Size distributions and scaling relations for heterogeneous nucleation and growth of atomic chains

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Abstract. An analytical model for one-dimensional islands growth was developed being inspired by experiments on growth of metallic atomic chains. On the basis of reported observations and simulations we considered the case of heterogeneous nucleation with linear on size rates for growth and decay. In this case the exact solution of the system of rate equation leads to Polya distribution for lengths of chains and corresponding scaling behaviour. These analytically computed dependences demonstrated good matching with experimental results.

1. Introduction
The group-III and IV metals [1, 2, 3, 7], several transition metals (like Mn, Pb)[8, 12] and some mixed dimers (like In − Sn) [13], being deposited in low coverage regime, are known to assemble into linear atomic chains. The substrate structure plays the key role in this case. The formation of metal chains was observed on Si(100) − 2 × 1 surface composed by silicon dimers arranged into rows. The deposited metal atoms arrange into the chains in a direction perpendicular to these substrate rows. Resulting surfaces could be observed by atomic resolved scanning tunnelling microscopy(STM). The STM technique gives the direct access to analysis of chains density, structure and such statistical characteristics as length distributions and their scaling [4, 14, 15]. The latter one could be also extracted from previously reported numerical simulations [7, 16, 5] and calculations based on analytical model which is presented in the following sections. A schematic image of metallic atomic chains on Si(100) − 2 × 1 substrate is shown on Fig.1. Where red full spheres corresponds to substrate atoms of Si dimers and semi-full spheres denotes chain atoms.

2. Analytical model
On the Si surface so called C-type defects play the important role. According to Hossein et al. and Okano and Oshiyama [19, 20] a defect of type C is interpreted as a dissociated water molecule with the H and OH group bonded to Si atoms of two adjacent surface dimers. These defects are reported to be chemically active and play the role of nucleation centres [3, 6].
Thus the theoretical model should imply the heterogeneous nucleation involving growth and decay of atomic clusters via the scheme $A_sB + A_1 \leftrightarrow A_{s+1}B$ with $s = 0, 1, 2, 3...$

Here, $B$ denotes the nucleation center, $A_1$ is the free metallic atom and $A_sB$ is the cluster consisting of $s$ monomers and one nucleation center. By definition, $A_0B \equiv B$ is the free seed. Since C-type defects are not appear or disappear during the metal deposition the total number of all clusters plus the number of free nucleation centres conserves in time and equals the total number of nucleation centres, so that the size distribution $f_s(t)$ can be normalized to one:

$$\sum_{s \geq 0} f_s(t) = 1 \quad (1)$$

Various cases of scenario of atom attachment to chain were discussed and simulated by Albao et al. [7]. According to their approach a randomly deposited atom diffuse along the chain after reaching it, so the probability of atom attachment is proportional to chain length. For our model it means that (as in [21]) the growth ($k^+_s$) and decay ($k^-_s$) rate for whatever material depends linearly on the number of monomers in the cluster:

$$k^+_0 = k^+ b$$
$$k^+_s = k^+ (a - 1 + s)$$
$$k^-_s = k^- s; \ s \geq 1 \quad (2)$$

with some positive dimensionless $a, b$, and the constants $k^+, k^-$ having the dimensions inverse time. The process could be considered in terms of the dimensionless time $\tau = k^-t$. Within these notations the set of corresponding discrete rate equations for the size distribution $f_s(\tau)$ (according to [21]) could be expressed as:

$$\frac{df_0}{d\tau} = -b(\zeta + 1)f_0 + f_1$$
$$\frac{df_1}{d\tau} = b(\zeta + 1)f_0 - f_1 - a(\zeta + 1)f_1 + 2f_2$$
$$\frac{df_s}{d\tau} = (a - 2 + s)(\zeta + 1)f_s - 1 - (a - 1 + s)(\zeta + 1)f_s + (s + 1)f_s; \ s \geq 2 \quad (3)$$

Where $\zeta \equiv (\frac{k^+}{k^-})f_1$ is a function of time with a clear sense of the effective supersaturation of a free monomer vapor with the concentration $f_1$.

In view of (2) the growth rate is:

$$\frac{ds}{d\tau} = (a - 1)(\zeta + 1) + \zeta s \quad (4)$$

which distinguish the cases of $a > 1$ and $a < 1$. The latter case, with a positive supersaturation, leads to the growth instability such that smaller clusters decay and larger clusters grow, as in nucleation theory, with a supersaturation-dependent critical size $s_c = (1 - a)(\zeta + 1)/\zeta$. Since such critical size and such behaviour were not observed in experiments, further we assume $a > 1$ which corresponds to stable unlimited or limited growth [17, 18].

Time evolution of mean clusters size, $<s> = \sum_{s \geq 1} f_s s$, follows the equation:

$$\frac{d <s>}{d\tau} = \zeta <s> + (1 - a)(\zeta + 1)(qf_0 - 1) \quad (5)$$
with parameter $q \equiv \frac{b+1-a}{1-a}$

The material balance in neglect of desorption leads to:

$$\Theta = <s> + \left(\frac{k^-}{k^+}\right)\zeta$$  \hspace{1cm} (6)

Where $\Theta$ is the normalized coverage.

For further analysis we introduce the generating function for discrete size distribution function $f_s$:

$$f(x, \tau) = \sum_{s=0}^{\infty} f_s(\tau)x^s$$  \hspace{1cm} (7)

with properties $f(0, \tau)$ and $f(1, \tau) = 1$.

Differentiating Eq. (7) with respect to $\tau$ and using (3) we arrive to differential equation for generating function $f(x, \tau)$:

$$\frac{\partial f}{\partial \tau} = (x-1) \left[ (\zeta + 1) \frac{\partial f}{\partial x} - (1-a)(\zeta + 1)f + (b+1-a)f_0 \right]$$  \hspace{1cm} (8)

$$f(x, \tau = 0) = 1$$

Further it is more convenient to use the new function $F(x, \tau) = f(x, \tau) - qf_0(\tau)$ In these terms the exact solution of (8) has a form:

$$F(x, \tau) = (1 + \alpha(\tau)(1-x))^{1-a} \left[ 1 - q - q \int_0^\tau d\tau' (1 + \frac{e^{-z(\tau')}}{\Psi} \alpha'(\tau'))^{1-a} \frac{\partial f_0}{\partial \tau'} \right]$$  \hspace{1cm} (9)

Here we denote the functions $\Psi(x, \tau)$ as:

$$\Psi(x, \tau) = e^{-z(\tau)} \left( \frac{1}{1-x} - \alpha(\tau) \right)$$  \hspace{1cm} (10)

with

$$z(\tau) = \int_0^\tau d\tau' \zeta(\tau')$$  \hspace{1cm} (11)

$$\alpha(\tau) = e^{z(\tau)} \int_0^\tau d\tau' [\zeta(\tau') + 1] e^{-z(\tau')}$$  \hspace{1cm} (12)

We now consider the asymptotic solution to Eq.(8) which corresponds to the approximation $1 + \frac{e^{-z(\tau)}\alpha(\tau)}{\Psi} \simeq 1$ under the integral. This reduces the integral to $1 - qf_0$. This kind of approximation is equivalent to applying the Laplace method for calculating the integral, so the validity requires $\frac{\partial f_0}{\partial \tau}$ to be a steep function near $\tau = 0$. In this case the solution has the form:

$$F(x, \tau) = (1 + \alpha(\tau)(1-x))^{1-a} [1 - qf_0(\tau)]$$  \hspace{1cm} (13)

For chains size distribution it means:

$$f_0(\tau) = \frac{(1+\alpha(\tau))^{1-a}}{1-q(1+\alpha(\tau))^{1-a}}$$  \hspace{1cm} (14)

$$f_s(\tau) = \frac{<s>(\tau)}{\alpha(\tau)} f_{s-1}[\alpha(\tau)], \ s \geq 1$$  \hspace{1cm} (15)

Putting the free parameter $b > 0$ to $b = a - 1$ (which requires the stable case $a > 1$ [21, 18]) we arrive to Polya distribution for lengths of chains:
Here it is worth for further applications to notice that the Polya distribution is a kind of universal function which could be the purely decreasing with \( s \) (for \( b < 1 \)) or have a maximum (for \( b > 1 \)). Both such distributions were observed in experiments.

### 3. Scaling

The derived form of size distribution could be rewritten in a scaling form. For this let us use the Stirling formula and the large \( s \) and \( \alpha \) asymptote \( \frac{\alpha^s}{(1+\alpha)} = e^{-s/\alpha} \). In this way we arrive at the continuum form of the Polya distribution:

\[
\begin{align*}
  f^{(b)}(s, \alpha) &= \frac{s^{b-1}}{\Gamma(b)\alpha^b} e^{-s/\alpha} \\
  \int_0^\infty ds f^{(c)}(s, \alpha) &= 1; \quad \int_0^\infty ds s f^{(c)}(s, \alpha) = ca
\end{align*}
\]

This form of size distribution preserves the previously fixed normalisation and correct mean size:

\[
\begin{align*}
  \frac{1}{<s>} &\phi_b \left( \frac{s}{<s>} \right) ; \quad \phi_b(x) = \frac{b^b}{\Gamma(b)} x^{b-1} e^{-bx} \\
\end{align*}
\]

with \( b \)-dependent scaling function \( \phi_b(x) \).

The obtained scaling \( f^{(b)}(s, <s>) = \frac{1}{<s>} \phi_b \left( \frac{s}{<s>} \right) \) at small enough \( \zeta \) when \( <s> \simeq \Theta \) satisfy well-known scaling relation \( f^{(b)}(s, <s>) = \frac{\Theta}{<s>} \phi_b \left( \frac{s}{<s>} \right) \) suggested by Vicsek and Family [9] and discussed in quite recent review of Einax et al. [10].

It is important to mention that the scaling given by Eq.(20) is the intrinsic property of the growth model with the size-linear rate constants and does not require any other assumptions. It works in case heterogeneous nucleation but could an object of further investigation whether this condition is necessary or the model, in some extent, could be applied in case of homogeneous nucleation.

### 4. Comparison with experiment

For the systems of metal atomic chains described in first section the experimentally obtained data could be fitted with analytical solution derived in previous sections.

The most of theoretical models predict the monomodal size distributions with single well-defined maximum around the mean size while the purely decreasing distributions also were observed in experiments [7]. The monomodal distributions are more usual for experiments. They were observed in many systems, for example, for one-dimensional \( Mn \) islands on \( Si(100) - 2 \times 1 \) surface reconstruction [11] or for Si homoepitaxy at low temperatures [22].

The systems of Mn atomic chains grown on \( Si(100) - 2 \times 1 \) substrates was found to be stable at room temperature [11]. The time-evolution of length size distributions of Mn chains is illustrated by Fig. 2. Due to the ambiguity of single Mn atom identification the size \( s \) enters in arbitrary units which correspond to distance between dimers of Si. The distributions are fitted with our model, Eq. (16), for three different deposition times: 2s, 7s and 12s. The value of the parameter
$b$ remains around 4 while $\alpha$ (which is proportional to mean size) is changing with time. The mean sizes in all three cases was calculated according to Eq. (17) and summarized in Table 1. The values obtained from the model fit was found to be inconsiderably smaller than the values extracted from experimental measurements which could be either due to the ambiguity of size units or due to lack of statistics (the data only about 100 - 300 chains were collected for each deposition time). Nevertheless, our simple model seems to fit the data quite well.

Let us next discuss the scaling of experimentally observed distributions. The Fig. 3 (a) shows the scaling form of dependences on Fig. 2 corresponding to 7s and 12s of deposition. The points of $f(s) < s >$ extracted from experimental data (ref. [11]) is plotted versus scaled size $\frac{s}{<s>}$ and fitted in accord with Eq.(20). For two cases of different times of deposition but the same growth conditions the dependences in a scaled form collapsed into one curve corresponding to $b = 4$. Large dispersion around the maximum could originates from lack of statistics, slight ambiguities in chain length measurement or impact of surface terraces.

Table 1

| Dep. time | $<s>$ | Model | Measured |
|-----------|-------|-------|----------|
| 2s        | 2.5   | 0.614 | 3.27     |
| 7s        | 4.96  | 1.24  | 5.3      |
| 12s       | 6.44  | 1.61  | 6.86     |

The process of Mn lines described previously could be compared with others for similar systems of other deposited materials on the same type of substrates. Obviously in these processes the value of $b$ parameter could be different. The Fig. 3 (b) shows the experimental points and corresponding fits of scaled size distributions for Mn (discussed above), In (ref. [3]) and two samples of Ga (ref. [7]) corresponding to coverages of 0.095 ML and 0.130 ML. All these processes were carried out under different growth conditions and, thus, not surprisingly, demonstrate different values of $b$. Scaled distributions has no peak when $b < 1$. When $b > 1$ and decreases the maximum shifts towards small sizes. In practice it could shifts to non-physical range when $s$ smaller than 2. So here the importance of unique property of Polya distribution (which could have or not to have the peak in positive range) is revealed.

In conclusion, the model for heterogeneously nucleated clusters with size-linear grow and decay rates has been presented in exactly solvable case. The obtained solution in asymptotic case leads to Polya form for size distributions with shapes controlled by dimerization parameter $b$. This obtained form is rather universal and provides the description for purely decreasing distributions when $b < 1$ as well as for monomodal ones with well defined peak when $b > 1$. Figure 2.
This property became useful in comparison of theoretical dependences and the distributions measured in experiments. The theory demonstrated agreement with experimentally observed time evolution of Mn chains length distribution and scaling for the systems of In, Ga and Mn lines on Si(100) − 2 × 1 substrates.

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