Supplemental Material

I. Dark-field LEEM imaging of the (6×6) surface phase

Here we confirm that the metastable domains with dark contrast in our bright-field (BF) images correspond to a (6×6) phase. Figure 1(a) displays a BF image obtained at an incident electron energy of 8.6 eV by filtering the $(0, 0)$ spot (encircled in red in panel (c)) with a contrast aperture. The corresponding dark-field (DF) image in panel (b) was obtained at 3.5 eV by filtering the $(0, 1/6)$ spot (encircled in blue in panel (c)). The chosen electron energies optimize contrast [22]. The complementary image contrast between (a) and (b) confirms that the dark patches correspond to the (6×6) phase.

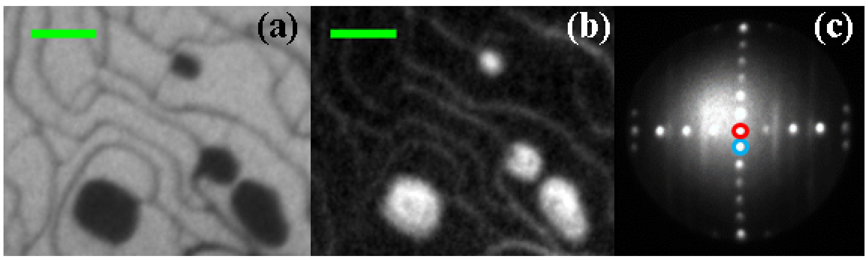

Figure 1: (a) BF image obtained at 8.6 eV from the $(0, 0)$ spot encircled in red in (c). (b) DF image obtained at 3.5 eV from the $(0, 1/6)$ spot encircled in blue in (c). (c) Representative LEED pattern of GaAs(001) revealing a superposition of $c(8 \times 2)$ and (6×6) patterns and indicating the diffraction spots used to obtain the images in (a) and (b). The scale bars in (a) and (b) are $0.3\,\mu$m.

II. Additional kinetic processes included in the Monte Carlo (MC) model

In this section we display snapshots from experimental LEEM movies which illustrate several secondary kinetic processes incorporated in our MC model. All images were obtained in the BF mode with an incident electron beam energy of 8.6 eV.

A. Lochkeim formation on (6×6)

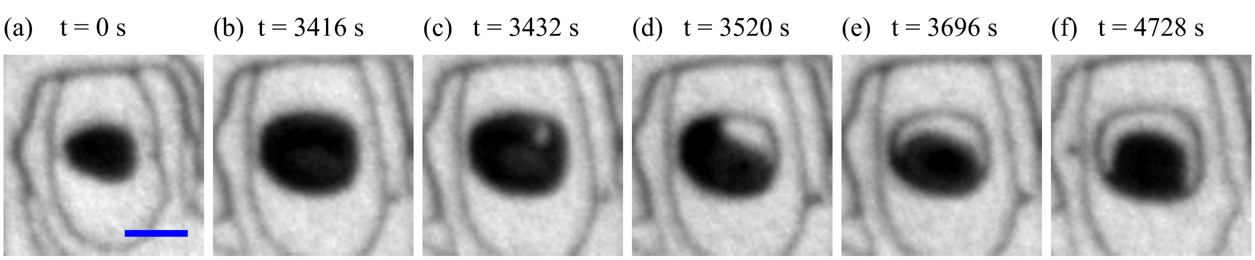

Figure 2: Sequence of LEEM images taken from a movie of a (6×6) terrace transforming to $c(8 \times 2)$. This initiates in panel (c) and continues through panels (d) and (e) until the transformation completes in (f), revealing a lower central (6×6) terrace. This indicates that multiple layers of (6×6) exist as inverted wedding cake structures and that Lochkeime form more readily on (6×6) than on $c(8 \times 2)$. Furthermore, we find it is always the outermost (uppermost) (6×6) terrace that transforms to $c(8 \times 2)$ first. The sample temperature is $T = 586\,^{\circ}$C, and the scale bar is $0.2\,\mu$m.

B. Systematic Lochkeim nucleation on critical-size $c(8 \times 2)$ terrace

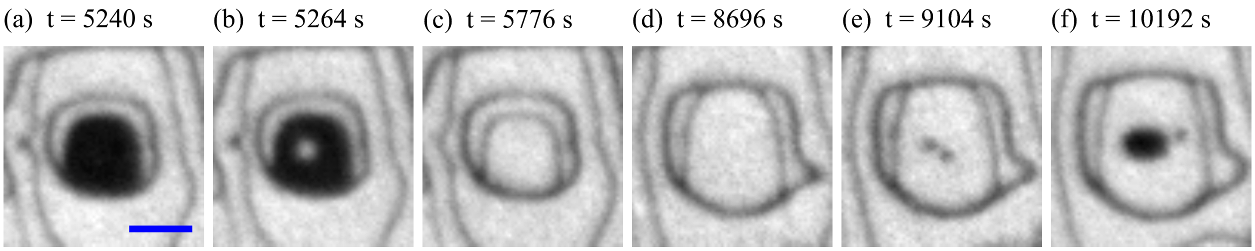

Figure 3: (Continued from Fig. 2) Sequence showing that one or more Lochkeime (in this case up to three) form almost simultaneously around the middle of a $c(8 \times 2)$ terrace upon it reaching a critical terrace radius R_c (panel (e)). The sample temperature is $T = 586\,^\circ$C, and the scale bar is $0.2\,\mu$m.

C. Coalescence of (6×6) terraces

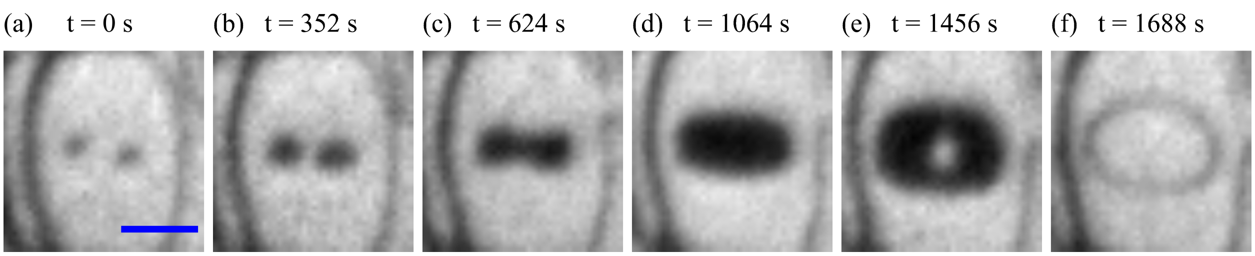

Figure 4: Sequence of LEEM images taken from a movie showing the coalescence of two (6×6) terraces, forming a larger (6×6) terrace. The combined (6×6) terrace transforms to $c(8 \times 2)$ as a single domain (panel (e), (f)). The sample temperature is $T = 592\,^\circ$C, and the scale bar in (a) is $0.15\,\mu$m.

D. Phase transformation by coalescence

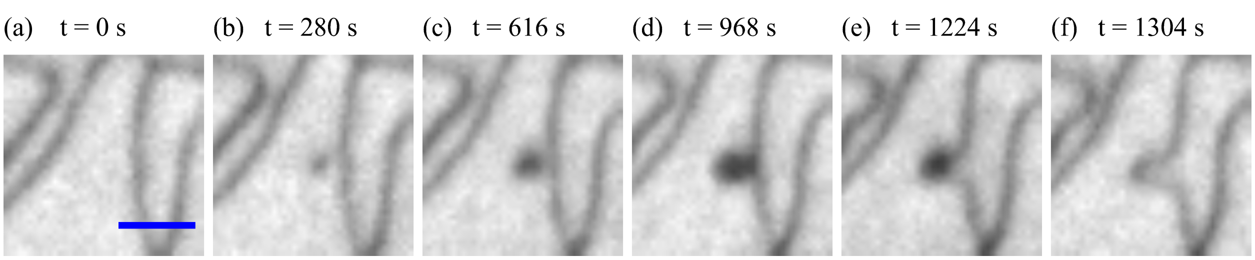

Figure 5: Sequence of LEEM images obtained from a movie showing that a (6×6) terrace transforms to $c(8 \times 2)$ on coalescing with a $c(8 \times 2)$ terrace. The sample temperature is $T = 586\,^\circ$C, and the scale bar is $0.15\,\mu$m.

III. Determining probabilities J_b and ρ from LEEM movies

Let ρ be the probability per unit area and time for nucleation of the stable phase on the metastable phase. If we have N metastable domains all with surface area A, after time $\mathrm{d}t$, the number of domains will have dropped by $\mathrm{d}N$, with

$$\mathrm{d}N = -\rho A N \mathrm{d}t. \tag{1}$$

Changing variables from from t to domain radius R, we have $\mathrm{d}t = \mathrm{d}R/v$, where v is the step velocity, and $A = \pi R^2$, giving

$$\mathrm{d}N = -\frac{\pi\rho}{v} N R^2 \mathrm{d}R. \tag{2}$$

Integrating Eq. (2) yields

$$N(R) = N_0 \exp\left(-\frac{\pi\rho}{3v} R^3\right), \tag{3}$$

where N_0 is the initial number of domains. Differentiating Eq. (3) yields

$$\mathrm{d}N = -N_0 \frac{\pi\rho}{v} R^2 \exp\left(-\frac{\pi\rho}{3v} R^3\right) \mathrm{d}R. \tag{4}$$

The probability distribution is hence

$$f(R) = 3\,\frac{R^2}{a^3} \exp\left(-\frac{R^3}{a^3}\right), \tag{5}$$

where a is

$$a = \left(\frac{3v}{\pi\rho}\right)^{1/3}, \tag{6}$$

and is related to the average domain radius upon phase transformation, $\langle R\rangle = \int_0^\infty R f(R)\,\mathrm{d}R$, via $a = \langle R\rangle / \Gamma(4/3)$, where Γ is the gamma function.

To calculate ρ at a certain temperature, we first perform measurements on our LEEM videos and produce a histogram of (6×6) terrace radius at which $c(8 \times 2)$ nucleates, as contained in Fig. 6(a). The value of ρ is then calculated by fitting the histogram to the distribution of Eq. (5), including an arbitrary proportionality constant. This yields a value for a, which is used together with the corresponding value of v to compute ρ from Eq. (6). Our histograms only include single (6×6) domains which undergo transformation to $c(8 \times 2)$ via the fundamental mechanism as in Fig. 1 of the main text.

A completely analogous argument applies to J_b, only that we consider Lochkeim nucleation instead of phase nucleation. The added difficulty is that it is not possible to observe the moment of Lochkeim nucleation, as $(6 \times 6)/(6 \times 6)$ steps show no contrast. Therefore we measure radii R_1 and R_2 of the upper and lower terraces, respectively, as soon as the upper terrace transforms to $c(8 \times 2)$ and the lower becomes visible (see Section II.A). In accordance with our assumption that step velocity v is independent of the nature of the phases on either side of the step, the radius of the upper domain at the moment the lower domain nucleated is $R_1 - R_2$. Therefore to calculate J_b at a certain temperature, we perform measurements on our LEEM videos and produce a histogram of (6×6) terrace radius $R = R_1 - R_2$ at which a Lochkeim nucleates on it, as contained in Fig. 6(b). We then fit the histogram to Eq. (5) (including an arbitrary proportionality constant) to obtain a value for a which is then used in Eq. (6) (with J_b in the place of ρ) to compute J_b.

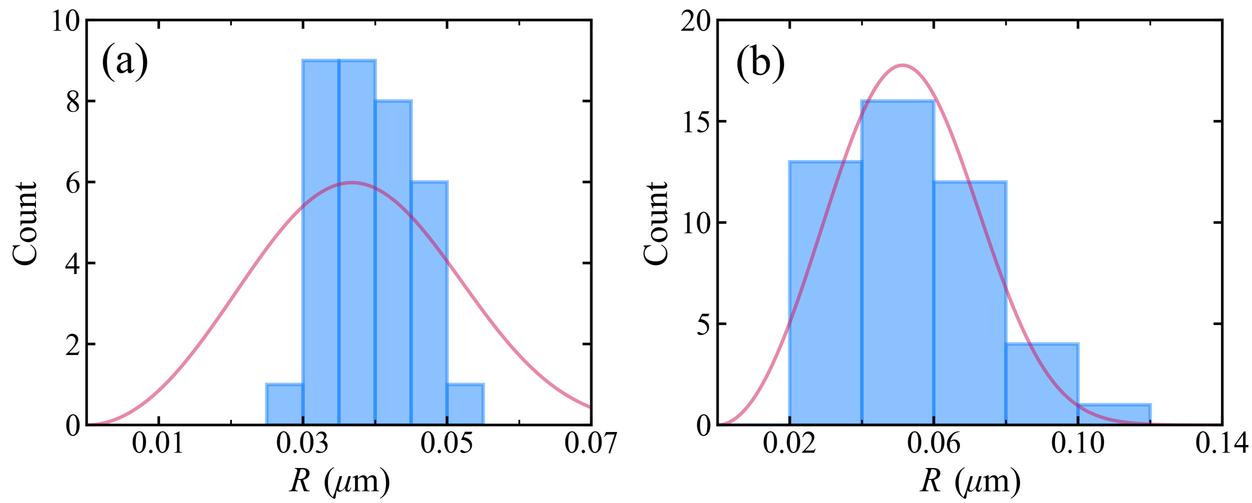

Figure 6: Histograms of (6×6) terrace radius upon (a) $c(8 \times 2)$ nucleation ($T = 628\,^{\circ}$C), and (b) Lochkeim nucleation ($T = 592\,^{\circ}$C), together with their fit to the distribution of Eq. (5).

IV. LEEM movie

Movie S1: LEEM movie taken under bright-field conditions revealing the fundamental mechanism of surface phase metastability. The movie corresponds to the image sequence displayed in Fig. 1 of the main text. The incident beam energy is 8.6 eV and the sample temperature 598 °C.

V. MC simulation movie

Movie S2: MC simulation movie of a $10 \times 10\,\mu$m region of GaAs(001) revealing the (6×6) coverage and evolving surface morphology at three different temperatures, $T = 581, 598,$ and $639\,^{\circ}$C. Dark areas correspond to $(6{\times}6)$ terraces. The simulation input parameters correspond to the kinetic rates shown in Fig. 4 of the main text, at the appropriate temperatures. The kinetic processes included in the simulations are described in the main text. Note, at lower temperatures the movies give the visual impression that (6×6) repetitively nucleates at the same location. However, this is a result of preferential nucleation of Lockheime on pre-existing (6×6) which creates inverted wedding cake structures. The sudden conversion of the outer (6×6) domains to $c(8 \times 2)$ combined with the growth of the inner (6×6) domains then mimics local nucleation (see main text).