Available online at www.sciencedirect.com
ScienceDirect
Surface Science 602 (2008) 62–66
SURFACE SCIENCE
www.elsevier.com/locate/susc

Quantum modulation of island nucleation on top of a metal nanomesa

Y. Han [a,*], M. Hupalo [b], M.C. Tringides [b], Feng Liu [a]

[a] Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84112, United States
[b] Ames Lab-USDOE, Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, United States

Received 24 July 2007; accepted for publication 26 September 2007
Available online 1 October 2007

Abstract

We present a theoretical analysis of selectivity of nucleation location for the two-dimensional island on top of a metal nanomesa. It has been observed experimentally that the nucleation can start either along the periphery of the mesa top or in the middle, depending on the mesa height. Such an intriguing nucleation behavior is shown to originate from the thickness-dependent mesa edge barrier for an adatom to jump off the mesa, which we attributed to be induced by the quantum size effect. Based on the experimentally observed nucleation locations, we estimate that the mesa edge barriers for the 5- and 6-layer Pb(1 1 1) mesas can differ by $\sim 19 \pm 5$ meV.

Keywords: Quantum size effect; Metal nanomesas; Island nucleation location; Surface diffusion

The nucleation of two-dimensional (2D) and 3D islands is an important subject in the fundamental study of epitaxial growth [1–4], because island nucleation plays a key role in controlling the thin film morphology. In layer-by-layer growth (in contrast to step-flow) of a multilayer film, the nucleation rate of 2D islands on top of existing islands governs the transition from 2D to 3D growth [1,3]. In general, enhancing island nucleation will roughen the film, while suppressing the second-layer island nucleation will smoothen the film.

The study of island nucleation in epitaxial growth also has important technological implications. The stochastic nature of island nucleation poses a limitation on self-assembly of islands [5], as the islands generally nucleate at random positions lacking spatial ordering. Thus, controlling island nucleation has become an important strategy in directed self-assembly. For example, in the heteroepitaxial growth of strained thin films, surface strain field can be modulated, e.g. by growth of a multilayer film with buried islands [6,7], or by growth on a patterned substrate [8], to direct island nucleation at preferred locations, leading to greatly improved island spatial ordering and size uniformity.

A recent experiment [9] has shown an intriguing nucleation behavior of 2D Pb island on top of a Pb nanomesa of only a few monolayers (ML) thick grown on the Si(1 1 1) α-$(\sqrt{3} \times \sqrt{3})$ phase at 180 K. On unstable odd-layer (e.g. 5-layer) Pb mesas, the growth of next layer (6th layer) proceeds with nucleation-growth along the edge of the mesa top, while on the stable even-layer (e.g. 6-layer) Pb mesas, the growth of next layer (7th layer) starts with nucleation of 2D islands in the middle of the mesa top (see Fig. 1 in Ref. [9], where a wetting layer is included in counting layer numbers). This odd–even alternation of island location was suggested to originate from an odd–even oscillation in surface diffusion barrier along with a postulated difference in mesa edge barrier (MEB) [9]. Here, we show that the observed thickness-dependent nucleation-growth location predominately originates from an odd–even oscillation of MEB for an adatom to jump off the mesa, possibly induced by the quantum size effect (QSE). Although the oscillation in surface diffusion barrier affects

* Corresponding author. Present address: IPRT and Ames Laboratory, US Department of Energy, 307D Wilhelm Hall, Ames, IA 50011, United States.
E-mail addresses: octavian2009@gmail.com (Y. Han), fliu@eng.utah.edu (F. Liu).

0039-6028/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2007.09.044

the overall nucleation rate of 2D islands on top of the mesa, it does not influence the *location* of the nucleated islands. Based on the experimentally observed different island locations on different mesas, we estimate that the MEB at a 5- and 6-layer Pb(1 1 1) mesa edge can differ by $\sim 19 \pm 5$ meV.

Several previous theoretical analyses [1,3,10–12] have been aimed at such 2D island nucleation on top of an existing 2D island. Most of them have focused on the overall nucleation rate of the second-layer islands, which competes with atoms descending into the lower layer to promote the growth of the first-layer islands. The issue of nucleation location has also been addressed on top of a square-shaped 2D island by Castellano and Politi [12]. One key prediction on the overall nucleation rate [3] is the existence of a critical minimum size (R_c) of the first-layer island, above which the adatoms land on top of the first-layer island will nucleate the second-layer islands before jumping off. This was confirmed, for example, by the experimental growth of Ag/Ag(1 1 1) [13]. R_c depends critically on the Ehrlich–Schwoebel (ES) step-edge barrier [14,15]. Here, we will focus on the preferred location of 2D island nucleation on top of a metal mesa in a cylindrical geometry.

We apply the mean-field rate equation approach [1,3] to analyze the preferred nucleation location. This approach will generally overestimate the total nucleation rate [10,11], but should be quantitatively more reliable in predicting the relative nucleation rate at different locations, which is of our interest here. There are some subtle differences between the current case and the previous studies [1,3,10,11]. The Pb mesa of finite thickness remains essentially of fixed radius R, larger than R_c for the "next-layer" nucleation during deposition. Only adatoms landing directly on top of mesa are included, no adatom climbing to the top of the mesa from sidewalls. The experimental conditions for this to be the case are either for deposition at lower temperature (less than 190 K) or high flux rates (larger than 0.5 ML/min) or larger deposited amounts in the stepwise deposition experiments. Otherwise it is possible to initiate the transfer of Pb from the wetting layer to the island tops and the build up of the next stable layer by forming rings. So, at the mesa edge, an adatom will either be reflected at the edge or hop off to the wetting layer, which implies that the boundary condition at the mesa edge can be expressed as [3,16][1]

$$\left(\frac{dn}{d\rho}\right)_{\rho=R} + \frac{n(R)}{a_s} e^{-\Delta/kT} = 0, \tag{1}$$

where $n(\rho)$ is the adatom density at the radial coordinate ρ of mesa top, a_s is the surface lattice constant (for Pb, $a_s = 0.35$ nm), and Δ is the MEB, i.e. the extra barrier in addition to surface diffusion barrier (E_d) for an adatom to jump off the mesa edge, as shown in the inset of Fig. 1.

Using the above boundary condition and solving the adatom diffusion equation, it is straightforward to derive the steady-state adatom density [1,3] as

$$n(\rho) = n_0\left(1 - \frac{\rho^2}{R^2} + \frac{2a_s}{R} e^{\Delta/kT}\right), \tag{2}$$

where $n_0 = FR^2/4D$ represents approximately the maximum density at the center of mesa top ($\rho = 0$) for small MEB (Δ); F is the deposition flux and D is the surface diffusion coefficient. According to the mean-field nucleation theory [2], the island nucleation rate at ρ is

$$\xi = \gamma D a_s^{2i-2} n^{i+1}, \tag{3}$$

where i is the critical nucleation size, and γ is a parameter dependent of i; for $i = 1$, $\gamma \approx 1$. Thus, the probability distribution function of island nucleation is

$$P(\rho) = \gamma D a_s^{2i-2} n_0^{i+1}\left(1 - \frac{\rho^2}{R^2} + \frac{2a_s}{R} e^{\Delta/kT}\right)^{i+1} (2\pi\rho). \tag{4}$$

From Eq. (4), the maximum peak nucleation probability P_m is obtained at

$$\frac{\rho_m}{R} = \sqrt{\frac{1}{2i+3}\left(1 + \frac{2a_s}{R} e^{\Delta/kT}\right)}. \tag{5}$$

It is important to notice that the total nucleation rate on the mesa top, $\Omega = \int_0^R P(\rho)d\rho$ obtained from Eq. (4), depends on surface diffusion coefficient (D), MEB (Δ), and the parameter γ. But the preferred nucleation location, given by ρ_m in Eq. (5), is only a function of Δ, but not D. This indicates that the experimentally observed alternating island nucleation locations on top of the odd and even Pb

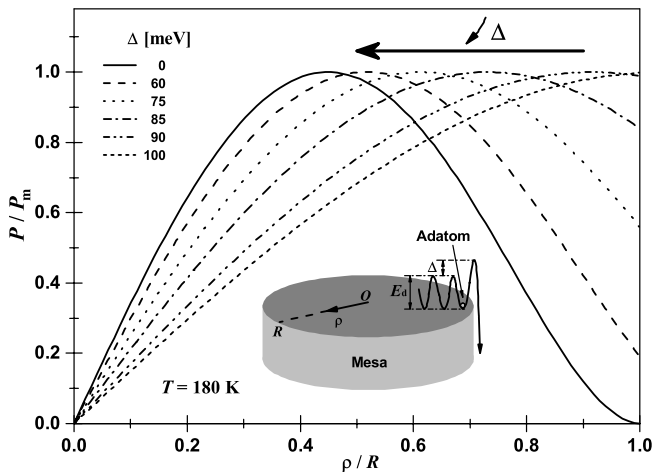

Fig. 1. Normalized probability distribution function P/P_m on a Pb mesa top with radius $R = 100$ nm for six different mesa edge barriers (MEB), for $i = 1$ and $T = 180$ K. The arrows indicate that with decreasing MEB (Δ), the peak nucleation probability moves towards the center of mesa top. The inset shows a schematic illustration of a mesa with the polar coordinate and the relationship between the surface diffusion barrier E_d and the MEB (Δ).

[1] This boundary condition is slightly different from that derived by Bales and Zangwill [16] at a step-edge bridging fluxes on two terraces. Nevertheless, the results are rather insensitive to this difference.

mesas is only an explicit function of the thickness-dependent MEB. Although the surface diffusion barrier has been shown in recent experiments to oscillate with mesa thickness [9,17], it does not enter Eq. (5) to directly influence the relative nucleation rate as a function of location.

Eq. (5) shows that if $\Delta \geqslant kT\ln[(i+1)R/a_s]$, the peak probability for island nucleation is always at the mesa edge ($\rho_m = R$). With decreasing Δ, the peak probability moves towards the center. At $\Delta = 0$, $\rho_m \approx R/\sqrt{2i+3}$, since $2a_s/R$ is small. For example, in Fig. 1, $P(\rho)$ is plotted for different values of Δ with $i = 1$, which shows the position of peak nucleation probability moving towards the middle of mesa top from the mesa edge with decreasing Δ. For $i > 1$, the behavior is qualitatively the same. In general, for a given Δ, the ρ_m moves towards the center of the mesa top with increasing i.

The dependence of island nucleation location on the MEB is related to the geometric feature on top of a cylindrical mesa. The adatom density is the highest but the weight of nucleation (local area) is the smallest at the center, as the latter is proportional to local radius. The combination of these two factors determines the radial dependence of the highest nucleation probability.

One interesting point is that in the case of small MEB, the peak probability never occurs at the center, and the smallest radius for peak probability is $\sim R/\sqrt{5}$ when $i = 1$. This is consistent with several experimental observations [3,9,11,13,18], which all showed that the nucleated 2D islands occur predominantly at the off-center positions on the mesa tops. Furthermore, it can be easily shown that in the presence of a small Δ when 2D nucleation starts in the middle of the mesa top, the subsequent nucleation of 2D islands will always remain in the middle. However, in the presence of a large Δ when the second-layer nucleation starts at the edge of the mesa top, the subsequent nucleation of 2D islands may occur as the second-layer in the middle as well as the third layer on top of the nucleated second layer along the edge, as observed in experiments [9,18].

The simple unique dependence of the preferred nucleation location ρ_m on Δ, as expressed in Eq. (5), allows us to determine the MEB, based on the experimentally observed island location without the complication from other factors, such as F, D, and γ. The previous experiment [9] was performed on Pb islands grown on Si(1 1 1)α-($\sqrt{3} \times \sqrt{3}$) with a larger amount added in the second-layer deposition of 1.3 ML (more than 1 ML). Consequently, it was difficult to locate the exact initial locations of island nucleation. Therefore, we have carried out new experiments with the second-layer deposition in the submonolayer regime to allow the measurement of the locations of initially nucleated islands, and from which we can further determine the MEBs as a function of mesa thickness.

The current experiments were performed on islands grown on Si(1 1 1)-(7 × 7). First a deposition of 1.5 ML at 240 K generated the initial Pb mesas of mostly 5- and 6-layer height. A second-layer deposition experiment similar to that in Bromann et al.'s [13] was performed first at 240 K followed by deposition at 180 K. Fig. 2 shows the typical experimental results. The second deposition at 240 K shows that no second-layer islands have nucleated on top of any mesas (see Fig. 2a), while the deposition at 180 K shows drastically different nucleation behavior of the second-layer islands on the mesas of different thickness (Fig. 2b). Specifically, five islands had nucleated on the 5-layer mesa, one island had nucleated on the two 6-layer mesa, and no island nucleated on the 8-layer island mesa. Also, at least three or four islands on the 5-layer mesa are at or very close to the edge, and the one island on the 6-layer mesa is in the middle. These morphologies are typical over larger areas and many terraces. Smaller islands are seen nucleated on the wetting layer between the mesas

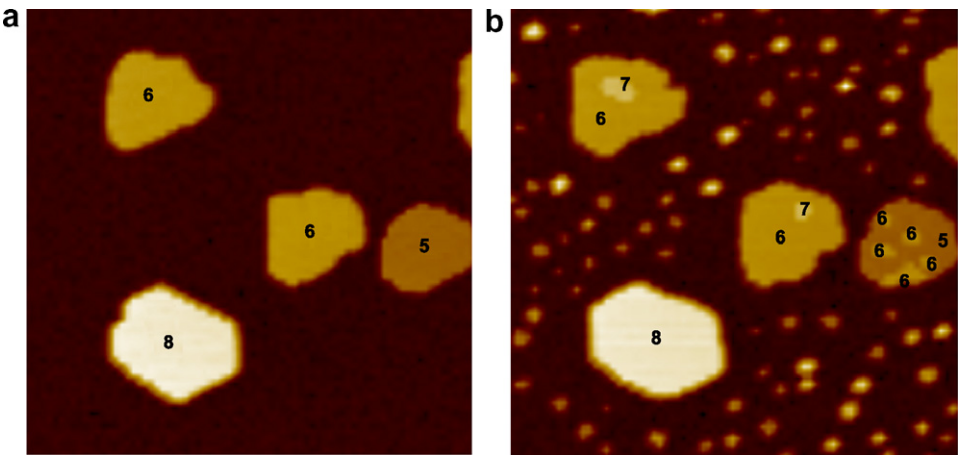

Fig. 2. (a) Pb islands prepared at 240 K on Si(111)-(7 × 7) surface, and then a second deposition of 0.1 ML/min at 240 K for 1 min. No nucleation is found on the islands. (b) The temperature is switched to 180 K, and the deposition time is still 1 min. The nucleation on the islands is observed. The STM image size is 300×300 nm^2. The heights of islands are marked numerically, including the wetting layer. STM images were taken at a tip bias of 1.5 V and tunnelling current of 1 nA.

indicating that the mobility of Pb on top of the wetting layer is smaller than the mobility on top of the mesas.

Based on our theoretical analysis, the results at 180 K have indicated that the MEB is higher on the 5-layer mesa than that on the 6-layer mesa because the islands preferentially nucleate closer to the edge on the 5-layer mesa than on the 6-layer mesa. This is also consistent with more islands on the 5-layer mesa than on the 6-layer mesa. For the same reason, the MEB is even smaller with 8-layer (the superstable height on the Si(111)-(7 × 7) substrate) mesa with no island even though its size is bigger (Fig. 2b). The absence of island nucleation at 240 K on all the mesas (Fig. 2a) suggests the MEB must be relatively small. We have estimated that the preferred nucleation locations on the 5- and 6-layer mesas are respectively having $\rho_{m,5}/R = 0.8$ and $\rho_{m,6}/R = 0.5$. Below, we will apply our theoretical model to analyze these experimental results, so as to quantitatively determine the MEB on each mesa.

In Fig. 3a, we plot the MEB Δ as a function of ρ_m/R, for $i = 1$–50, using the experimental values of $R = 33$ nm and $T = 180$ K. Now, taking the measured $\rho_m/R \approx 0.8$ on the 5-layer mesa, it gives rise to $\Delta_5 = 72$ meV for $i = 1$ and $\Delta_5 = 124$ meV for $i = 50$, as indicated by the dashed line at $\rho_m/R = 0.8$ in Fig. 3. Similar, taking the measured $\rho_m/R \approx 0.5$ on the 6-layer mesa,, it gives rise to $\Delta_6 = 38$ meV for $i = 1$ and $\Delta_6 = 110$ meV for $i = 50$, as indicated by the dashed line at $\rho_m/R = 0.5$ in Fig. 3. One sees that the absolute value of Δ depends sensitively on the value of i. If we use $i = 5 \pm 3$, as deduced from other experiments [19,20], we obtain the MEBs of 91 ± 8 meV, and 72 ± 17 meV for the 5- and 6-layer mesas, respectively.

Actually, we found that the difference of Δ on the two mesa tops is much less sensitive to i, which is ~34 meV for $i = 1$, and ~15 meV for $i = 50$. In general, the difference between Δ on a j-layer mesa and that on a k-layer mesa top can be calculated as

$$\Delta_k - \Delta_j = kT \ln \frac{(2i+3)\rho_{m,k}^2 - R^2}{(2i+3)\rho_{m,j}^2 - R^2}, \tag{6}$$

where $\rho_{m,j}$ and $\rho_{m,k}$ are the peak nucleation locations on the j- and k-layer mesa, respectively. From Eq. 6, we obtain the upper limit for the MEB difference on top of any two mesas is set by $i = 1$, as $\Delta_k - \Delta_j = kT \ln[(5\rho_{m,k}^2 - R^2)/(5\rho_{m,j}^2 - R^2)]$, and the lower limit is set by $i \to \infty$, as $2kT\ln(\rho_{m,k}/\rho_{m,j})$. Specifically, for experimentally observed $\rho_{m,5}/R = 0.8$ and $\rho_{m,6}/R = 0.5$ on mesas of $R = 33$ nm at $T = 180$ K, we plot in Fig. 4 the MEB difference, $\Delta_5 - \Delta_6$ as a function of i. For $i = 1$, $\Delta_5 - \Delta_6 = 34$ meV; it initially decreases rapidly with increasing i to ~19 meV at $i = 5$, and it then changes very little decreasing slowly to the asymptotic value of ~15 meV when $i \to \infty$. Since $i = 5 \pm 3$ is considered to be the most probable value of the critical size cluster [19,20], we deduce that the difference is 19 ± 5 meV.

The physical origin of different MEB on top of the 5-layer vs. 6-layer mesa is believed to be the QSE. In a seminal work [21], Schulte showed that in ultrathin metal films (thinner than the electron de Broglie wavelength) the QSE becomes prominent, with a unique manifestation of film properties oscillating as a function of film thickness with a "universal" period of $\lambda_F/2$, where λ_F is the Fermi wavelength. Because the film thickness can only vary discretely with an increment in unit of interlayer spacing (d), the actual oscillation pattern of film properties will depend on the matching (or mismatch) between $\lambda_F/2$ and d.

Coincidentally, for Pb(1 1 1) film, $2d \sim 3\lambda_F/2$, so that the properties of Pb(1 1 1) should exhibit an odd–even oscillations. This general behavior has indeed been confirmed by many experiments for the thermodynamic properties of Pb films [18,22–24]. More recently, experiments [17] and first-principles calculations [9] have also shown

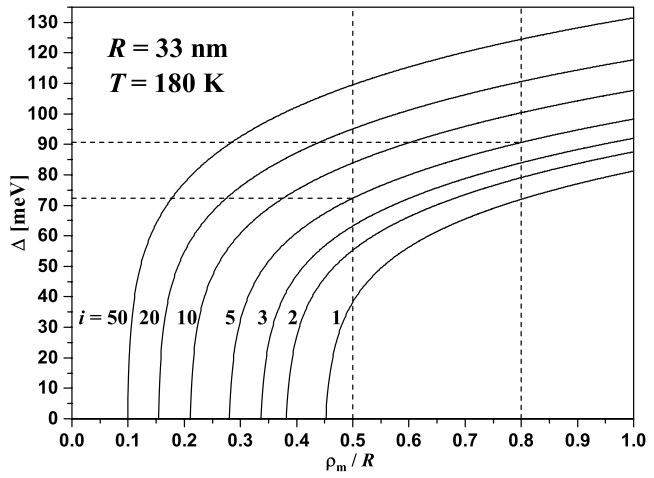

Fig. 3. The MEB Δ as a function of peak nucleation probability location ρ_m/R for different nucleation size i. In experiments, the preferred nucleation locations $\rho_{m,5}/R$ and $\rho_{m,6}/R$ for the 5- and 6-layer mesas are measured at 0.8 and 0.5, respectively, as indicated by two dashed vertical lines.

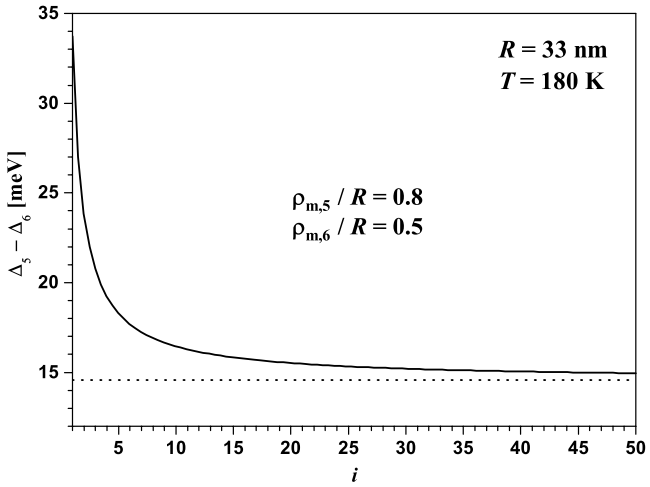

Fig. 4. The MEB difference $\Delta_5 - \Delta_6$ of the 5- and 6-layer mesas as a function of i. The dotted line indicates the asymptotic value at $i \to \infty$.

QSE-induced odd–even oscillations in surface diffusion barrier on surface of thin Pb(1 1 1) films due to QSE. Here, we further suggest the QSE-induced oscillation in MEB. Future first-principles calculations will be helpful to confirm this.

In conclusion, we have presented a theoretical analysis of selectivity of nucleation location for the two-dimensional island on top of metal nanomesas as a function of mesa thickness (stability). The nucleation can start either along the periphery of the mesa top or in the middle, depending on the mesa edge barrier (MEB). A large MEB (for unstable mesa heights) favors the nucleation along the periphery, and a small MEB (for stable mesa heights) favors the nucleation in the middle. The thickness dependent MEB is attributed to the QSE. Based on the experimentally observed varying nucleation locations on different mesas, we estimate that the MEB on the Pb(1 1 1) mesas differs by $\sim 19 \pm 5$ meV on a 5- vs. 6-layer mesa.

Acknowledgements

The work at Utah is supported by NSF (DMR-0307000). The work at Iowa is supported by DOE, the Director for Energy Research Office of Basic Energy Sciences. Ames Laboratory is operated by the DOE and by Iowa State University under Contract NO. W-7405-Eng-82.

References

[1] S. Stoyanov, I. Markov, Surf. Sci. 116 (1982) 313.
[2] J.A. Venables, Phys. Rev. B 36 (1987) 4153.
[3] J. Tersoff, A.W.D. van der Gon, R.M. Tromp, Phys. Rev. Lett. 72 (1994) 266.
[4] R.G.S. Pala, F. Liu, Phys. Rev. Lett. 95 (2005) 136106.
[5] F. Liu, A.H. Li, M.G. Lagally, Phys. Rev. Lett. 87 (2001) 126103.
[6] J. Tersoff, C. Teichert, M.G. Lagally, Phys. Rev. Lett. 76 (1996) 1675.
[7] F. Liu, S.E. Davenport, H.M. Evans, M.G. Lagally, Phys. Rev. Lett. 82 (1999) 2528.
[8] B. Yang, F. Liu, M.G. Lagally, Phys. Rev. Lett. 92 (2004) 025502.
[9] T.-L. Chan, C.Z. Wang, M. Hupalo, M.C. Tringides, K.M. Ho, Phys. Rev. Lett. 96 (2006) 226102.
[10] J. Rottler, P. Maass, Phys. Rev. Lett. 83 (1999) 3490.
[11] J. Krug, P. Politi, T. Michely, Phys. Rev. B 61 (2000) 14037.
[12] C. Castellano, P. Politi, Phys. Rev. Lett. 87 (2001) 056102.
[13] K. Bromann, H. Brune, H. Röder, K. Kern, Phys. Rev. Lett. 75 (1995) 677.
[14] G. Ehrlich, F.G. Hudda, J. Chem. Phys. 44 (1966) 1039.
[15] R.L. Schwoebel, E.J. Shipsey, J. Appl. Phys. 37 (1966) 3682.
[16] G.S. Bales, A. Zangwill, Phys. Rev. B 55 (1997) R1973.
[17] L.-Y. Ma et al., Phys. Rev. Lett. 97 (2006) 266102.
[18] W.B. Su et al., Phys. Rev. Lett. 86 (2001) 5116.
[19] W.B. Su et al., Phys. Rev. B 68 (2003) 033405.
[20] Z. Kuntova, M. Hupalo, Z. Chvoj, M.C. Tringides, submitted for publication.
[21] F.K. Schulte, Surf. Sci. 55 (1976) 427.
[22] V. Yeh, L. Berbil-Bautista, C.Z. Wang, K.M. Ho, M.C. Tringides, Phys. Rev. Lett. 85 (2000) 5158.
[23] M.H. Upton, C.M. Wei, M.Y. Chou, T. Miller, T.-C. Chiang, Phys. Rev. Lett. 93 (2004) 026802.
[24] Y.-F. Zhang et al., Phys. Rev. Lett. 95 (2005) 096802.