

Morphological Symmetry Breaking during Epitaxial Growth at Grazing Incidence

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(Received 18 November 1999)

It is shown that, in submonolayer growth at off-normal incidence, even much less than 1% of transfer from the condensation energy of the deposited atoms into adatom motion is sufficient to induce a net adatom current from the illuminated edge of a two-dimensional island to the other edges, thereby breaking the island symmetry. Such a symmetry breaking phenomenon is most pronounced for deposition at grazing incidence. Comparison between our theoretical predictions and existing experimental results confirms the general validity of the model.

PACS numbers: 68.55.Jk, 68.35.Bs, 68.70.+w

Because of their application potentials in future electronic devices, a great deal of effort is being devoted to developing novel methods for fabrication of organized low-dimensional structures, such as ordered arrays of quantum wires or quantum dots [1]. Epitaxial growth and its inverse process, atom removal by sputtering or etching, are two of the most promising approaches for mass production of controlled nanostructures on various substrates. Typically, ordered structures are obtained in heteroepitaxial systems, and the long-range elastic field associated with the lattice mismatch between the two systems plays an essential role in leading to self-organized growth [2]. However, in recent studies of Cu(100) homoepitaxy, an intriguing phenomenon about island formation and ordering has been discovered, i.e., the average island symmetry varies with the incident angle of deposition, leading to the formation of elongated islands, or ripples, of twofold symmetry [3]. In contrast, earlier studies of Cu(100) homoepitaxial growth at normal incidence resulted in only square-shaped islands of fourfold symmetry [4,5]. Such a symmetry breaking phenomenon is already present even in the submonolayer growth regime and is more dramatic at grazing incidence [3]. For atom removal by sputtering under ion bombardment at off-normal incidence, formation of coherent ripples has also been observed on different substrates [6–8].

In earlier attempts to understand these symmetry breaking phenomena, some qualitative suggestions have been proposed, all of which rely on atoms climbing down from steps as an essential atomic process [3,8]. In this Letter, through a detailed study of a simple model, we offer an alternative and quantitative interpretation of the widely observed incidence geometry induced symmetry breaking. Our model is based on an experimentally widely invoked concept, namely, transient mobility of deposited atoms on various surfaces [9–11]. Through studying shape evolution of monolayer-high islands on an fcc (100) surface, we demonstrate that even much less than 1% of transfer of the condensation energy from the deposited atoms into

adatom motion is sufficient to induce a net adatom current transferring adatoms from the illuminated island edge to neighboring edges. As a consequence, the symmetry of the growing islands changes from an initially square shape to a rectangular shape elongated perpendicularly to the incident direction. Such a symmetry breaking phenomenon is most pronounced for deposition at grazing incidence. A comparison between theory and experiment confirms the general validity of the model. We also make several specific predictions that can be tested in future experiments.

We use Fig. 1 to schematically show the growth process of a monolayer-high island on an fcc (100) surface during deposition at off-normal incidence. We denote the island width and length by $W = m_x a$ and $L = m_y a$, respectively, where a is the surface lattice constant. We name the four island edges as x^+ , x^- , y^+ , and y^- edges. Atoms are deposited onto the surface at an angle α with respect to the surface normal, with a deposition flux F . We consider the three most important kinetic processes for adatom motion, i.e., the surface diffusion, the island edge diffusion, and the island corner crossing, with rates $q_i = \nu_i \exp(-V_i/kT)$, where V_i and ν_i ($i = s, e, c$) are the corresponding barriers and attempt frequencies. In

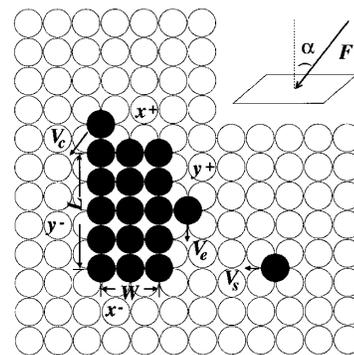


FIG. 1. Schematic illustration of island growth on an fcc (100) surface at off-normal incidence (see text for notations).

general, one has $V_c = V_e + \Delta V$, with $\Delta V > 0$ because an adatom has to lower its coordination in crossing an island corner [12,13].

In the case of deposition at off-normal incidence, the effective flux for depositing atoms on the surface is $F \cos \alpha$. The adatoms diffuse on the surface and attach to an existing island with a flux $f_s = \frac{F \cos \alpha}{N}$, where N is the island density. Following classical nucleation theory [14], we have

$$f_s = \left(\frac{\nu_s a^2 F^2 \cos^2 \alpha}{3\theta} \right)^{1/3} \exp\left(-\frac{V_s}{3kT}\right), \quad (1)$$

where θ is the coverage. Because of the isotropic nature of adatom diffusion on an fcc (100) surface, the fluxes for adatom attachment at the x (x^+ or x^-) and y (y^+ or y^-) island edges are given by $f_x = \frac{m_x}{2(m_x + m_y)} f_s$ and $f_y = \frac{m_y}{2(m_x + m_y)} f_s$, respectively. A remarkable feature for the off-normal deposition is that it directly deposits atoms on the island edge facing the incident beam (the illuminated edge), with a flux $f_d = F m_y a^2 \sin \alpha$, valid in the low coverage limit.

It is easy to conjecture on the island shape evolution without considering the contribution of the condensation energy. Because of the existence of the direct landing flux f_d , the illuminated edge (the y^+ edge in Fig. 1) has more arriving atoms than the other three edges. In the low temperature regime where island-corner crossing is not frequent enough to establish equilibrium adatom distribution along the four edges, the islands would elongate parallel to the incident direction. In contrast, at higher temperatures, frequent edge diffusion and corner crossing can take place, leading to adatom transfer from one edge to the other edges. This yields a uniform adatom distribution on the four island edges. Therefore, without the contribution of condensation energy, one would find only compact islands of either square shape or rectangular shape elongated parallel to the incident direction.

Now let us consider the effect of the condensation energy transfer to adatom diffusion. As stated above, the illuminated island edge has more landing atoms than the other three edges. The existence of the transient mobility [9–11] implies that those adatoms directly deposited at the illuminated edge will have higher mobility to cross the two island corners bounding this edge. Such anisotropic island corner crossing induces a net current transferring adatoms from the illuminated edge to its neighboring edges and may therefore change the symmetry of the initially square-shaped islands. As a result, the islands can elongate along the direction perpendicular to the incident direction, which is just the opposite to the expectation given above without consideration of condensation energy transfer.

To quantify the above picture, next we derive a set of equations describing the island evolution in the presence of condensation energy transfer. In a unit time, the total condensation energy given up by the atoms directly deposited at the illuminated edge amounts to $f_d U_0$, where U_0 is the condensation energy for each atom. During the

same time, the number of atoms landing on the illuminated edge is $f_d + f_y$. Because only a portion of the condensation energy is transferred into diffusional motion, we write the average energy gain of an adatom on the illuminated edge as $\Delta E = \beta f_d U_0 / (f_d + f_y)$. Here β is a parameter describing the transfer efficiency from the condensation energy of the incident atom to its diffusional motion, with $\beta = 1$ corresponding to complete transfer and $\beta = 0$ to zero transfer. It should be noted that, besides its being finite based on the experimental evidences for transient mobility [9–11], very little is known about this parameter β . Nevertheless, it is known to possess the following qualitative features, based on simple physical considerations. First, β is weakly temperature dependent for a given system, because the condensation energy is much larger than the thermal energy at typical growth temperatures. Second, β is also weakly dependent on the incident angle, because the primary angular dependence of the problem has already been incorporated into the flux expression f_d . Third, β is expected to be strongly system dependent, larger for a larger mass mismatch between the incident atom and the substrate atom. This last point is transparent within the simple picture of elastic collision between the incident atom and a surface atom and is still qualitatively correct even if the frictional forces due to vibrational and/or electronic damping are included.

With the above considerations, here we can treat β as a fitting parameter and approximate the higher rate of an adatom on the illuminated island edge by $q_h = \nu_c \exp(-\frac{V_c}{kT + \Delta E})$ when crossing an island corner to a neighboring edge. The average frequency for an adatom on an island edge of length m to cross the island corner with rate q_c can be well approximated [15] by $\frac{1}{m} q_c$ when $V_c > V_e$. Assume that the numbers of adatoms on the x^+ , x^- , y^+ , and y^- edges at time t are n_x^+ , n_x^- , n_y^+ , and n_y^- , respectively. Because of the higher island corner crossing rate for adatoms on the illuminated island edge, there must exist a net adatom current j_1 , which transfers adatoms from the y^+ edge to its neighboring x^+ or x^- edge. As a consequence, one has $n_x^+ > n_y^-$ and $n_x^- > n_y^+$, which further induce another net adatom current j_2 , carrying adatoms from the x^+ and x^- edges to the y^- edge. All together, the growth of the island is described by

$$\begin{aligned} \frac{dn_y^+}{dt} &= f_y + f_d - 2j_1, \\ \frac{dn_y^-}{dt} &= f_y + 2j_2, \\ \frac{dn_x^+}{dt} &= \frac{dn_x^-}{dt} = f_x + j_1 - j_2, \end{aligned} \quad (2)$$

where

$$j_1 = \frac{n_y^+}{m_y} q_h - \frac{n_x^+}{m_x} q_c, \quad j_2 = \left(\frac{n_x^+}{m_x} - \frac{n_y^-}{m_y} \right) q_c. \quad (3)$$

Variations of the island width $\Delta m_x a$ and island length $\Delta m_y a$ are given by $\Delta m_x = \frac{n_y^+ + n_y^-}{m_y}$ and $\Delta m_y = \frac{n_x^+ + n_x^-}{m_x}$. The ratio $r \equiv \frac{\Delta L}{\Delta W} = \Delta m_y / \Delta m_x$ predicts the evolution of the island shape. A square-shaped island will remain a square if $r = 1$ (stable growth) and will elongate perpendicularly to the incident direction if $r > 1$ or parallel to the incident direction if $r < 1$ (unstable growth).

Because ΔE reaches its maximum when α approaches 90° , the effect of the condensation energy is most pronounced in the case of grazing incidence. In the following, we first focus our attention on the growth at grazing incidence. Typical behaviors of r versus T for different β are shown in Fig. 2, where the growth parameters are $F = 0.1 \text{ ML s}^{-1}$, $\nu_s = \nu_c = 10^{12} \text{ s}^{-1}$, $V_s = 0.35 \text{ eV}$, $V_e = 0.1 \text{ eV}$, $\Delta V = 0.3 \text{ eV}$, $U_0 = 5 \text{ eV}$, and $t = 0.1 \text{ s}$. Figure 2(a) is for an initial square island of size $m_x^0 = m_y^0 = 2$. Figure 2(b) is for an intermediate rectangular island with $m_x^0 = 2$ and $m_y^0 = 8$. As expected, without contribution of the condensation energy, i.e., $\beta = 0$, the ratio r remains a constant $r = 1$ when $T \gg T_c$ and $r < 1$ when $T < T_c$, where $T_c \approx 190 \text{ K}$ is the freezing temperature for island-corner crossing defined by $tq_c(T_c) \sim 1$. For a nonzero β , we find three different r - T behaviors upon changing the energy transfer coefficient β . In the case of a very small β , e.g., $\beta = 10^{-4}$ in Fig. 2, r increases with decreasing temperature until it reaches T_c . Further decreasing T rapidly turns r to zero. A notable feature of r in the temperature regime $T > T_c$ is $1 < r < 2$. For larger β , e.g., $\beta = 6 \times 10^{-4}$ in Fig. 2, when T approaches T_c , r increases from $r = 1$ at high temperatures to a ratio $r = 2$. After that, a highly anisotropic growth with $r > 2$ appears until the temperature reaches another critical value $T_a \approx 170 \text{ K}$. When T goes down further, r drops to zero. We identify T_a to be the freezing temperature for condensation energy assisted island-corner defined by $tq_h(T_a) \sim 1$. In the case of a much larger coefficient β , e.g., $\beta = 0.05$, a steady growth regime characterized by $r \equiv 2$ exists at moderate temperatures, and the strongly anisotropic growth mode $r > 2$ remains in the whole temperature range of $T < T_c$. We note that the steady growth regime exists for all $\beta > 0.05$. Figure 2 also shows that the value of r is larger for a larger value of m_y^0/m_x^0 (except for the steady state regime where $r \equiv 2$), indicating that the elongation instability is more pronounced for already developed rectangular islands.

The observed different behaviors of r for different β can be rationalized based on the competition of the three rate processes: surface diffusion, thermally activated island-corner crossing (without the assistance of the condensation energy), and condensation energy assisted island-corner crossing. In the temperature regime $T > T_c$, frequent corner crossing with $q_c \gg 1$ and $q_h > q_c$ induces a net current j_1 transferring adatoms from the illuminated edge to its neighboring edges. On the other

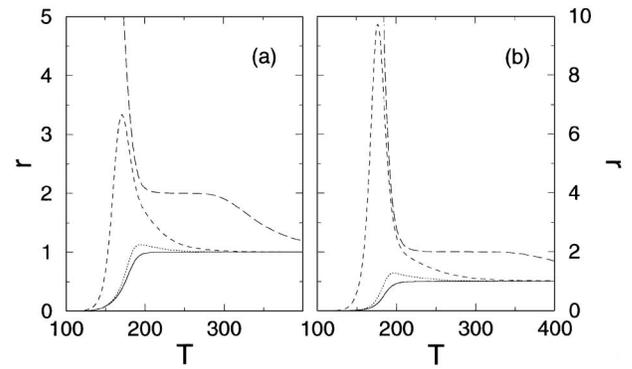


FIG. 2. Temperature dependence of island growth on an fcc (100) surface with different contributions of condensation energy. The initial island size is $m_x^0 = m_y^0 = 2$ in (a) and $m_x^0 = 2$, $m_y^0 = 8$ in (b). Atoms are deposited at a grazing angle of $\alpha = 85^\circ$. Solid, dotted, dashed, and long dashed lines correspond to $\beta = 0, 0.0001, 0.0006$, and 0.05 , respectively. Curves for $\beta = 0.05$ are truncated for $r \geq 5$ in (a) and $r \geq 10$ in (b).

hand, $q_c \gg 1$ also results in a uniform adatom distribution on the x^+ , x^- , and y^- edges, with $j_2 = 0$. From Eqs. (2) and (3), we have $r = 2/[1 + (1 + 2m/n)\xi]$, where $\xi = (f_y + f_d - 2j_1)/(2f_x + f_y + j_1)$. Because typically $V_s \leq V_c$, surface diffusion is activated when $q_c \gg 1$, leading to $f_s \gg f_d$. Moreover, for a small β , the net current is small with $j_1 < (f_d + f_s)/2$. Therefore, we have $1 < r < 2$ for $T > T_c$, as shown in Fig. 2 for $\beta = 10^{-4}$. By increasing β , j_1 reaches the maximum current $j_1 = (f_s + f_d)/2$ upon decreasing T toward T_c . In this case, we find $r = 2$, as shown in Fig. 2 for $\beta = 6 \times 10^{-4}$ and $\beta = 0.05$. In the temperature regime $T < T_c$ for small β , corner crossing and surface diffusion are frozen with $q_c \ll 1$, $q_h \ll 1$, and $q_s \ll 1$. The landing atoms from the direct flux f_d accumulate on the illuminated edge, leading to $0 \approx r < 1$. For $T_a < T < T_c$, we have $q_c \ll 1$ and $q_s \ll 1$ but $q_h \gg 1$. Such a regime of strongly anisotropic island-corner crossing leads to $j_1 = (j_s + j_d)/2$, which in turn results in strongly anisotropic growth with $r > 2$, as shown in Fig. 2 for $\beta = 6 \times 10^{-4}$. Finally, for even larger β , we have $q_h \gg 1$ for any temperature below T_c , leading to $r > 2$ for $T < T_c$ (see Fig. 2 for $\beta = 0.05$). The above discussions are valid as long as the islands are compact [15].

Finally, through studying Cu/Cu(001) growth, we examine how the aspect ratio r depends on the incident angle. Figure 3 is obtained for various temperatures with the same flux $F = 0.0042 \text{ ML s}^{-1}$ as used in the experiments [3]. The barriers are $V_s = 0.505 \text{ eV}$, $V_e = 0.265 \text{ eV}$, and $\Delta V = 0.29 \text{ eV}$, as suggested by experiments [4] and embedded-atom model calculations [15]. The condensation energy [9] is taken as $U_0 = 3 \text{ eV}$ and a reasonably small energy transfer coefficient $\beta = 8 \times 10^{-5}$ is used. Figure 3 indicates that, at room temperature, the elongation is not easily measurable for smaller α . A significant change of the island shape occurs at larger grazing angles ($\alpha > 80^\circ$). This explains why one

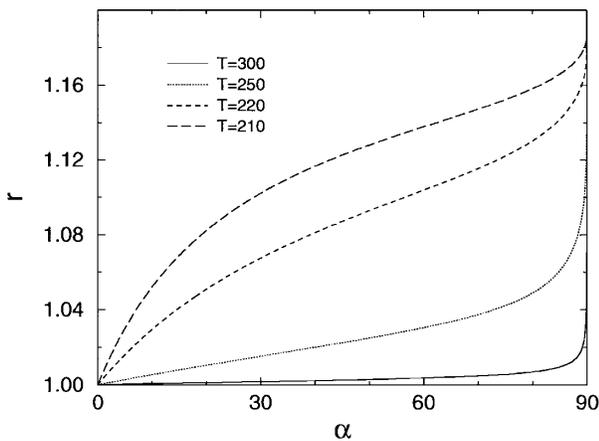


FIG. 3. Island growth on a Cu/Cu(001) surface at off-normal incidence and four different temperatures.

usually observes square-shaped islands during deposition at normal incidence or small-angle incidence [4,5] but elongated islands at grazing incidence [3]. Furthermore, after integration of Eq. (2) to a coverage $\theta = 0.5$, we found that the aspect ratio has a value $r \equiv \frac{L}{W} = 1.05$ for $T = 250$ K at $\alpha = 80^\circ$, as found in the experiments [3]. Moreover, Fig. 3 shows that r can be greatly enhanced by slightly decreasing the growth temperature, a prediction to be confirmed in future experiments. We also note that if β increases weakly with α , the crossover shown in Fig. 3 will be even sharper.

In summary, through studying monolayer-high island shape evolution on an fcc (100) surface, we have shown that the condensation energy of deposited adatoms can play an important role in controlling the island shape during epitaxial growth. In the case of deposition at off-normal incidence, the component of the deposition flux parallel to the surface provides additional atoms on the illuminated island edge and thus more condensation energy. This leads to an enhancement of the mobility of the adatoms on the illuminated edge and results in island elongation perpendicular to the incident direction. Such an island symmetry breaking phenomenon is most pronounced at grazing incidence. A comparison between the theoretical predictions and the experimental findings in Cu/Cu(001) growth confirms the general validity of the model. We have also found strong temperature dependence of the aspect ratio and the existence of a well-defined incident angle above which the

elongation instability is most pronounced. These latter predictions are to be verified in future experiments.

We thank Dr. W. F. Egelhoff, Jr. for a careful reading of the manuscript and for his helpful comments and suggestions. This research was supported by the U.S. National Science Foundation under Grant No. DMR-9702938, by Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. for the Department of Energy under Contract No. DE-AC05-96OR22464, and by the Natural Science Foundation of China under Grants No. 19810760328 and No. 19928409.

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