaller stable 2D islands are observed after growth near room temperature [9].

The dynamics of Si(001) above ~ 500 °C appears now to be well understood. Capillary fluctuations of step edges are well described by step-terrace exchange kinetics [1], and Ostwald ripening of a population of 2D islands can also be understood in this framework. The rate of change of an island area is limited by step-terrace exchange kinetics, while equilibration of the dimer sea is limited by surface diffusion [2]. The same ingredients describe 2D nucleation if we supplement the step-terrace exchange kinetics with classical homogeneous nucleation theory. The resulting critical nucleus size is surprisingly large, and depends on the local adatom chemical potential. At a given incoming adatom flux, the exponential temperature dependence of $a^2 D c_0$ leads to a strong temperature dependence of the critical nucleus size. Thus, while below 500 °C the critical nucleus is small, at technologically relevant growth temperatures the notion of a small, fixed critical nucleus must be abandoned. The substrate contribution to the mobile adatom sea can be much larger than that due to the incoming flux and must be taken into account explicitly. We expect this to be the case not just in Si homoepitaxy, but in a wide range of epitaxial growth systems.

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