Growth and Coalescence in Submonolayer Homoepitaxy on Cu(100) Studied with High-Resolution Low-Energy Electron Diffraction

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By measuring the dependence of the island separation L on the flux F during submonolayer epitaxy on Cu(100), the scaling exponent p in $L \sim F^{-p/2}$ is determined in the steady-state and island coalescence regimes. In both regimes at low temperature (223 K), a crossover of p is observed from a low-flux value of $\frac{1}{3}$ to a high-flux value of $\frac{1}{2}$. At elevated temperatures (263-305 K), $p \sim \frac{3}{5}$ is obtained. These results agree with classic nucleation theories and recent Monte Carlo simulations, and imply that the smallest stable island changes directly to a tetramer from a low-temperature dimer with increasing temperature. Dissociation energy calculations using the embedded-atom method support these results.

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Nucleation, growth, and coalescence of islands are three fundamental physical processes involved in thin film growth. Although many phenomena in these processes have been studied [1-4], the central result obtained is a simple scaling relationship among the stable island density N, deposition flux F, and surface diffusion constant D of the form

$$N \sim (D/F)^{-p}. \tag{1}$$

In this equation, the exponent p depends on the island dimensionality, the number of atoms i in a critical nucleus, competition between adatom diffusion and flux, mobility of islands, and the completeness of condensation. Therefore, the determination of p allows us to gain insight into the physics involved in these growth processes. Equation (1) and the exponent p can be derived from rate equations with the approximate form [4-6]

$$\frac{d\rho}{dt} = F - D\rho N, \tag{2a}$$

$$\frac{dN}{dt} = D\rho\rho_i. \tag{2b}$$

As implied by these equations, the adatom density ρ first increases due to the incident flux of atoms during the initial stage of homoepitaxial deposition. Upon supersaturation of the deposited atoms, small critical nuclei of density ρ_i and size i are formed, which grow by capturing diffusing adatoms to become stable islands with the island creation rate ($\sim D\rho\rho_i$). When an appreciable number of islands exist on the surface, adatom attachment to these islands becomes the dominant adatom loss term ($\sim D\rho N$) limiting the adatom density [4]. If the island density N increases to roughly equal ρ, the scaling relationship of Eq. (1) may then be characterized by an exponent of the form [2,5,6]

$$p = (i+1)/(i+3). \tag{3a}$$

Equation (3a) is usually valid only for the early stages of growth, i.e., for very low coverages. A crossover to the steady-state regime occurs when the adatom density saturates. Continuing deposition of atoms balances the loss of adatoms absorbed by existing islands without significant further nucleation; i.e., N saturates also. In this regime, N is usually larger than ρ [2,6]. The exponent is then predicted to be [1-4,6]

$$p = i/(i+2). \tag{3b}$$

A third regime, which is not included in Eqs. (2), occurs at higher coverage when islands start to contact each other, which results in island coalescence, and ultimately a reduction of N to zero as the first monolayer fills in. Equations (3a) and (3b) are derived for two-dimensional growth under the assumption of complete condensation (no desorption from the surface) and immobile islands. Because of variation of the dissociation energy of islands with their size, the smallest stable island size $(i+1)$ can change with sample temperature. This change will be reflected in the scaling exponent p.

Theoretical modeling of the growth processes with Monte Carlo simulations has suggested that the steady-state island growth starts at a coverage between 0.01 and 0.1 ML (monolayer) depending on the deposition flux [7] and that the growth for the minimal model of $i = 1$ in the steady-state regime can be described by an exponent $p \sim \frac{1}{3}$ [6-10], in agreement with Eq. (3b). Using He-atom scattering, Ernst, Fabre, and Lapujoulade recently reported an exponent of $p \sim \frac{1}{2}$ obtained in the steady-state regime for Cu/Cu(100) at $\sim$220 K [11]. Their result disagrees with the simulation results and is interpreted in terms of Eq. (3a) with $i = 1$, suggesting that the nucleation saturates at $N \sim \rho$. For that case, the saturated island density will extend throughout the steady-state regime so that Eq. (3a) should apply rather than Eq. (3b). However, a similar experiment for Pb/Cu(100) at 150 K gives a smaller exponent of $p \sim \frac{1}{4}$ [12]. These inconsistencies motivated the present investigation.

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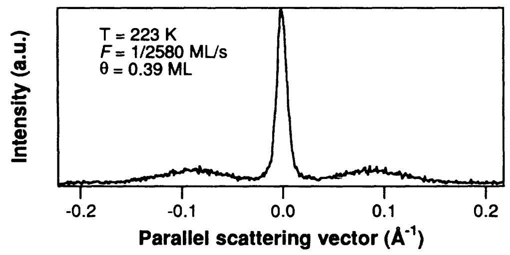

FIG. 1. A typical angular profile cut across the diffraction ring along the [110] direction through the (00) peak in an out-of-phase condition with an electron energy of 141.6 eV.

In this Letter, we present new experimental results for both the steady-state and island coalescence regimes from the same system, Cu/Cu(100), that of Ernst, Fabre, and Lapujoulade [11]. Using time-resolved high-resolution low-energy electron diffraction (HRLEED) with a transfer width of ~1000 Å, we have studied the scaling relationship of Eq. (1) as a function of deposition flux for sample temperatures ranging from 223 to 305 K. In both growth regimes, we found that Eq. (3b) can describe the growth processes at low flux. The smallest stable island is the dimer ($i=1$) at low temperature, while at an elevated temperature the smallest stable island changes directly to a tetramer ($i=3$). This observation is further supported by our dissociation energy calculations using the embedded-atom method (EAM) [13]. At low temperature and high flux, we found an exponent compatible with Eq. (3a) with $i=1$. The physical rationales for these new observations will be discussed and compared with existing theories and simulations.

Experiments were performed in an ultrahigh vacuum chamber (base pressure $\sim 5\times 10^{-11}$ Torr) equipped with instruments for HRLEED, Auger electron spectroscopy (AES), an ion sputter gun, and Cu evaporator. The Cu(100) surface was cleaned by Ne sputtering and subsequently annealed at ~750 K for a few minutes. After that, we deposited a few Cu buffer layers followed by annealing to ~750 K in order to eliminate residual defects created during sputtering. After cleaning and Cu deposition, no impurities were detected in AES. The average terrace width on the Cu(100) surface was estimated to be ~700 Å by HRLEED. Copper was evaporated from a 99.9999% pure Cu disk heated by electron bombardment from the backside of the disk. The sample could be heated by electron bombardment and cooled with liquid nitrogen to 150 K. The temperature was measured by a chromel-constantan thermocouple with an accuracy better than ±2 K.

Angular profiles centered on the (00) beam were scanned during interruptions of the deposition, similar to the procedure in the scanning tunneling microscopy study by Mo *et al.* [8]. In the study by Ernst, Fabre, and Lapujoulade [11], the diffraction profiles were obtained during deposition. Each HRLEED profile took about 2 min to measure during which time no change in profile shape was detected. The coverage was calibrated using the intensity oscillation of the specular beam with the first minimum corresponding to $\theta=0.5$ ML [14]. Above a coverage of $\theta\sim 0.2$ ML, a first-order diffraction ring becomes obvious around the (00) beam in an out-of-phase diffraction condition at 141.6 eV, which is visible in Fig. 1 as two side peaks in a typical angular profile scanned along the [110] direction. The diameter S of this ring structure defines a characteristic length associated with the island separation, $L\sim 4\pi/S$, which is plotted versus θ in Fig. 2 for various values of F at $T=223$ K. The ring is round due to a uniform distribution of island separations in all directions [15]. The positions of the (00) peak and the side peaks were determined by a least-squares fit with three power Lorentzians. As can be seen, for a given flux, L initially remains constant up to a critical coverage θ_c. After that, it starts to increase. Constant L below θ_c indicates that the diffraction ring reflects a narrow distribution of island separations peaked at the mean value of L. This is consistent with the steady-state regime in which L, and hence N ($\sim 1/L^2$) is invariant, while the island sizes grow with coverage [16]. From Fig. 2, we can also extract additional features: (1) Above θ_c, the increase in L reflects the occurrence of the coalescence among islands; (2) within experimental accuracy, θ_c is constant between 0.45 and 0.50 ML except for an apparent shift to lower coverages at high flux.

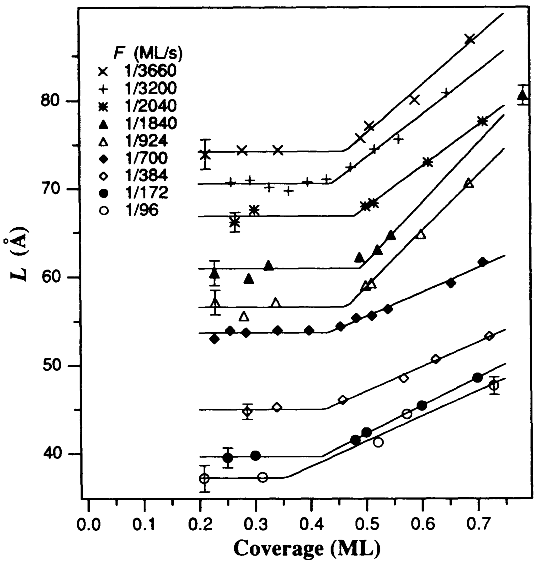

FIG. 2. Island separation vs coverage for various fluxes at a fixed $T=223$ K, where solid lines are fits of two connected line segments to the data.

The island separation is a characteristic length which is related to the stable island density via $L\sim 1/\sqrt{N}$. Therefore, the following relationship can be established using Eq. (1):

$$L=4\pi/S\sim 1/N^{1/2}\sim (D/F)^{p/2}. \tag{4}$$

By measuring the dependence of S on F, we are able to extract the scaling exponent p, and gain insight into the growth behavior. The results for two growth temperatures are shown in Fig. 3, where L is plotted vs $1/F$ on a log-log scale and the slope gives $p/2$ according to Eq. (4). The open and solid circles represent data measured in the steady-state regime (0.3 ML) and the island coalescence regime (0.63 and 0.7 ML), respectively.

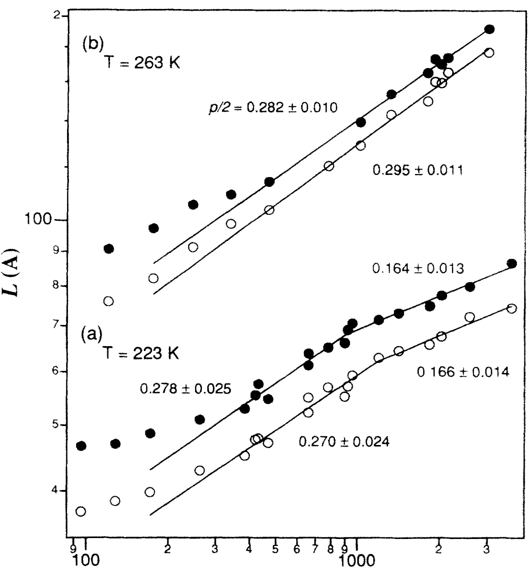

FIG. 3. The log-log plots of island separation vs inverse flux, where the slope gives $p/2$ with the value marked in each data regime: (a) $T=223$ K and (b) $T=263$ K. Open circles correspond to $\theta=0.3$ ML. Solid circles correspond to $\theta=0.63$ and 0.70 ML, for temperatures of 263 K and 223 K, respectively.

Figure 3(a) shows the data at 223 K. In order to obtain a satisfactory fit, we have to use a two segment linear fit in the regime of $1/F > 350$ s/ML. The deviation of the data for $1/F < 350$ s/ML will be discussed later. In the steady-state regime (0.3 ML), the exponent obtained from the slope is $p \sim \frac{1}{3}$ for $1/F > 900$ s/ML, which corresponds to Eq. (3b) with $i=1$. This indicates that the smallest stable island is the dimer which is immobile and the island growth at low flux is governed by the irreversible capture of hopping adatoms via long-range diffusion. Interestingly, for $1/F < 900$ s/ML, the exponent crosses over to $p \sim \frac{1}{2}$ within experimental uncertainty. Recently, a crossover of p from $\frac{1}{3}$ to $\frac{1}{2}$ has also been found in Monte Carlo simulations by Ghaisas and Das Sarma [9], who argued that $p \sim \frac{1}{2}$ at high flux is a result of island growth via either island coalescence or direct absorption of atoms from the vapor [9]. In the steady-state regime considered here, the crossover due to coalescence can be excluded. Therefore, one possibility responsible for our observation might be due to the direct absorption from vapor or via short-range diffusion of atoms which land very close to existing islands. This can be explained as follows: With increasing F, the island density will increase with a corresponding decrease in the island size and separation, thus increasing the total number of sites along the perimeters of the islands. This will enhance the probability of incident atoms directly absorbed at or near the edges of existing islands. Therefore, the dependence of nucleation rate on diffusion length L will be weakened, leading to the crossover of p to $\frac{1}{2}$. In the work of Ernst, Fabre, and Lapujoulade [11], a value of $p \sim \frac{1}{2}$ was obtained at $\theta \sim 0.5$ ML, but no crossover was observed. Based on Eq. (3a) with $i=1$, they argued that the exponent is a result of nucleation saturated at $N \sim \rho$. In their data at $T=220$ K, there are only four data points in the range from $1/F \sim 250$ to 1500 s/ML which is associated primarily with the $p \sim \frac{1}{2}$ range observed here. Furthermore, their data at $T=230$ K might not correspond to the minimal model of $i=1$, since it has been found [15] that the dimer dissociation has already begun at 230 K. It has also been suggested that $p \sim \frac{1}{2}$ may be explained using Eq. (3b) with $i=2$; i.e., the smallest stable island is a trimer [4,10]. However, variation of i with flux for a given temperature is unlikely within the rate equation treatment [1-4] and a value of $i=2$ is inconsistent with the low flux value of $i=1$ obtained here. In Ref. [12], a smaller value of $p \sim \frac{1}{4}$ was obtained for Pb/Cu(100) at 150 K. This is a more complicated system and one possible explanation for the smaller p might be an insufficient thermal activation at this low temperature according to the observations by Ernst, Fabre, and Lapujoulade [11] and us.

Surprisingly, the exponents obtained in the island coalescence regime (0.7 ML) are, within experimental uncertainty, identical to the values in the steady-state regime. Taking into account the island coalescence in the rate equation for N in Eq. (2), Stoyanov and Kashchiev have obtained a scaling exponent identical to Eq. (3b) for the early stage of coalescence [1], which agrees with our results, at least in the low flux regime. This implies that, in addition to capturing diffusing adatoms, islands grow via coalescence between islands.

With further increasing flux ($1/F < 350$ s/ML), the slope of the data in Fig. 3(a) is reduced. In this regime, the deposition rates are so high that the deposited atoms might not have enough time to complete the diffusion process during deposition, reducing the flux dependence of L as observed in computer simulations [6,8]. An additional effect could be the development of small second-layer islands atop the first-layer islands at high flux in competition with the first-layer island growth rate. This is implied by the fact that the deviation becomes more pronounced at 0.7 ML than at 0.3 ML.

Figure 3(b) shows the data obtained at a temperature of 263 K. Another data set taken at 305 K gives similar results, except for finite-size effects in the coalescence regime where island sizes become comparable to the terrace widths on the surface. For the island coalescence regime at 0.63 ML, $p \sim \frac{3}{5}$ is obtained within experimental uncertainty, which corresponds to Eq. (3b) with $i=3$ for early-stage coalescence [1,4]. This means that the smallest stable island at the higher temperatures is the tetramer instead of the dimer and that dimers could become unstable and dissociate with increasing temperature. An exponent of $p \sim \frac{3}{5}$ is also obtained for the steady-state regime at 0.3 ML. This value can be given from both Eqs. (3a) and (3b) for $i=2$ and $i=3$, respectively. However, a value of $i=2$ is inconsistent with the value $i=3$ obtained for the coalescence regime and should be excluded, since the critical nucleus size i cannot vary with coverage. In a recent Monte Carlo study, Ratsch *et al.* [17] also found a variation of the exponent p with the lateral bond strength which can be scaled with temperature, indicating that the smallest stable island size could vary with temperature. For $1/F$ below 470 s/ML, a deviation from $p \sim \frac{3}{5}$ takes place for similar reasons as discussed in the low-temperature case.

The data discussed above indicate that the critical nucleus size i will vary with sample temperature due to a variation of dissociation energy with island size. To confirm that, we have calculated the dissociation energies for removal of one atom from various-size clusters on Cu(100) using the embedded-atom method at 0 K, which give upper limits for the true dissociation energies due to the neglect of entropy effects at finite temperatures [18]. Details of the calculations will be presented elsewhere [13]. The dissociation energy, which reflects the relative stability of islands, is similar for the dimer (0.88 eV), trimer (0.96 eV), and pentamer (0.93 eV), but there is a big jump for the tetramer (1.42 eV) where each atom has two nearest neighbors in a square array. This explains why the observed value of the smallest stable island size changes from the dimer ($i=1$) at 223 K to the tetramer ($i=3$) at elevated temperatures without a distinct trimer stage ($i=2$). The fact that small islands with an odd number of atoms are less stable is due to the detailed binding structure and has also been seen in island density calculations on Cu/Cu(100) [7].

In summary, using HRLEED, the scaling relationship of Eq. (1) has been investigated in the steady-state and island coalescence regimes for submonolayer homoepitaxy on Cu(100). In both growth regimes, a crossover of the scaling exponent p is observed at low temperature (223 K) from $\frac{1}{3}$ at low flux to $\frac{1}{2}$ at high flux, consistent with recent simulation results. At elevated temperatures (263–305 K), $p \sim \frac{3}{5}$ is obtained in the flux range considered, indicating that the smallest stable island changes from a low-temperature dimer to a tetramer. This observation is further explained by our EAM calculations. Our results for p, at least in the low-flux regime, are consistent with Eq. (3b), which reflects island growth via long-range adatom diffusion.

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[1] S. Stoyanov and D. Kashchiev, in *Current Topic in Materials Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. 7, p. 69.

[2] J. A. Venables, G. D. T. Spiller, and M. Hanbucken, Rep. Prog. Phys. **47**, 399 (1984).

[3] J. Villain, A. Pimpinelli, and D. E. Wolf, Comments Condens. Matter Phys. **16**, 1 (1992).

[4] A. Zangwill, in *Evolution of Surface and Thin Film Microstructure*, edited by H. A. Atwater, E. Chason, M. Grabow, and M. Lagally, MRS Proceedings Vol. 280 (Materials Research Society, Pittsburgh, 1993).

[5] M. J. Stowell, Philos. Mag. **21**, 125 (1970); B. Lewis and D. S. Campbell, J. Vac. Sci. Technol. **4**, 209 (1967); T. Irisawa, Y. Arima, and T. Kuroda, J. Cryst. Growth **99**, 491 (1990).

[6] L. H. Tang, J. Phys. I (France) **3**, 935 (1993); J. G. Amar, F. Family, and P.-M. Lam, in "Mechanisms of Thin Film Evolution," Proceedings of the MRS, Boston, 1993, edited by S. M. Yalisove, C. V. Thompson, and D. J. Eaglesham (Materials Research Society, Pittsburgh, to be published), and references therein.

[7] G. T. Barkema, Ofer Biham, M. Breeman, D. O. Boerma, and G. Vidali, Surf. Sci. **306**, L569 (1994).

[8] Y. W. Mo, J. Kleiner, M. B. Webb, and M. Lagally, Phys. Rev. Lett. **66**, 1998 (1991); Surf. Sci. **268**, 275 (1992).

[9] S. V. Ghaisas and S. Das Sarma, Phys. Rev. B **46**, 7308 (1992).

[10] M. Bartelt and J. W. Evans, Phys. Rev. B **46**, 12675 (1992); M. Bartelt, M. C. Tringides, and J. W. Evans (to be published).

[11] H.-J. Ernst, F. Fabre, and J. Lapujoulade, Phys. Rev. B **46**, 1929 (1992).

[12] G. Vidali, Ofer Biham, H. Zeng, J.-S. Lin, and Wei Li, in *The Structure of Surfaces 4*, edited by S. Y. Tong and X. Xide (World Scientific, Singapore, 1994); (private communication).

[13] C.-L. Liu (to be published).

[14] J. M. Pimbely and T.-M. Lu, J. Appl. Phys. **58**, 2184 (1985).

[15] H. Dürr, J. F. Wendelken, and J.-K. Zuo (to be published).

[16] P. Hahn, J. Clabes, and M. Henzler, J. Appl. Phys. **51**, 2079 (1980).

[17] C. Ratsch, A. Zangwill, P. Smilauer, and D. D. Vvedensky (to be published).

[18] L. B. Hansen, P. Stolze, K. W. Jacobsen, and J. K. Nørskov, Surf. Sci. **289**, 68 (1993).