PHYSICAL REVIEW B **73**, 245425 (2006)

Equilibrium island-size distribution in one dimension

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(Received 24 February 2006; revised manuscript received 24 April 2006; published 20 June 2006)

We derive an analytical expression for the size distribution of monoatomic wires in the framework of a one-dimensional lattice gas model at thermodynamic equilibrium. The theoretical results are compared with the size distribution of one-dimensional Ag wires obtained via nucleation at the step edges of the Pt(997) surface.

DOI: 10.1103/PhysRevB.73.245425 PACS number(s): 81.16.Dn, 82.60.Nh, 68.55.Ac, 68.43.De

I. INTRODUCTION

Surfaces with a periodic step structure are employed in molecular beam epitaxy as deposition templates to produce dense arrays of one-dimensional (1D) atomic wires.[1–4] The investigation of such systems is a very active research field that includes the theory of nucleation in 1D,[5–10] the investigation of atomistic diffusion[11–17] and epitaxial growth[1–3,18–21] in the presence of steps, the catalytic activity of step sites,[22] electron confinement in 1D states,[23–26] and the behavior of 1D magnetic materials.[27–35]

Owing to the increase of binding energy at step sites, and depending on the substrate temperature, adatoms deposited on vicinal surfaces can self-assemble into chainlike structures by decorating the step edges.[19,21] Step decoration is a general phenomenon that has been observed for metals[1–3,18] as well as noble gases[36,37] and molecules.[22,38] An advantage of this growth method is that by adjusting the adatom coverage and the average step spacing one can independently control the width and separation of the atomic wires in a fast parallel process. So far, growth investigations have focused on tailoring the width of the wires while maintaining their uniformity and linearity across macroscopic regions of the sample.[2,3] However, since many of the wire physical properties—notably the electronic structure and magnetic behavior—depend also on their finite dimensions,[35,39] it is desirable to understand and possibly control the factors determining the wire length.

Recently, we have shown that by using Pt vicinal surfaces with a narrow terrace-size distribution and tuning the sample temperature to control diffusion activation we can grow uniform[2,3] as well as compositionally modulated[21] arrays of 1D metal wires in a row-by-row fashion. Continuous monoatomic wires are obtained for an adatom coverage $\Theta_w = 1/t$, where t is the average terrace width (in atoms) and Θ is measured in ML (monolayer). Such linear, continuous monoatomic wires are interrupted by step defects [see Fig. 1(a)], so that their length is ultimately determined by the density of defects along the step edges. Depending on the quality of the surface miscut and surface preparation, this density can be the order of 5×10^{-3} Å^{-1} on metal[2] and 6×10^{-5} Å^{-1} on Si[23] substrates. Scanning tunneling microscopy (STM) has shown that the formation of continuous monoatomic wires proceeds via the coalescence of increasingly long 1D islands that grow at the steps due to the diffusion of step-trapped adatoms. The length of these islands generally depends on the coverage, the substrate temperature, the adatom-step binding energy, and the kink (island boundary) energy.

To address this issue, we present here a straightforward determination of the theoretical equilibrium island size distribution in 1D derived analytically by means of simple thermodynamics arguments. The equilibrium size distribution for 1D islands as well as gaps is shown to depend only on the island density and coverage. The theoretical distributions so obtained are compared with STM measurements for 0.04 ML Ag deposited on Pt(997) at 400 K (Θ_w=0.13 ML for this surface) and discussed in comparison with the assumptions of the model.

II. EQUILIBRIUM ISLAND AND GAP SIZE DISTRIBUTIONS IN 1D

The statistical distribution of adatoms adsorbed at an ideal step edge, i.e., on a linear array of lattice sites is derived in terms of observables that can be readily extracted, e.g., from STM images. We consider a 1D lattice consisting of N sites with M adsorbed atoms distributed in K islands

$$\ldots000AAAA00000AA00AAAAA0AAA00\ldots \qquad (1)$$

where 0 and A represent free and occupied sites, respectively. Let n_i be the number of islands containing i atoms (or,

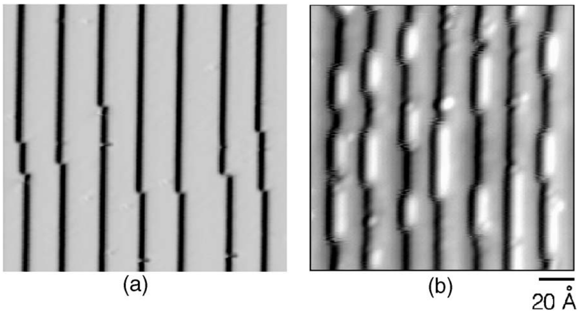

FIG. 1. (a) STM image of the Pt(997) surface prior to Ag deposition. (b) STM image of 0.04 ML Ag deposited on Pt(997) at 400 K. Step down direction is from right to left in both images. The images are shown in the derivative mode to evidence the nucleation of 1D Ag islands (bright stripes) at the step edges in (b).

equivalently, of length i), we define the total number of islands

$$K = \sum_{1}^{\infty} n_i, \tag{2}$$

and the total number of adatoms

$$M = \sum_{1}^{\infty} i n_i. \tag{3}$$

The free energy of the adatoms in (1) is

$$F = 2KE_b + (E_{ad} - \mu)M - TS \tag{4}$$

where E_b is the island boundary energy, E_{ad} the adsorption energy at steps, μ is the chemical potential of the adsorbed atoms, T the substrate temperature, and S the entropy term. In writing this expression for F we implicitly assume that interactions between island boundaries are negligible. The term $2KE_b$ in Eq. (4) contains the assumption that adatoms incorporated into islands have a lower free energy compared to monomers.

In order to calculate S, it is convenient to map the 1D lattice (1) into a lattice of reduced length $L=N-M$ obtained by replacing the lattice of occupied sites with the kink lattice, each kink now being associated with the length i of the corresponding island. In this way (1) rewrites as

$$\ldots 00\langle 0AAAA\rangle 0000 < 0AA > 0 < 0AAAAA > < 0AAA > 00\ldots$$

or

$$\ldots 0040000205300\ldots .$$

The above is equivalent to considering an ideal gas mixture of particles $\{i\}$ whose only interaction is the forbidden occupancy of the same site. The entropy of the system is, therefore, equal to the entropy of a substitution solution of particles of type $\{i\}$. The entropy expression can be easily derived by considering first only n_1 indistinguishable particles with $\frac{L!}{(L-n_1)!n_1!}$ allowed configurations; adding n_2 particles we obtain $\frac{L!}{(L-n_1-n_2)!n_1!n_2!}$ configurations, and so on, obtaining

$$S = \ln\left(\frac{L!}{(L-K)!\prod_0^\infty n_i!}\right)$$

$$\approx L\ln L - (L-K)\ln(L-K) - \sum_{1}^{\infty} n_i \ln n_i. \tag{5}$$

Minimization of F with respect to the distribution function $n_i(i>0)$ gives

$$n_i = Ax^i \tag{6}$$

with

$$A = (L-K)\exp\left(-\frac{2E_b}{T}\right),$$

$$x = \exp\left(\frac{-(E_{ad}-\mu)}{T}\right). \tag{7}$$

It follows that Eqs. (2) and (3) can be rewritten as

$$K = \sum_{1}^{\infty} n_i = A\sum_{1}^{\infty} x^i = A\frac{x}{1-x}, \tag{8}$$

$$M = \sum_{1}^{\infty} i n_i = A\sum_{1}^{\infty} i x^i = Ax\frac{d}{dx}\sum_{1}^{\infty} x^i = A\frac{x}{(1-x)^2}. \tag{9}$$

From Eqs. (6)–(9) one can work out the relation between the parameters E_b, $E_{ad}-\mu$ and the numbers K and M

$$E_b = \frac{T}{2}\ln\frac{(M-K)(N-M-K)}{K^2}, \tag{10}$$

$$E_{ad} - \mu = T\ln\frac{M}{M-K}, \tag{11}$$

and obtain the final result

$$n_i = K^2(M-K)^{i-1}M^{-i}. \tag{12}$$

An analog derivation gives the distribution function f_j of the free sites (gaps) interspersed between the 1D islands

$$f_j = K^2(N-M-K)^{j-1}(N-M)^{-j}. \tag{13}$$

Division of Eqs. (12) and (13) by N yields the normalized distributions as a function of the island and adatom concentration K/N and M/N, respectively. We note that n_i and f_j depend only on the coverage, through M/N, and the total number of islands K.

III. COMPARISON WITH EXPERIMENT

The n_i and f_j theoretical values can be compared with those extracted from the STM images of the type presented in Fig. 1(b). The image shows 1D islands that have nucleated at the lower step edges in the initial stages of row-by-row growth of Ag on Pt(997) upon deposition of 0.04 ML Ag ($=0.3\Theta_w$) at 400 K with a deposition rate of 0.003 ML s^{-1}. The STM images were recorded at 77 K. Ag islands can be identified and characterized, within the resolution limits of the experiment, as they present a larger apparent height in STM compared to Pt steps[2] and appear brighter in the derivative mode image shown in Fig. 1(b). The deposition temperature was chosen such as to stay well below the surface-confined mixing of Ag and Pt,[40] situated between 550 and 600 K on densely stepped surfaces, but also well above the activation temperature for Ag diffusion along Pt{111} step facets (200 K),[2] in order to minimize kinetic effects on the growth of continuous 1D wires.

A set of STM images with total values $N=5816$, $M=1811$, and $K=211$ was used to derive the experimental

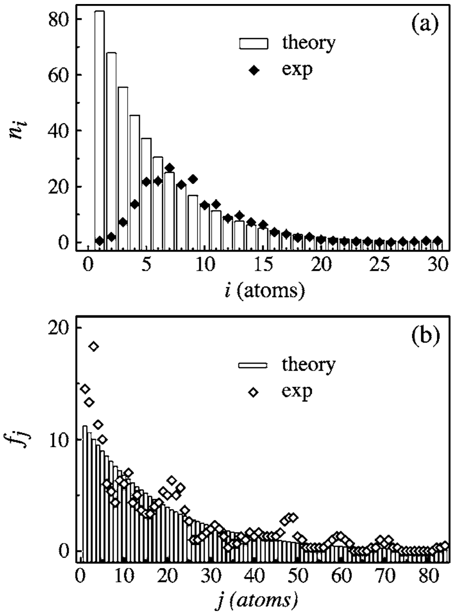

FIG. 2. (a) Theoretical (bars) and experimental (diamonds) 1D island size distributions. (b) Same for the 1D gap size distributions.

distributions n_i and f_j shown in Fig. 2. The theoretical n_i, f_j distributions were calculated from Eqs. (12) and (13) using the above values of N, M, and K. Due to the finite lateral resolution of the STM in the present experimental conditions, islands (gaps) with size i (j)$\leqslant 2$ could not be determined with sufficient accuracy. For the same reason, the experimental data for i and $i \pm 1$, j and $j \pm 1$ have been averaged in Fig. 2. One can notice that the theoretical n_i closely reproduces the decrease of the experimental data for $i > 5$ in Fig. 2(a), while there is no agreement for $i \leqslant 5$. For f_j, [Fig. 2(b)], the theoretical and experimental data follow the same trend, even though there is more scattering around the theoretical values.

Not withstanding the simplicity of the theory and the absence of any adjustable parameter, the 1D lattice model presented in the previous section is able to capture part of the physics that enters into the island-size distribution function, notably that related to the adsorption energy, the formation of island boundaries and the entropic contribution. In the model, the increase of n_i for $i \rightarrow 0$ is related to the term $K \ln(L-K)$ contained in Eq. (5), which, at fixed M/N coverage, favors the configurations where K is large, i.e., where the size of the islands is small. In the experiment, this entropy term is likely balanced by interactions either between islands and island boundaries or by an additional potential term arising from the misfit between Ag adatoms and the substrate lattice spacing. In the latter case, the inclusion in Eq. (4) of an additional energy term describing an elastic interaction with substrate sites due to epitaxial strain is indeed expected to lead to a better agreement between theory and experiment for small values of i,[5] although at the expense of an additional parameter not directly related to experimental observables.

In general, the experimental island size distribution can also be influenced by the kinetics of diffusion and nucleation events. To match the assumptions of the lattice gas model and thermodynamic equilibrium conditions, Ag adatoms should be strictly confined to the step sites and be able to diffuse freely along the step edges, while island nucleation should be a reversible process. As confinement to step sites requires a moderation of the substrate temperature, contrary to diffusion and cluster dissociation events, it is not clear whether these three requirements can be simultaneously fulfilled. It is generally established that the edge diffusion energy barriers for atoms adsorbed on the lower side of a step on a metal surface are significantly smaller than the barriers for edge detachment (evaporation on terrace sites), typically by about a factor two.[14,17] A temperature window, therefore, exists where atoms are confined to step sites but nonetheless mobile in 1D. For Ag adatoms diffusing along the $\{111\}$ edge of Ag islands on Pt(111), the diffusion barrier was estimated to be 0.37 eV by comparing the experimental island branch width with kinetic Monte Carlo simulations,[41] which is consistent with the formation of smooth 1D Ag wires observed on Pt(997) for $T \geqslant 200$ K.[2] Detachment from an Ag step edge should, therefore, be activated between 300 and 400 K, as indeed reported for Ag submonolayer films grown on Pt(111) (Ref. 42) and roughening of Ag islands on Pt(111).[43] However, the binding energy of Ag adatoms at Pt step sites is calculated to be larger by about 0.35 eV compared to Ag step sites,[21] thus suggesting an effective confinement of the first row of Ag atoms along the steps of Pt(997) at 400 K. Regarding the reversible nucleation of 1D Ag islands, one can consider the dissociation of Ag dimers adsorbed at a step edge as the necessary condition leading to ripening of Ag islands in 1D. Tight-binding calculations for Au and Ag homoepitaxial systems indicate that dimer dissociation at step edges implies overcoming significantly larger activation barriers compared to edge diffusion.[14] However, for Ag on Pt(111) dimer dissociation starts already at 120 K,[44] while both density functional calculations[45] and experiments[46] indicate that, for certain systems, dimers might break up more easily at step sites rather than on terrace sites. Finally, it is interesting to note that the dimer bond energy per Ag atom on Pt(111) estimated by STM, 75 ± 10 meV,[47] compares well with $E_b = 83$ meV calculated using Eqs. (8)–(10) and the experimental N, M, K values. Based on these arguments, we believe that kinetic factors do not play a dominant role in determining the island size distribution in the present experimental conditions.

IV. CONCLUSIONS

In summary, we have developed a statistical lattice gas model to calculate the equilibrium island and gap size distribution function in 1D. The distribution function is given in terms of the total number of lattice sites N and occupied sites M, and on the total number of islands K. All other parameters that enter into the model, such as the adatom adsorption energy, the island boundary energy, the chemical potential, and the substrate temperature are expressed through N, M, and K, thereby allowing for a straightforward comparison with experiments. We have studied the nucleation of monoatomic Ag wires at the step edges of Pt(997) at $T=400$ K as a 1D model system. The experimental and theoretical island distribution functions are in good agreement for islands containing more than five atoms. We attribute the disagreement between theory and experiment in the small island limit to the presence of epitaxial strain that has not been considered in our model.

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