

Entropy-Driven Effects in Self-Organized Formation of Quantum Dots

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Finite-temperature thermodynamic theory is developed for equilibrium arrays of two-dimensional monolayer-high islands in heteroepitaxial systems at submonolayer coverage. It is shown that the entropy contribution to the Helmholtz free energy of the system favors formation of smaller islands at higher temperatures which results in a decrease of the average number of atoms in the islands (the island volume) with temperature. The characteristic temperature T_{char} , at which the island volume is significantly decreased compared to its value at $T = 0$ K, is found to be far below the characteristic energy of the island formation and to lie in a region of several hundreds of K. Such a temperature dependence can be the basis for decisive experiments aimed at distinguishing between thermodynamic and kinetic effects in the formation of arrays of 2D islands. Results of high resolution electron microscopy and photoluminescence spectroscopy of a submonolayer InAs/GaAs(001) system are in agreement with the theory. It confirms that the formation of a submonolayer array of InAs/GaAs(001) islands is predominantly influenced by thermodynamics.

The recent breakthrough in quantum dot (QD) technology, allowing a new generation of optoelectronic devices such as semiconductor diode lasers, relies on effects of self-organization at semiconductor surfaces [1]. During the initial years of QD research its main objective was to study basic effects of self-organization, to investigate the optical properties of QD arrays, and to demonstrate the possibility of fabricating QD lasers. To ensure further progress in the fabrication of QD heterostructures one has to master the way of controlling the process of self-organized growth in order to intentionally tune the morphology of QD arrays. To achieve this goal it is necessary to understand the formation mechanisms of QD arrays for any heteroepitaxial system.

There exist two basic classes of theoretical models of self-organized formation of QD arrays: thermodynamic models, which describe an array of strained islands as the equilibrium state of a heteroepitaxial system [2, 3], and kinetic models, which emphasize strain-driven barriers for adatoms to attach to islands [4, 5] or for a new atomic layer to nucleate on facets [6]. The barriers eventually lead to the self-limited growth of the islands. In this connection, the relative importance of thermodynamic and kinetic effects in the self-organized formation of arrays of strained islands still remains a highly debated issue [7]. To elucidate the relative roles of thermodynamic and kinetic effects in

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QD formation is one of the key experimental challenges in the study of any particular QD structure.

The experimentally observed morphology of QD arrays depends strongly on the temperature of array formation. However, previous phenomenological thermodynamic theories (e. g. [2,3]) have taken into account temperature dependencies only in an implicit form, whereas first-principles theories (e. g. [8]) have focused only on the equilibrium morphology at $T = 0$ K. To distinguish the relative roles of the thermodynamic and kinetic effects, it is necessary to obtain theoretically the dependence of the parameters of the QD arrays on the formation temperature in an explicit form.

A comparatively simple and theoretically tractable system, for which a finite-temperature thermodynamic theory can be developed, is an array of strained islands having a 2D-like shape, i.e. an array of islands for which the height is fixed and small compared to the lateral dimensions. An example of such an array is a system of monolayer-high islands obtained in the submonolayer (SML) heteroepitaxy. Optical [9] and structural [10] studies of SML of InAs deposited on GaAs(001) have revealed the formation of nanometer-scale islands. Photoluminescence (PL) spectroscopy of SML CdSe/ZnSe(001) islands [11] have demonstrated discrete lines from single islands thus proving the QD-like electronic spectrum of such islands.

It has been theoretically established [12–15] that the discontinuity of the intrinsic surface stress tensor at the island boundaries in SML heteroepitaxial systems results in elastic relaxation. The total energy of the system, normalized per atom in the islands, equals

$$E(N) = -W + \frac{C_1}{\sqrt{N}} - \frac{C_2}{\sqrt{N}} \ln \left(\frac{\sqrt{N}}{e} \right), \quad (1)$$

where the first term is the binding energy, the second term is the energy of the island boundaries due to additional broken chemical bonds, and the third term is the elastic relaxation energy, N being the number of atoms in the island. The constant C_1 is proportional to the energy of the boundaries normalized per one boundary atom, and the constant C_2 is proportional to the square of the elastic forces acting at the island boundaries and resulting in an elastic relaxation. The energy per atom (1) has a minimum at the optimum number of atoms in the island (the optimum volume of the island) $N_0 = \exp [2(C_1/C_2 + 1)]$. The energy per atom in the optimum island is lower than that in a ripened ($N \rightarrow \infty$) island by the quantity

$$\Delta E_{\text{opt}} = \frac{C_2}{\sqrt{N_0}}. \quad (2)$$

The corresponding energy normalized per optimum island equals

$$\Theta \equiv N_0 \Delta E_{\text{opt}} = C_2 \sqrt{N_0}. \quad (3)$$

The two energies (2) and (3) define a characteristic energy scale for an array of SML islands.

Kinetic theories developed for SML islands in homoepitaxial systems yield that a kinetically controlled ensemble of SML islands can also reveal an optimum island size at a relatively slow steady-state stage of growth which follows the nucleation stage. Kinetic theory yields a scaling behavior of island volume distribution [16–18] which

appears to fit well experiments on homoepitaxy for Si/Si(001) [19] and Cu/Cu(001) [20]. Kinetic theories developed for homoepitaxial systems can, in principle, be applied to heteroepitaxial systems if the elastic relaxation at island boundaries is a weak effect, the optimum number of atoms in the island N_0 is too large (say, $N_0 \ll 10^4$), and the actual islands contain considerably less atoms than N_0 . Several experiments have revealed scaling to be valid also for some heteroepitaxial systems, e.g. Ag/Si(111) [21] and Pb/Cu(001) [22].

In the present paper we propose a direct experimental tool which allows to distinguish between thermodynamically-controlled arrays of SML islands and kinetically-controlled ones. The method is based on opposite temperature behavior for the two types of arrays. For kinetically-controlled arrays, the nucleation phase mainly determines the islands density (see also [23]). The larger the temperature is, the larger is the diffusivity. This promotes adatoms to arrive at existing islands rather than to form new ones. Thus, with increasing temperature, the island density should decrease and the average island volume should increase. For equilibrium arrays, the larger the temperature, the larger the entropy contribution to the Helmholtz free energy. Since entropy favors small islands (in the ultimate case individual adatoms), the temperature increase should result in the shrinkage of the islands.

To obtain an equilibrium distribution of island volumes, or, in other words, a distribution of the number of atoms in the islands, we focus on a strongly dilute array of islands and neglect elastic interaction between the islands. We further assume that the islands have identical shape, thus omitting possible shape fluctuations. In equilibrium, under the constraints of a given areal coverage q , the areal concentration of islands consisting of N atoms, P_N , obeys the Gibbs-Boltzmann distribution

$$P_N = \exp \left\{ \frac{\mu N - \tilde{E}(N)}{k_B T} \right\} = \exp \left\{ \frac{[\mu - E(N)] N}{k_B T} \right\}, \quad (4)$$

where $\tilde{E}(N)$ is the energy of the island consisting of N atoms, $E(N)$ is the island energy per atom given by Eq. (1), μ is the chemical potential, and k_B is the Boltzmann constant. The temperature dependence of the chemical potential is determined by the conservation of the total number of atoms, which equals the number of atoms deposited

$$q = \sum_{N=1}^{\infty} N P_N. \quad (5)$$

The solution of Eq. (5) gives the chemical potential as a function of temperature, and its substitution into Eq. (4) gives the equilibrium distribution function of the number of atoms in the islands. Detailed analysis presented elsewhere [24] yields the following. The characteristic temperature, at which the number of atoms in the optimum island decreases by a half with respect to its value at $T = 0$ K, equals

$$T_{\text{char}} = \frac{\Theta}{k_B} \frac{1}{\ln \frac{\pi N_0^4}{q^2}}. \quad (6)$$

This implies the following two points. First, the logarithmic factor in the denominator of Eq. (6) demonstrates the entropy nature of the decrease of the number of atoms in the islands. With decreasing surface coverage (smaller q), more empty sites are found on

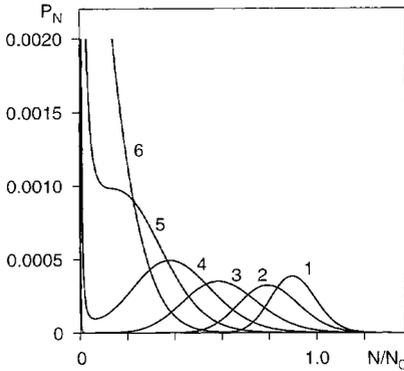


Fig. 1. Equilibrium distribution of the number of atoms in two-dimensional islands in a heteroepitaxial system. The optimum island at $T = 0$ consists of $N_0 = 625$ atoms, and the surface coverage is 0.1. Θ is the characteristic energy of the formation of the optimum island consisting of N_0 atoms; curves correspond to temperatures $k_B T / \Theta = 0.005$ (curve 1), 0.01 (curve 2), 0.02 (curve 3), 0.03 (curve 4), 0.04 (curve 5), and 0.05 (curve 6)

the surface. These empty sites pull atoms from the islands at finite temperature. Second, Eq. (6) gives one more energy scale relevant to an array of islands, in addition to the energy per atom in optimum islands ΔE_{opt} and to the energy of the optimum islands Θ . The characteristic temperature is an intermediate quantity,

$$\Delta E_{\text{opt}} \ll k_B T_{\text{char}} \ll \Theta. \quad (7)$$

An estimate of the characteristic energies for a dilute ($q = 0.1$) array of SML InAs islands on a GaAs(001) surface yields (for $N_0 = 625$) the energy per atom in the optimum islands of about 40 K, and the energy per optimum island of about 25000 K. Then the characteristic temperature T_{char} equals $T_{\text{char}} \approx 800$ K which is in the range of a typical growth temperature of InAs/GaAs QDs.

Figure 1 displays the equilibrium distribution of the number of atoms in the islands at different temperatures calculated for $N_0 = 625$ and $q = 0.1$. With increasing temperature, the local maximum shifts towards smaller islands, and another maximum for individual adatoms evolves. An equilibrium distribution of the number of atoms in the islands is in fact, a bimodal one. At a critical temperature (curve 5) the local maximum for nanometer scale islands disappears and the size distribution becomes a monotonously decreasing function.

For a bimodal distribution, it is natural to split the distribution function in two parts as shown in the inset of Fig. 2. We can attribute the local minimum in the volume distribution function as the volume separating nanometer-scale islands (shaded region) and small clusters (unshaded region). Curve 1 in Fig. 2 gives the temperature dependence of the number of atoms in optimum nanometer-scale islands corresponding to

the local maximum of the distribution function of the island volumes. It decreases approximately linearly with temperature and disappears where the bimodal distribution disappears.

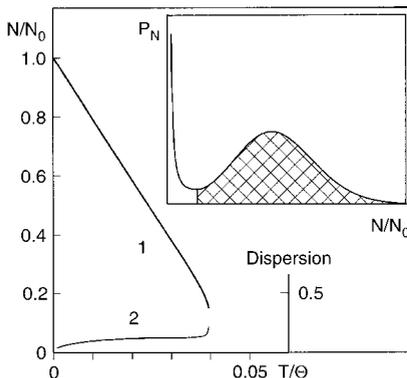


Fig. 2. Temperature dependence of the number of atoms in an optimum island (curve 1) and of the dispersion of the number of atoms in the islands (curve 2). The distribution function of the number of atoms in the islands shown in the inset is divided into two parts: the shaded region corresponds to nanometer-scale islands, and the unshaded region corresponds to small clusters

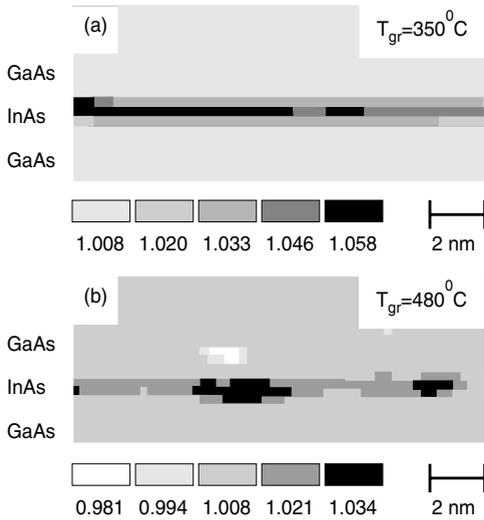


Fig. 3. Cross-sectional images of InAs/GaAs submonolayer insertion obtained by high resolution electron microscopy followed by the DALI evaluation program. The structure grown at lower temperature (350 °C) (a) reveals larger islands than the one grown at higher temperature (480 °C) (b)

appears. Curve 2 in Fig. 2 shows the dispersion of the distribution function of island volumes. The dispersion is nearly temperature-independent in a wide range of temperatures and equals $\approx 15\%$. Experiments have been carried out for InAs/GaAs submonolayer structures grown by MBE at different temperatures. A 0.3 monolayer of InAs was deposited, a growth interruption of 10 s was introduced, and the structures were capped by GaAs. Figure 3 displays cross-sectional high resolution transmission microscopy (HREM) images processed by the DALI evaluation program. Darker regions in Fig. 3 correspond to a larger local lattice parameter in the vertical direction, or, in other words, to a larger content of indium. For a sample grown at 350 °C, rather large islands (> 8 nm) are revealed by HREM (Fig. 3a). For a sample grown at 480 °C, the islands shrink, and a typical size is less than 4 nm (Fig. 3b). Figure 4 displays PL spectra of the structures grown at 350, 450, and 480 °C. With the increase of the growth temperature, the PL peak shifts towards higher energies, which corresponds to smaller sizes of submonolayer islands localizing excitons.

To conclude, we have developed a thermodynamic theory of the temperature dependence of the equilibrium distribution of the number of atoms in submonolayer islands (island volumes). The entropy contribution to the Helmholtz free energy is the driving force of the broadening of the volume distribution and of the decrease of the average island volume. Thus, results of our thermodynamic theory are in contrast to predictions of kinetic theories where an increase in temperature results in an increase of the island

volume, the total number of atoms in the islands remaining constant. Shrinkage of islands with temperature is confirmed qualitatively by HREM and PL

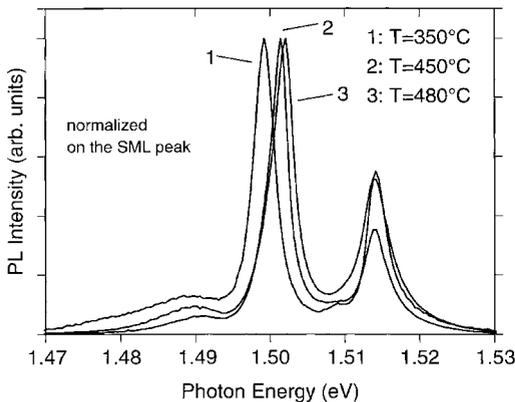


Fig. 4. Photoluminescence (PL) spectra of submonolayer InAs/GaAs structures grown at different temperatures. With the increase of the growth temperature, the PL peak shifts towards higher energies which corresponds to smaller lateral sizes of the islands

data for 0.3 monolayer InAs/GaAs islands, which indicates the thermodynamic nature of this array of islands. Opposite temperature dependencies for thermodynamically-controlled arrays of SML islands and for kinetically-controlled ones create the possibility to experimentally distinguish between the dominating formation mechanisms for any given array of islands.

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