Equilibrium island-size distribution in one dimension

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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.

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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 diffusion11–17 and epitaxial growth1–3,18–21 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 metals1–3,18 as well as noble gases36,37 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.23 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 uniform33 as well as compositionally modulated21 arrays of 1D metal wires in a row-by-row fashion. Continuous monoatomic wires are obtained for an adatom coverage Θw=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 metal2 and 6×10−5 Å−1 on Si23 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 (Θw=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

\[ \ldots 000AAAA00000A00AAAA00AAAAAA00 \ldots \] (1)

where 0 and A represent free and occupied sites, respectively. Let \( n_i \) be the number of islands containing \( i \) atoms (or,
equivalently, of length $i$), we define the total number of islands

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

(2)

and the total number of adatoms

$$M = \sum_{i=1}^{\infty} in_j.$$  

(3)

The free energy of the adatoms in (1) is

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

(4)

where $E_b$ is the island boundary energy, $E_{ad}$ the adsorption energy at steps, $\mu$ 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

\ldots00(0AAAA)0000 < 00AA > 0 < 0AAAAA > < 0AAA > 00\ldots

or

\ldots0040000205300\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

$$S = \ln \left( \frac{L!}{(L-K)! \prod_{i=1}^{\infty} n_i!} \right)$$

$$= L \ln L - (L-K)\ln(L-K) - \sum_{i=1}^{\infty} n_i \ln n_i.$$  

(5)

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

$$n_i = Ax^i$$

(6)

with

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

(7)

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

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

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

(8)

$$M = \sum_{i=1}^{\infty} in_i = A \sum_{i=1}^{\infty} ix^i = A \frac{x}{(1-x)^2}.$$  

(9)

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

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

(10)

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

(11)

and obtain the final result

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

(12)

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

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

(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 ($=0.30\Theta_a$) 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
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.\textsuperscript{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,\textsuperscript{41} which is consistent with the formation of smooth 1D Ag wires observed on Pt(997) for $T \approx 200$ K.\textsuperscript{5} 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).\textsuperscript{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,\textsuperscript{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.\textsuperscript{14} However, for Ag on Pt(111) dimer dissociation starts already at 120 K,\textsuperscript{44} while both density functional calculations\textsuperscript{45} and experiments\textsuperscript{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,\textsuperscript{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.