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Thermodynamic modeling of island size distributions for InGaAs/GaAs self assembled quantum dots: a quantitative effort to understand ensemble size nonuniformity

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ABSTRACT

Experimental island count histograms as a function of SAQD volume have been evaluated using an established model. The experimental data was obtained for 51 mm wafers grown by MOCVD and analyzed over the center 26 x 26 mm square of the wafer with AFM. More than one distribution is required for all conditions investigated to obtain adequate representations of the experimental data. Consistent parameters are obtained for samples grown with a variable InAs thickness. Higher growth temperatures results in material being converted into relaxed islands. Extended annealing without AsH_3 eliminates small islands, suggesting that they are not a stable distribution.

INTRODUCTION

InGaAs self-assembled quantum dots (SAQD) have been studied extensively over the past 15 years addressing fundamental questions related to their three-dimensional quantum confinement and a variety of applications. Initial research of InGaAs-based SAQD was motivated by the possibility of achieving active regions that emit at 1.3 or 1.55 μm to replace and improve upon InP-based quantum well devices.[1, 2, 3] SAQD discrete characteristics naturally lead into applications utilizing them for single photon detectors.[4] SAQD have been utilized to demonstrate middle infrared detectors [5,6] and emitters [7].

The optimization of InGaAs SAQD on GaAs (100) has been largely an empirical effort. Basic phenomenological models have provided insight into SAQD formation and development as of function of growth parameters.[8, 9, 10] This can be contrasted to the even more widely studied Ge(Si) on Si (100) system, where extensive fundamental modeling has been undertaken.[11] There is a need for quantitative modeling addressing experimentally determined SAQD size distributions in the InAs/GaAs (100) material system.

A general thermodynamic model for SAQD size distributions was first posed by Shchukin, *et al.*[12] With this model they evaluated the stability of SAQD with respect to ripening. They determined the importance of the surface energy and the dipole interaction energy to distribution stabilization and determined regions where distributions would be stable and unstable. Daruka and Barbási extended this model providing a phase plot of the different regimes of island formation as a function of strain and deposit thickness.[13] More recently Rudd, *et al.* has combined the previous developments into a tractable model that allows fitting experimental histograms of island count versus island size.[14] They applied their model to fitting Ge on Si (100) where the pyramid to dome transition produces bimodal distributions that vary with the growth temperature and Ge thickness deposited.

This article utilizes the thermodynamic model as developed by Rudd, *et al.* and applies it to the InAs on GaAs (100) system. An overview of the derivation leading to development is provided. The conditions relating to sample formation by metal-organic chemical vapor deposition (MOCVD) are given and the details of how the histograms are generated from

extensive atomic force microscopy (AFM) images. The histograms and their fits are compared for a variety of conditions.

MODEL DEVELOPMENT

Since the system under consideration is open and isothermal we use the grand canonical ensemble to describe island evolution. The partition function of interest is given as:

$$\Xi = \sum_{configurations} e^{-(E_{total} - N\mu)\beta} \quad (1)$$

Ξ is the grand partition function for an open system exchanging material and energy with its surroundings. β represents $1/kT$, where T is the absolute temperature of the system, and k is Boltzmann's constant, and μ is the chemical potential of the InAs film. E_{total} is the total internal energy of the ensemble and can be expressed as:

$$E_{total} = \sum_{v} nE_v \quad (2)$$

Where n is the number of islands containing v atoms and E_v is the energy of an island with size v. N is the total number of atoms in all islands and can be expressed as:

$$N = \sum_{v} vn \quad (3)$$

Substituting (2) and (3) into (1) and converting the sum over configurations to a sum over the number of molecules gives:

$$\Xi = \sum_{n} \frac{e^{-\sum_{v} n(E_v - v\mu)\beta}}{n!} = \sum_{n} \frac{\prod_{v} e^{-n(E_v - v\mu)\beta}}{n!} \quad (4)$$

The factorial denominator results from the conversion of the sum over configurations to the sum over states. Ensemble averages for the island size $<n>$ are expressed as:

$$< n >= \frac{\sum_{n}\prod_{v} e^{-n(E_v - v\mu)\beta}\frac{n}{n!}}{\sum_{n}\prod_{v}\frac{e^{-n(E_v - v\mu)\beta}}{n!}} = \frac{\prod_{v}\sum_{n} e^{-n(E_v - v\mu)\beta}\frac{n}{n!}}{\prod_{v}\sum_{n}\frac{e^{-n(E_v - v\mu)\beta}}{n!}} = e^{-(E_v - v\mu)\beta} \quad (5)$$

The energy of an individual island containing v molecules can be expressed as:

$$E_v = (Av + Bv^{2/3} + Cv^{1/3} + D) + (2\lambda\xi^2 v^{2/3}\theta) \quad (6)$$

The coefficients associated with (6) require explanation. In the first term, A represents the elastic energy of the island. It is interpreted in this work as the additional energy the island has due to strain relative to the bulk film. B incorporates surface physics such as the reconstruction and the

surface energy. C introduces edge effects of the island and the surface stress. A more rigorous expression for the edge energy might include an additional logarithmic term to multiply the term included here, but this is neglected in this development to simplify fitting. The volume independent term D can be considered as the energy of the wetting layer relative to the island distribution. The second term incorporates the energy dipole between islands. The elastic coefficients is represented by $\lambda\xi$ is the elastic strain dipole energy of the island, and θ is the thickness deposited. The mathematical expression used for the dipole energy is open to debate, but must be considered for dense ensembles.

The procedure adopted to fit equation (5) and (6) to a distribution of islands involves performing a minimization of the sum of squared differences between the experimentally determined island count for a specific island volume and the calculated number of islands. Island volume was used as the dependent parameter, because it can be calculated from measured data and doesn't require the atomic density of the material to be known. The minimization of the sum of squared differences was performed using the *Solver* routine in *Excel* allowing as many as five variable coefficients for each distribution. Since both A and μ vary with v, only the difference between these coefficients was evaluated. Due to the uncertainty introduced by alloying of the InAs with the GaAs substrate no effort was made to separate λ and ξ. The temperature and material coverage are both treated as known, fixed parameters. A check was performed after a fit is obtained to see how close the calculated coverage based on $\theta = \Sigma_v(v<n>)$ was to the experimental coverage. This was used along with the sum of squared differences to judge the quality of the fit. Since the distributions obtained experimentally showed more than a single island type, two or more distributions are summed together with different coefficients for each distribution. This gives rises to as many as 15 variable coefficients to describe the experimental data.

EXPERIMENTAL DETAILS

The InAs SAQD evaluated were deposited by MOCVD. The surface SAQD samples considered were grown on top of an GaAs/AlGaAs heterostructure containing buried SAQD. The thickness separating the buried SAQD from those of the surface was such that the buried layer should not impact the surface SAQD. The growth sequence follows closely a previously published procedure.[15] A post-growth purge without AsH_3 was introduced after InAs deposition to all SAQD. Two temperatures were considered for InAs SAQD formation: 480°C and 500°C. At 480°C the thickness of InAs deposited was varied: 5.4 Å, 6.0 Å, and 6.6 Å, with a constant post-growth purge without AsH_3 of 10 seconds after deposition. At 500°C the InAs thickness was fixed at 6.0 Å and the post-growth purge time without AsH_3 varied:10 seconds and 60 seconds. These two sample sets allows assessment of coefficients generated by the model to determine if they are consistent when experimental conditions are held constant.

The SAQD density and height were measured using AFM. Imaging was performed under ambient conditions with commercial pyramidal Si tips in tapping mode. Each specimen was analyzed by taking measurements at an array of 81 points, which covered the central 26 x 26 mm^2 region of the wafer. The corners of the array are 7 mm from the wafer edge, and the centers of the array sides are 12.4 mm from the wafer edge. A scan size of 9 μm^2 was used to eliminate the effect of small-scale local variations.

The model developed uses the volume of the SAQD as the independent variable. Experimentally, the volume cannot be determined accurately from AFM because the volume determination is subject to evaluation of island diameter. Instead we have evaluated the

minimum and maximum aspect ratios, α, defined as the ratio of the height to the base diameter ($\alpha \equiv h/d$) of a subset of islands as a function of their height and applied geometric formulas for a spherical cap to determine island volume. The island volume was then calculated as $v = 12\pi h^3 / \alpha^2$. The aspect ratio transformation has been considered as a discontinuous first-order phase transformation, but discontinuous functions introduce mathematical difficulties into the fitting procedure. In our analysis, the dependence of the aspect ratio on island height was defined as $\alpha = \alpha_1 + \Delta\alpha \arctan(h/h_c)$. This assumes a single aspect ratio transformation of the islands consistent with our results. Larger islands relax and grow monotonically [16] which would introduce a third aspect ratio, but this observation is not implemented.

RESULTS AND DISCUSSION

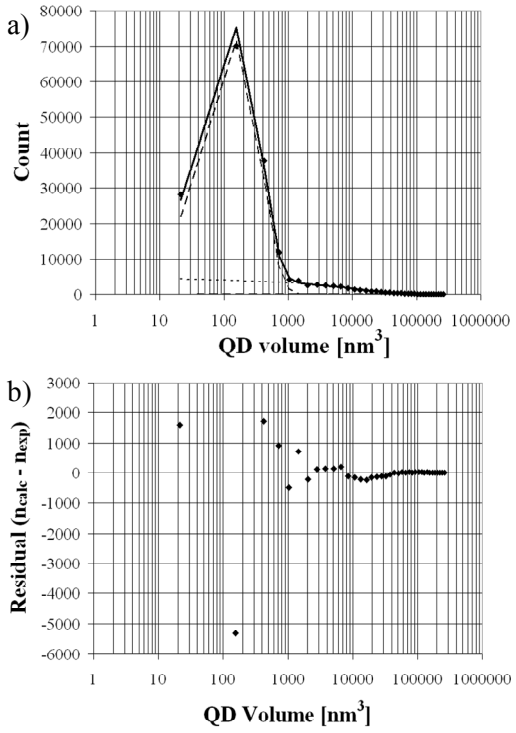

Figure 1. a) Comparison of model to experimental histogram . b) Residual, defined as the difference between the fit and experimental data.

Figure 1a shows the island volume histogram and the associated fit obtained with the model for the sample grown at 480°C with 6.0 Å of InAs. Two distributions are required for adequate fitting of the histogram which is consistent with reports which identify a pyramid to dome transition in InAs/GaAs SAQD.[17] Figure 1b shows the residual defined as the difference between the calculated and experimental counts. At low island volumes large absolute deviations between the fit and the data exist corresponding to about 8 percent of the experimental value. At larger island sizes the absolute fit is much better, but the percentage deviation can be as large as 16 percent.

Figure 1a can be compared to the other conditions observed for smaller and larger depositions of InAs. Figure 2a displays the histogram and its fit for 5.4 Å of InAs. Again two distributions are needed to fit the data adequately. The number of islands involved in the second distribution is lower. For the 5.4 Å sample no clear peak is observed for the first distribution, instead a broad shoulder is observed. When 6.6 Å of InAs is deposited (Figure 2b) for SAQD formation the number of islands in the first distribution decreases and the number of islands associated with the second distribution increases.

The validity of the model requires a quantitative comparison of the model parameters for constant conditions where one of the model variables is changed. In our case the sample thickness was varied. Table I summarizes the coefficients obtained for fits displayed in Figures 1 and 2. Analysis of the results concluded that $\lambda_2\xi^2$ needed to be fixed at a value of zero. This is physically realistic because the large islands have a low enough density that they do not interact elastically as the smaller, denser islands do. In addition to the coefficients obtained, the

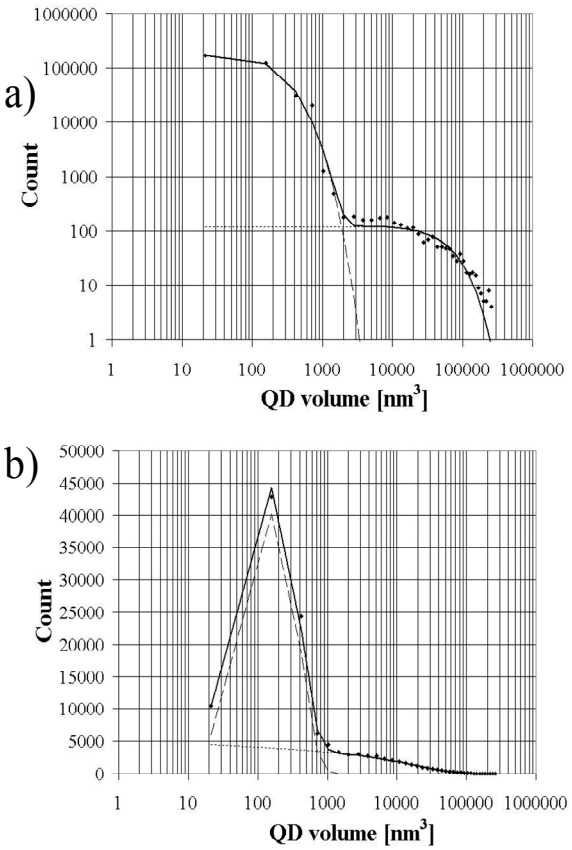

Figure 2. Experimental distributions with fits for samples grown with an InAs thickness of a) 5.4 Å and b) 6.6 Å.

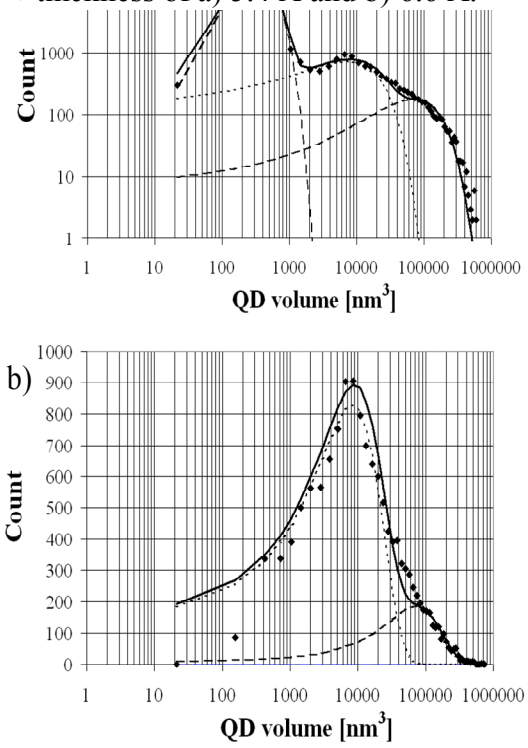

Figure 3. Experimental distributions with fits for samples grown at 500°C with a) 10 sec PGP without AsH_3 and b) 60 sec PGP without AsH_3.

Tabel I. Summary of parameters for the samples grown at 480°C.

	T [K]	753	753	753
	θ [Å]	6.6	6.0	5.4
	AsH_3 pressure [torr]	0.27	0.27	0.27
	PGP time [seconds]	10	10	10
A1[eV/atom]	x 10^6	-4.13	-1.24	-1.30
B1[eV/atom$^{2/3}$]	x 10^4	-2.85	-2.91	-3.10
C1[eV/atom$^{1/3}$]	x 10^2	-6.7	-4.7	1.6
D1[eV]		-0.20	-0.4	-0.72
$\lambda_1\xi^2$[eV/Å/atom$^{2/3}$]	x 10^3	1.20	0.99	0.68
A2[eV/atom]	x 10^7	1.11	1.22	1.11
B2[eV/atom$^{2/3}$]	x 10^6	-5.72	-4.37	-7.29
C2[eV/atom$^{1/3}$]	x 10^3	1.12	1.12	0.076
D2[eV]		-0.55	-0.55	-0.31
θ_1 [Å]		0.3	0.45	0.67
θ_2 [Å]		6.01	4.64	0.75

calculated planar thickness of InAs that makes up each distribution is given at the bottom of the table. Most of the coefficients are reproduced well, with the exception being C_2.
Increasing the growth temperature to 500°C for a deposition of 6 Å requires a third distribution to be included to fit the data adequately. The fit obtained in shown in Figure 3a. The physical origin of the third distribution is speculated to be the strain relaxation of a significant number of the islands. Extending the purge time at 500°C to 60 seconds eliminates the first distribution as shown in Figure 3b, indicating that the small islands are unstable with respect to ripening for long anneals without AsH_3.

CONCLUSION

We have evaluated island count histograms as a function of volume for two MOCVD conditions using an established model. More than one distribution is required for all conditions investigated. InAs thicknesses near the critical thickness for island formation and temperatures at or below 480°C are necessary to minimize the second distribution. Consistent parameters are obtained for samples grown with variations in the InAs thickness. Higher growth temperature results in material being converted into what we propose to be relaxed islands. Extended annealing without AsH_3 eliminates small islands and leaves the distributions with larger islands unchanged, suggesting that the distribution composed of small islands is not stable for all volumes.

ACKNOWLEDGEMENTS

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