Self-limiting growth and bimodal size distribution of Au nanoislands on InAs(111)B surface

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Abstract. Gold nanoparticles are widely used for catalytic growth of different semiconductor nanowires. It is important therefore to have a full appreciation of the factors influencing the size distribution of such particles on semiconductor substrates. Here, we describe some interesting phenomena observed during low-temperature deposition of Au onto InAs(111)B substrates where Au islands are solid. In particular, we find a bimodal character of the size distribution of these islands. We then develop a nucleation model which is based on a specific form of the island formation energy. The model yields a self-limiting growth behavior in which the growth rate of large islands is suppressed e.g. due to dislocations. We show that the regime of self-regulated nucleation with a few pulses is observed for short growth times, leading to a bimodal size distribution or even a more complex shapes. For longer growth times, the system acquires a steady-state regime with a time-independent supersaturation and hence the pulses disappear.

1. Introduction

Au-catalyzed growth of nanowires allows for fabrication of a variety of sophisticated non-planar nanostructures suitable for optical and electronic applications. These applications usually require a good control over the nanowire diameters and thus the size distribution of the catalytic particles from which the nanowire growth starts [1,2]. Usually, Au is deposited on semiconductor surfaces at low temperatures where the initial Au nanoparticles are solid (before anneal). In this case, the strain-induced effects due to the lattice mismatch between the islands and the substrate becomes very important [3-5] and may strongly influence the size distribution. The latter determines the initial condition for the annealing step and thus influences the resulting surface assembly of the nanowire seeds. If we restrict ourselves to solid Au nanoparticles, the strain-induced effects may lead to a suppression of the growth rate for large sizes and consequently to the regime of self-limiting growth with secondary nucleation. This was previously discussed, e.g., in Ref. [6] in connection with the bimodal size distribution of three-dimensional (3D) Ge islands on Si(100). However, in this work the strain-induced suppression of the growth rate was introduced in modeling without changing the island formation energy. On the other hand, several studies revealed a saturation of the size of Au [7] and some other metal nanoislands [8] at a certain steady-state value in the course of growth. Similar
phenomenon was reported for dislocated 3D GaN islands on Si(111) surfaces covered with AlN mismatching layer [9] or even for dislocation-free 3D GaN islands on an amorphous SiN interlayer (without any strain) [10-12] before the island-to-wire growth transformation. The last example suggests that the self-limiting growth behavior is not necessarily associated with strain relaxation but may be caused by other reasons such as the surface energy balance and shape transformation.

Consequently, here we study the morphology of 3D Au nanoislands deposited on InAs(111)B substrates at a low temperature of 350°C where the islands are solid. We find experimentally a bimodal character of the size distribution of such islands. We then develop a nucleation model which is based on a specific form of the island formation energy with a strain-induced contribution. The model describes a self-limiting growth and enables us to explain the experimental findings. Furthermore, from theoretical point of view, we present an unusual behavior of supersaturation with damped oscillations which produce two differently shaped peaks of the size distribution which are well-separated at the beginning but merge together on a later stage of growth.

2. Experiment

The deposition of Au on InAs(111)B substrates was performed at 350 °C which is below the melting point for these materials [13,14]. We thus deal with solid strained Au nanoislands with a huge lattice mismatch (ε₀ = 33%) with the substrate which is expected to induce misfit dislocations in the islands soon after their nucleation. In the growth time series, the Au deposition was stopped after 0.5, 1, 2, 2.5, 4 and 5 min. Low resolution transmission electron microscopy (TEM) images shown in Fig. 1 did not allow us to confirm precisely the presence or absence of crystalline defects or dislocations. This will be elaborated elsewhere.

Figure 1(a)-(d) SEM images of Au nanoislands on InAs(111)B substrate for the deposition times of 0.5, 1, 2.5 and 4 min, respectively; (e) TEM image and (f) diffraction pattern of Au nanoislands on InAs(111)B substrate

The analysis of scanning electron microscopy (SEM) images (Fig. 1 a-d) reveals several interesting features of the time-dependent growth behaviour. First, within the time interval from 0.5 to 4 min, the
mean diameter of the island bases remains within the interval from 75 to 100 nm but increases to 125 nm after 5 min of deposition. Thus, we observe a quick saturation of the island size with a slow increase at a later growth step. At the same time, the island density gradually increases with time from 2.2 $\mu m^{-2}$ at 0.5 min to 16 $\mu m^{-2}$ at 4 min. Surprisingly, in the 2.5 min sample (Fig. 1c) we can see a coexistence of large islands with much smaller islands having the mean diameter of only 10 nm. The corresponding distribution over lateral sizes has two separate peaks which are not observed for shorter or longer deposition times.

The island density and the mean size at different growth times are summarized in Table 1. Since the island density only increases with time, the evolution of the size distribution has nothing to do with the Ostwald ripening [1]. In a qualitative way, one could think of the two generations of islands whose nucleation events are separated in time. The first generation quickly emerges and grows until reaching a steady-state size which is stabilized by some inhibition of the material consumption by larger islands. Since stable islands cannot continue growing and the material influx remains on, supersaturation starts increasing again and this gives rise to nucleation of the next generation of islands, as described in Ref. [6].

Table 1 Experimental data on the island density and size at different deposition times

| Deposition time | Island density ($\mu m^{-2}$) | Mean size (nm) |
|----------------|-------------------------------|----------------|
| 0.5 min        | 2.2                           | 81             |
| 1 min          | 6.8                           | 78             |
| 2 min          | 5.8                           | 94             |
| 2.5 min        | 15                            | 75             |
| 4 min          | 16                            | 72             |

3. Theoretical model

Standard macroscopic expression for the island formation energy $F$ as a function of the number of monomers (Au adatoms in our case) $i$ yields a function with one maximum after which the islands grow infinitely [1,15,16]. In order to describe the observed self-limiting growth, we modify the formation energy of a 3D island with the linear size $r$ by adding the new $i^{4/3}$ term which dominates at large enough $i$. If we attribute the inhibition of growth to the lattice mismatch, $i^{4/3}$ is proportional to $r^4$ and can be considered as the energy of interaction between a linear dislocation of length $r$ with the island volume $r^3$. On the other hand, the residual strain is known to modify the volume term in the formation energy.

Therefore, our model for $F(i)$ has the form

$$F(i) = A i^{2/3} - [B + \ln(1 + \zeta)] i + C i^{4/3}.$$  \hspace{1cm} (1)

Here $A$, $B$ and $C$ are the material-related constants and $\zeta = n_1/n_{eq} - 1$ is the supersaturation of 2D adatom sea with concentration $n_1$ with respect to their equilibrium concentration $n_{eq}$. The $A i^{2/3}$ term stands for the surface energy and $B i$ is volume energy gain due to strain relaxation. With an obvious relationship between the coefficients in Eq. (1), the formation energy has a maximum at the critical size as in the standard theory [1] and a minimum at a certain steady-state size which corresponds to the growth equilibration [5,6,17-19]. The typical shape of the formation energy versus the base size $r$ is shown in Fig. 2.

Following the standard procedure described in detail in Refs. [1,15,16], we obtain the growth ($W_i^+$) and decay ($W_i^-$) rates in the form

$$W_i^-(t) = W_{i-1}^+ exp\left(\frac{dF(i)}{dt}\right); \quad W_i^+ = \frac{m}{r} (1 + \zeta)^{\frac{m-1}{m}}.$$  \hspace{1cm} (2)
Here, the growth index \( m \) depends on the mechanism of material transport of Au adatoms into the islands and \( \tau \) is the characteristic diffusion time of adatoms on the substrate. The rate equations describing the time evolution of the surface concentration of differently sized islands \( n_i(t) \) is taken in the standard form \([1,15,16]\):

\[
\frac{dn_i}{dt} = W^{+}_{i-1}(\zeta)n_{i-1} + W^{-}_{i+1}(\zeta)n_{i+1} - \left(W^{+}_{i}(\zeta) + W^{-}(\zeta)\right)n_i. \tag{3}
\]

The time evolution of supersaturation \( \zeta = \zeta(t) \) is obtained from material balance equation

\[
\zeta(t) + \sum_{i=2}^{\infty} i n_i(t) = \Phi(t), \tag{4}
\]

where \( \Phi(t) \) is the so-called “ideal supersaturation” which equals the appropriately normalized total volume of the deposited material and increases linearly with time \([20]\).

**Figure 2** Formation energy \( F(r) \) versus the base size of 3D nanoisland \( r = r^{1/3} \) (measured in the units of lattice spacing) with the critical size \( R_c \) and the steady-state size \( R_* \). This shape corresponds to \( A=0.7, B + \ln(1 + \zeta) = 0.055 \) and \( C = 0.001 \) in Eq. (1)

The nucleation rate gives the number of islands emerging per unit surface area per unit time and is obtained from the Zeldovich expression \([1]\):

\[
l(\zeta(t)) \sim (1 + \zeta)^2 \ln(1 + \zeta) \exp \left[ -\frac{\alpha}{\ln^2(1+\zeta)} \right], \tag{5}
\]

where \( \alpha \) is a material-related constant corresponding to the maximum of the formation energy. The most important feature of Eq. (5) is that the nucleation rate is extremely sensitive to the value of supersaturation \( \zeta \) due to the exponential dependence on the nucleation barrier with a large parameter \( \alpha >> 1 \).

**4. Results and discussion**

Numerical solution of Eqs. (3) to (5) was performed by introducing the dimensionless time \( z \equiv m t / \tau \), scaled size \( s = l / l_0 \) and concentrations \( f_i \equiv n_i / n_{eq} \) and implementing the explicit finite
difference method. The parameter values used in calculations were the following: \( m = 1.5, A = 10, B = 3.6, C = 0.34 \). The time dependences of supersaturation, size distribution, mean size and density of islands were obtained and compared with the experimental data.

In particular, Fig. 3 (a) shows the dependence of supersaturation \( \zeta \) on the dimensionless time \( z \). It is seen that this dependence has the form of damped oscillations whose amplitude rapidly decreases with the number of pulses. After that, supersaturation stabilizes at a certain value corresponding to a time-independent nucleation of the new islands (at a low rate) and a slow growth of all previously formed islands.

![Figure 3](image)

**Figure 3** (a) Time dependence of supersaturation, (b) Size distribution shapes at different times \( z \)

A much more informative picture of the growth process can be deduced from the analysis of the size distributions shown in Fig. 3 (b). Following the pulsed behavior of supersaturation, the initial distribution at short times (\( z = 200 \)) is monomodal which corresponds to the time interval before the growth stabilization. After that (at \( z = 360 \)) we observe the bimodal distribution with a lower peak at smaller sizes caused by secondary nucleation. At longer times, this second peak moves toward larger sizes and merges with the first peak, as demonstrated by the curve at \( z = 440 \). The curve at \( z = 540 \) illustrates the follow-up evolution of the system: the distribution becomes monomodal again and is taller than the others, corresponding to a steady-state process with a slowly increasing mean size.

![Figure 4](image)

**Figure 4** Time dependences of the islands mean diameter, with error bars corresponding to half-widths of the size distributions
As regards the interpretation of our experimental data, we believe that the two populations of islands seen in our SEM images correspond to the situation with two distribution peaks soon after secondary nucleation. After that, the two peaks merge as shown in Fig. 3 (b) and we do not observe any size separation on a later growth stage. The fits to the mean island size versus the deposition time are shown Fig. 4. With our model parameters, we are able to reproduce the observed behavior. The first generation of islands features growth at a decreasing rate from 0.5 to 2. Around 2.5 min, secondary nucleation of new islands occurs and then the two generations become indistinguishable in terms of their mean size.

In conclusion, we have shown experimentally an interesting growth behavior of Au nanoislands deposited onto InAs(111)B surfaces at 350 °C. We clearly observe the initial nucleation step with a monomodal size distribution, then the two populations of islands with a distinct size separation, transformed to a monomodal system again in the course of deposition. Such a behavior is well-described by a theoretical model where the island formation energy is modified to yield the growth inhibition for large islands. Our model describes a very unusual growth with self-regulated nucleation pulses producing multiple populations of differently sized islands which merge together on a later growth stage.

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