Regimes of GaAs quantum dot self-assembly by droplet epitaxy

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Two regimes are observed for the density of strain-free GaAs quantum dots (QDs) grown by Ga droplet epitaxy. QDs grown from liquid Ga droplets deposited at temperatures up to 200 °C exhibit densities that qualitatively agree with classical nucleation theory and are quantitatively reproduced by a rate equations based growth model under consideration of dimer break off. In contrast, at higher growth temperatures, the onset of coarsening by Ostwald ripening [Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **34**, 495 (1900)] causes drastically reduced QD densities. Extension of the growth models and consideration of Ostwald ripening allow the quantitative prediction of QD densities in this regime, as well.

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I. INTRODUCTION

The fabrication of quantum dots (ODs) in a selfassembled fashion by applying droplet epitaxy is an interesting alternative to the established technology of strain-driven InAs OD formation in Stranski-Krastanov mode. During droplet epitaxy, the QD formation process consists of two stages. First, liquid Ga or In droplets are grown in a Volmer-Weber-like mode, followed by crystallization and transformation into semiconductor QDs under As pressure. In comparison to the Stranski-Krastanov QDs, the method of droplet epitaxy is more flexible with regard to the choice of the QD material. For example, fabrication of strain-free GaAs QDs,^{1,2} InGaAs QDs with controlled In content,^{3,4} and InAs QDs⁵ has been demonstrated. Furthermore, besides QD-like structures, recent experimental droplet-epitaxy studies demonstrate, e.g., the generation of QD molecules,¹ quantum rings,⁶ and concentric double rings.^{2,7,8}

However, so far, to the best of our knowledge, no theoretical description of the underlying growth mechanism is available, which would enable the precise prediction of the QD density as a function of growth parameters. Therefore, we study the processes responsible for the droplet epitaxial formation of GaAs QDs on AlGaAs by atomic force microscopy (AFM) combined with a kinetic rate equations based growth model and scaling analysis.

II. EXPERIMENTS

The growth experiments were performed in a solid-source molecular beam epitaxy system equipped with an effusion cell for Ga evaporation and a valved-cracker cell for As. On (001) GaAs wafers, a 100 nm thick AlGaAs layer with Al content of 0.3 was grown at 580 °C. Subsequently, the As flux was stopped and the substrate temperature was reduced down to T=140, ..., 300 °C. In the next step, liquid Ga droplets were formed during Ga deposition without As flux. Deposition of Ga with flux F=0.025, ..., 0.79 ML/s for a time t resulted in a Ga surface coverage of $\theta=Ft$. We would

like to note that the initial AlGaAs substrate surface is As terminated. Due to the strong binding energy to As in the substrate, the first Ga monolayer (ML) is consumed for the formation of a Ga terminated surface structure and does not contribute to the formation of Ga droplets. This picture is supported by our coverage dependent experiments, which indicate that no GaAs QDs are formed on samples with a Ga surface coverage of less than 1 ML.

After Ga droplet formation, a 60 s pause was applied for equilibration followed by the crystallization of the droplets and their transformation into GaAs QDs during As₄ supply for 120 s at growth temperature. The As₄ pressure during crystallization corresponded to a flux gauge reading of about 1×10^{-4} Torr. After crystallization, the QDs were annealed for 10 min at T=350 °C.

Ga droplets after quenching as well as crystallized GaAs QDs are inspected with atomic force microscopy in tapping mode. Examples are shown in Fig. 1. Investigations of the influence of the growth conditions on the shape of the GaAs QDs are described elsewhere.⁹ The QD surface density N measured with AFM gives the number of GaAs QDs per cm², whereas the Ga droplet density n in our growth model



FIG. 1. (Color online) $5 \times 2.5 \ \mu\text{m}$ AFM images of GaAs QDs grown by droplet epitaxy at F=0.025 ML/s, $\theta=3.75 \text{ ML}$, and indicated *T*.



FIG. 2. Surface density *N* of GaAs QDs as a function of Ga flux *F* at T=200 °C and $\theta=3.75$ ML. Symbols reflect results of AFM measurements, the continuous line is calculated with model 2, and the dotted line is calculated from the scaling law of Eq. (8).

yields the number of droplets per surface site. In order to compare both quantities, we use $N=nN_s$, with the density $N_s=6.25 \times 10^{14}$ cm⁻² of sites on a (001) GaAs surface.

Figure 2 shows measured QD surface densities as function of the Ga flux F. We find a rise of N with F, which is in agreement with commonly observed nucleation behavior and is caused by the increasing number of nucleation processes at higher adatom density. The decrease of N with increasing Tin Fig. 3 reflects the well known effect that with higher surface activity, the adatoms will rather attach to existing clusters instead of nucleating new ones.

III. GROWTH MODELS

For a quantitative interpretation of the data, we now introduce two rate equations based models of QD formation by droplet epitaxy. Model 1 considers irreversible aggregation,



FIG. 3. Surface density *N* of GaAs QDs vs growth temperature *T* at θ =3.75 ML and indicated *F*. Symbols reflect results of AFM measurements, the continuous line is calculated with model 2, the dashed line considers, in addition, Ostwald ripening, and the dotted line is calculated using the scaling law of Eq. (8).

whereas model 2 allows dimer break off. Rate equations are established as a powerful tool for modeling complex growth processes such as, e.g., the self-assembled formation of InAs QDs.^{10,11}

We assume that all Ga droplets transform into GaAs QDs during As_4 exposure. This assumption is confirmed by several reference samples which were grown at $T = 200, ..., 260 \,^{\circ}\text{C}$ and quenched without a crystallization step directly after Ga droplet formation. The Ga droplet densities of these samples agree with the GaAs QD densities of samples where the Ga droplets have been formed under identical conditions but with a crystallization step. Thus, we assume that the Ga droplet densities calculated with our growth models can be directly compared to GaAs QD surface densities measured with AFM.

As discussed above, the first Ga monolayer is consumed for the transition from an As terminated to a Ga terminated surface. Only the excessive Ga atoms for $\theta > 1$ ML contribute to Ga droplet formation. After finishing the Ga terminated surface structure, impinging Ga atoms perform a thermally activated random walk on the surface, which is characterized by the surface diffusion coefficient D $= \nu \exp[-E_s/(k_B T)]$, with the surface diffusion activation energy E_s , the vibrational frequency¹² $\nu = 2k_BT/h$, Boltzmann's constant k_B , and Planck's constant h. Collisions between diffusing monomers lead to formation of dimers which act as nuclei for the generation of Ga droplets. Model 1 considers irreversible aggregation; i.e., a dimer is assumed to be already stable. In this case, the dimers are counted as smallest possible droplets. The time evolution of the density of mobile Ga monomers n_1 on the surface and of the density of Ga droplets *n* is described by

$$\dot{n}_1(t) = F - Dn_1(2\sigma_1 n_1 + \sigma n),$$
 (1)

$$\dot{n}(t) = D\sigma_1 n_1^2, \tag{2}$$

with the capture numbers of monomers σ_1 and droplets σ . These capture numbers reflect the depletion of the monomer density around the droplets^{13,14} $\sigma = 2\pi (r/\lambda)k_1(r/\lambda)/k_0(r/\lambda)$, with the modified Bessel functions k_0 , k_1 , the effective droplet radius r, and the surface diffusion length¹⁴ $\lambda^{-2} = (F/D)$ $+ 2\sigma_1 n_1 + \sigma n$. We assume that prior to crystallization, the Ga droplets are hemispherically shaped, leading to an effective radius of $r = \sqrt[3]{(3/2\pi)V}$, where $V = (\theta - 1 - n_1)/n$ is the droplet volume. This approach for V considers that the first Ga monolayer is consumed for the transition from an As terminated to a Ga terminated surface. For monomers, we take $V_1=1$.

Equations (1) and (2) are calculated self-consistently with respect to λ according to the approach of Bales and Chrzan.¹⁴ We would like to emphasize that in model 1 the only free parameter is the surface diffusion barrier E_s . Figure 4 shows values of N calculated as a function of E_s for F = 0.2 ML/s and T = 200 °C.

Qualitatively, the decrease of N with E_s is in accordance with the results of Fig. 3, and reflects that the reduction of an energy barrier is equivalent to a temperature rise. However, the most important result of Fig. 4 establishes, even for very



FIG. 4. QD surface density calculated for F=0.2 ML/s, T=200 °C, and $\theta=3.75$ ML as a function of E_s using model 1 and model 2 with $E_2=0.5$, 0.4, 0.3, and 0.2 eV. The dashed line represents the experimental density determined with AFM at corresponding growth parameters.

low E_s , that model 1 yields significantly higher QD densities in comparison to the experimental result. Theoretical studies compute values of E_s in the range from 0.14 up to 0.60 eV.^{15,16} We, thus, conclude that the assumption of irreversible aggregation during nucleation of Ga droplets is unrealistic.

As an extension to model 1, in model 2 we consider dimer break off with rate $R = \nu \exp[-(E_s + E_2)/(k_BT)]$. That means a dimer can either break into two monomers or becomes stable by capturing an additional adatom. The volume of stable Ga droplets is now $V = (\theta - 1 - n_1 - 2n_2)/N$, and the rate equations are extended by the dimer density n_2 :

$$\dot{n}_1(t) = F - Dn_1(2\sigma_1n_1 + \sigma_2n_2 + \sigma_n) + 2Rn_2, \qquad (3)$$

$$\dot{n}_2(t) = Dn_1(\sigma_1 n_1 - \sigma_2 n_2) - Rn_2, \qquad (4)$$

$$\dot{n}(t) = Dn_1 \sigma_2 n_2. \tag{5}$$

Model 2 has two free parameters E_s and E_2 . Figure 4 shows N vs E_s calculated for different values of E_2 and demonstrates that model 2 is able to quantitatively reproduce the experimental QD density. Agreement with the experimental value is obtained for several combinations of E_s and E_2 . Interestingly, every set of parameters that fits experimental data follows the condition $2E_s+E_2 \approx 0.9$ eV. This observation will be confirmed below by the scaling analysis. Reasonable values of E_s are expected in the range from 0.14 eV (Ref. 16) up to 0.4 eV according to the above condition.

IV. REGIMES OF QUANTUM DOT DENSITY

In Figs. 2 and 3, measured values of N as a function of F and T are compared to results calculated using model 2 with $E_s=0.3 \text{ eV}$ and $E_2=0.3 \text{ eV}$. Two regimes can be distinguished concerning the degree of agreement between model results and experimental data. Very good agreement is demonstrated for the flux dependent data at T=200 °C (Fig. 2) using the above values of E_s and E_2 . The temperature dependent data (Fig. 3) in the range of $T \le 200$ °C are quantitatively reproduced by model 2, as well. This very good agreement indicates that model 2 with only two free energy values quantitatively describes the major processes during Ga droplet epitaxy in this regime. On the other hand, for T > 200 °C, the measured QD densities are drastically reduced in comparison to the model predictions. In the following, this interesting deviation will be discussed.

Classical nucleation theory¹³ predicts the density of stable three-dimensional clusters by a scaling law

$$n \propto F^p \exp[E/(k_B T)]. \tag{6}$$

In the case of complete condensation of three-dimensional clusters, p=i/(i+2.5) and $E=p(E_s+E_i/i)$, with the critical cluster size *i* and the energy of a critical cluster E_i . In the regime at $T \le 200$ °C, the slope of our flux dependent data in Fig. 2 fits p=0.50 and thus i=2.5. This value of *i* confirms our finding that dimers are unstable and trimers represent the smallest stable island size. The slope of the temperature dependent data for T < 200 °C agrees with a value of *E* of about 0.225 eV. Assuming $E_2=2E_i/i$, we get an analytical derivation of the above empirical finding, $E_2+2E_s=2E/p=0.90$ eV. Since this condition does not depend on the growth parameters, we conclude that an independent determination of E_s and E_2 from measurements of the QD density is not possible.

On the other hand, in the regime of T > 200 °C, the measured values of N deviate from the predictions of model 2 with the above parameters. We will show now that this change cannot be understood within the framework of classical nucleation theory. Regarding the scaling law in Eq. (6), the stronger slope of N vs T at T > 200 °C fits a significantly higher E of about 1 eV. Furthermore, at T=260 °C, the experimental flux dependence yields a higher p of about 0.95. The higher *p* corresponds to an increase of the critical cluster size to a value of $i \simeq 50$. Assuming at this stage unchanged E_s and E_i/i , the higher value of *i* would lead to E=0.43 eV. This value is still significantly smaller than the observed value of E=1 eV. From a mathematical point of view, the higher E in Eq. (6) requires higher values of E_s or E_i/i . However, an increase of both energy values physically makes no sense. A higher value of E_i/i would represent stronger bonds inside the clusters, which is not consistent with the observation of an increase of the critical cluster size. An increase of i indicates that detachment of atoms even from large clusters becomes significant and, thus, points out a small value of E_i/i . As is visible in Fig. 4, a higher E_s yields an increase of N and not the observed strong reduction. These considerations demonstrate that the experimental QD densities at T > 200 °C are not consistent with classical nucleation theory.

We attribute the reduction of the measured QD densities at T > 200 °C in comparison to the results of model 2 to the onset of coarsening by Ostwald ripening.¹⁷ Ostwald ripening means growth of large clusters on the cost of smaller ones and hence causes a decrease of the total cluster density. In the present experiments, Ostwald ripening might take place during the late stage of droplet growth,¹⁸ the growth interruption between droplet formation and crystallization,¹⁹ or during the crystallization step. In order to clarify this point, we refer to the above experiments showing the equality of Ga droplet densities and GaAs QD densities for identical growth conditions. These experiments demonstrate that at T > 200 °C, also the Ga droplet density is reduced in comparison to results of model 2 and that the density remains nearly constant after droplet formation has finished. Considering these experiments, we conclude that Ostwald ripening takes place mainly during the process of Ga droplet formation.

From classical mean field theory¹⁸ of Ostwald ripening under mass conservation, the evolution of the cluster density as a function of time t_r is predicted¹⁹ as

$$n(t_r) = n_0 (1 + t_r / \tau_r)^{-m}, \tag{7}$$

where n_0 is the droplet density as calculated with model 2, and *m* is a scaling exponent that is equal to 1 for threedimensional islands coupled via adatom diffusion on a twodimensional surface in the interface-reaction-limited case.¹⁹ We assume an activated temperature dependence τ_r $= \nu^{-1} \exp[E_r/(k_B T)]$, where E_r is a constant.

Figure 3 shows values of N calculated under consideration of Ostwald ripening with model 2 and Eq. (7). The ripening time is $t_r = (\theta - 1)/F$. For the droplet growth related energies, the above values of $E_s = 0.3$ eV and $E_2 = 0.3$ eV are used. The value of the only free parameter $E_r = 1.5$ eV is chosen with respect to best agreement with the experimental data. The very good reproduction of the experimental temperature dependence and the fact that the only Ostwald ripening related parameter E_r fits both our measurements at F = 0.79 ML/s and at F = 0.025 ML/s suggest the validity of our model.

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Furthermore, by combining Eqs. (6) and (7), an extended scaling law is obtained that considers Ostwald ripening:

$$n = jF^{p} \left[\nu^{-1} \exp\left(\frac{-E}{k_{B}T}\right) + t_{r} \exp\left(\frac{-E-E_{r}}{k_{B}T}\right) \right]^{-1}$$
(8)

with constant *j*. As is demonstrated in Figs. 2 and 3, results of the scaling law using $j=5 \times 10^{-6}$ and the above values of p=0.5, E=0.225 eV, and $E_r=1.5$ eV agree very well with the experimental behavior, too.

V. CONCLUSIONS

In conclusion, the nucleation of liquid Ga droplets and their crystallization into GaAs quantum dots are studied experimentally and theoretically. We find that all droplets transform into crystalline QDs, which establishes that the QD density can be calculated directly with our model of droplet growth. The growth model is based on kinetic rate equations and reproduces QD densities correctly up to growth temperatures of $T < 200 \,^{\circ}$ C. Higher growth temperatures require the consideration of coarsening by Ostwald ripening. The QD density also in this regime is successfully reproduced by an extended model. At high growth temperatures and slow growth speed, drastically reduced QD densities enable the fabrication of samples which are compatible with microscopy based setups for photoluminescence spectroscopy of single QDs.²⁰

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