# Ripening of single-layer InGaAs islands on GaAs (001)*

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The present paper discusses our investigation of InGaAs surface morphology annealed for different lengths of time. After annealing for 15 min, the ripening of InGaAs islands is completed. The real space scanning tunneling microscopy (STM) images show the evolution of InGaAs surface morphology. A half-terrace diffusion theoretical model based on thermodynamic theory is proposed to estimate the annealing time for obtaining flat morphology. The annealing time calculated by the proposed theory is in agreement with the experimental results.

**Keywords:** scanning tunneling microscopy, morphology of films, annealing, diffusion in nanoscale solids

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## 1. Introduction

Ostwald ripening[1] plays an important role in two-dimensional (2D) layer-by-layer growth and heat treatment of samples. The ripening process has been studied by experiment and computer simulation.[2–7] In Ostwald ripening, the diffusion of the surface adatoms between islands of different sizes is a two-way process in which adatoms can detach from either small islands or big ones. The larger islands have lower free energies because the Gibbs–Thomson chemical potential of an isolated 2D island is inversely proportional to its area.[8] Total free energy of the system always decreases, larger islands grow and small islands gradually disappear so that the system can reach equilibrium.[9] During annealing, if the diffusion distance of adatoms is shorter than the terrace width, adatoms will nucleate on the terrace, forming islands to relieve strain.[10]

Thermodynamic theory can be applied to predict surface morphology phenomenologically.[11–15] According to thermodynamic theory, the average diffusion speed of surface adatoms is determined by migration ratio and driving force, where migration ratio can be calculated by thermodynamic formulas and the driving force of the ripening is closely related to the surface energy.[11] The anisotropic diffusion of InGaAs adatoms during annealing has been studied.[16] Reflection high-energy electron diffraction (RHEED) can be used to monitor the surface morphology *in situ*,[17] however, a real space image cannot be obtained by this method. During InGaAs/GaAs annealing, higher $As_4$ beam equivalent pressure (BEP) will lead to small islands forming bigger ones and the surface coverage of islands will be lowered.[18] Also, the miscut angle of GaAs substrate, which determines the average terrace width on the substrate, can suppress Ostwald ripening.[6]

During epitaxial growth, adatoms of In, Ga, and As nucleate on the surface. Immediately after the growth ends, adatoms form single-layer-isolated islands that evenly distribute on the terraces at different heights. There are always several terraces at different heights in one STM image. Theoretically, isolated islands on a terrace can be treated as a whole and imagined as a point of mass; movement of the center of mass can be used to indicate the diffusion process. Since the islands distribute evenly on the terrace, the center of mass of islands should be in the center of the selected area. During annealing, the center of mass moves along $[1\bar{1}0]$ and this unidirectional movement goes toward the step edge of a terrace that is one layer higher. For this reason, the maximum diffusion distance of the center of mass is half of the terrace width in selected areas.

Past research was mainly focused on theoretical calculation,[11–15] while little attention has been paid to the effective diffusion distance of surface adatoms based on experimental results of semiconductor surfaces during the ripening process. In this study, we apply thermodynamic theory to the annealing process of InGaAs islands, and we propose a half-terrace diffusion model based on thermodynamic theory to explain the experimental phenomenon of annealing, according

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to the analysis of real space scanning tunneling microscopy (STM) images. In the half-terrace diffusion model, the effective diffusion distance and average diffusion speed of adatoms on the terraces can be calculated; in this way, the annealing time for the flat terrace can be estimated. Furthermore, the half-terrace diffusion model can be applied to predict the necessary annealing time for obtaining a flat terrace of InGaAs.

## 2. Experiment

The epitaxial growth and surface morphology analysis were carried out by a molecular beam epitaxy (MBE)–STM combined system. During epitaxial growth, the sample was monitored by RHEED to obtain the growth rate and the surface morphology *in situ*. First, a GaAs buffer layer of approximately 150 nm was grown on GaAs (001) substrate at 560 °C under $As_4$ BEP of $1.06\times10^{-3}$ Pa. Then $In_{0.15}Ga_{0.85}As$ film was grown at 450 °C under $As_4$ BEP of $1.06\times10^{-3}$ Pa. RHEED oscillation of InGaAs film growth is shown in Fig. 1. The growth rate of InGaAs film was determined to be 0.344 monolayer/s (ML/s). The growth process lasted 46 seconds, and approximately 16 layers of $In_{0.15}Ga_{0.85}As$ film were deposited on the surface.

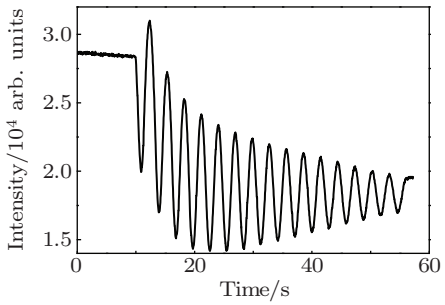



**Fig. 1.** RHEED oscillation curve of $In_{0.15}Ga_{0.85}As$ film at 450 °C and $As_4$ BEP = $1.06\times10^{-3}$ Pa, growth rate = 0.344 ML/s.

After deposition, the $In_{0.15}Ga_{0.85}As$ film was annealed *in situ* at 450 °C under $As_4$ BEP of $1.06\times10^{-3}$ Pa. After annealing, the sample was cooled down to room temperature at the fastest speed and transferred to the STM chamber for scanning. We repeated the growth and annealing process mentioned above for three experiments, each experiment with a different annealing time: 0 min, 5 min, and 15 min. After annealing for 15 min, an $In_{0.15}Ga_{0.85}As$ surface with flat terraces was obtained. Three 1000 nm×1000 nm STM images were obtained at about −3 V gap voltage, as shown in Fig. 2.

## 3. Results and discussion

Figure 1 shows that the RHEED oscillation of $In_{0.15}Ga_{0.85}As$ remains stable with precisely the same periodicity even after 16 periods. It also indicates that the $In_{0.15}Ga_{0.85}As$ film was grown layer by layer[19] and the surface is in good condition.

STM images of $In_{0.15}Ga_{0.85}As$ film with different annealing time are shown in Fig. 2. Figure 2(a) indicates the disordered surface morphology of $In_{0.15}Ga_{0.85}As$ film without annealing; small islands with one monolayer height are evenly distributed on terraces. During annealing, driven by thermal activation energy, adatoms diffuse from one island to another. Because larger islands are more stable, the quantity of adatoms in smaller islands becomes lower and lower. When the sample was annealed for 5 min, as shown in Fig. 2(b), due to Ostwald ripening of the islands, adatoms detach from smaller islands and attach to larger islands, so the average size of islands becomes larger than that in Fig. 2(a) and island coverage decreases. For a longer annealing time of 15 min in Fig. 2(c), ripening of surface islands continues; finally, the island coverage decreases to 6.3%, nearly a clean and flat surface. This indicates the islands have gathered to form a flat morphology.

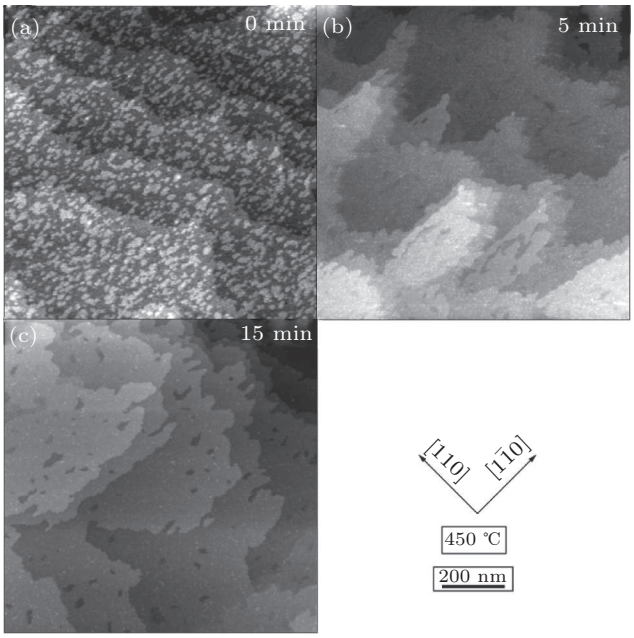



**Fig. 2.** The STM images of $In_{0.15}Ga_{0.85}As$/GaAs films with different annealing time at 450 °C, $As_4$ BEP = $1.06\times10^{-3}$ Pa. (a) $In_{0.15}Ga_{0.85}As$/GaAs, without annealing, gap voltage = −2.7 V, $I$ = 120 pA; (b) $In_{0.15}Ga_{0.85}As$/GaAs, annealing time 5 min, gap voltage = −2.7 V, $I$ = 150 pA; (c) $In_{0.15}Ga_{0.85}As$/GaAs, annealing time 15 min, gap voltage = −2.9 V, $I$ = 150 pA.

Island coverage was calculated by choosing ten 100 nm×100 nm areas cropped from STM images which contain single-layer terraces from Figs. 2(a), 2(b), and 2(c), 30 images were chosen in total, island coverage was calculated by averaging ten values in three groups. Figure 3 indicates the $In_{0.15}Ga_{0.85}As$ islands coverage decreased as annealing time extended. The data points can be fitted in a solid line with a simple exponential decay function. The fitted time constant is 17.3 min, which is longer than the experimental annealing time. In our experiment, when annealing time is increased to 15 min, the surface morphology is almost flat and the island coverage is very low.

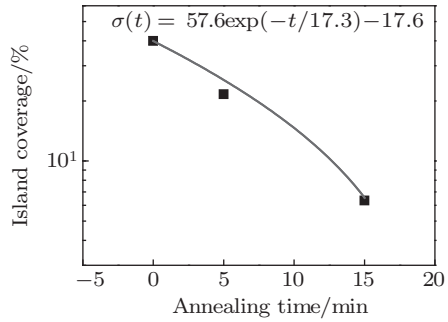



**Fig. 3.** $In_{0.15}Ga_{0.85}As$ island coverage on GaAs (001) as a function of annealing time. The data points were fitted to an exponential function.

According to thermodynamic theory,[11] the average diffusion speed $v$ can be expressed as

$$v \approx M \times F, \tag{1}$$

where $M$ is the migration ratio, $F$ is the driving force. Migration ratio is defined as follows:[11]

$$M \approx \kappa\left(\frac{D}{RT\lambda}\right), \tag{2}$$

where $\kappa$ is the adaption coefficient, $D$ is the diffusion coefficient, $R = 8.314$ J/mol·K, is the mole gas constant, $T$ is temperature of the substrate, which is 723.16 K, and $\lambda$ is the unit hopping distance of adatoms, which is considered to be the space between two nearest top atoms on the surface of $In_{0.15}Ga_{0.85}As$, as shown in Fig. 4. Here, we ideally consider that the diffusion atoms do not exchange with the under-layer atoms, so the diffusion atoms meet the top layer adatoms of $In_{0.15}Ga_{0.85}As$ only. Because the temperature of the substrate remains constant and top atoms do not change with under-layer atoms, we can suppose the energy of adatoms remains the same if the adatoms hop and move toward larger islands in the overall migration of adatoms.

During annealing, we assume the adatoms that detach from small islands can firmly attach to larger islands; we can take that $\kappa \approx 0.5 \times 10^{-4}$ according to the results by Nishizawa.[11] The diffusion coefficient of the surface adatoms $D^{\mathrm{surf}}$ can be estimated by the formula[11]

$$D^{\mathrm{surf}} \approx 7 \times 10^{-6} \exp\left[-\frac{56}{R}\left(\frac{T_{\mathrm{m}}}{T}\right)\right], \tag{3}$$

where $T_{\mathrm{m}}$ is the melting point of a single element. Considering atomic composition of $In_{0.15}Ga_{0.85}As$ film, we denote the surface diffusion coefficient of the three elements as $D^{\mathrm{surf-In}}$, $D^{\mathrm{surf-Ga}}$, $D^{\mathrm{surf-As}}$, respectively. The average $D^{\mathrm{surf-av}}$ is calculated by the weighted mean value of the $In_{0.15}Ga_{0.85}As$ composition:

$$\begin{aligned} D^{\mathrm{surf-av}} &= (0.15D^{\mathrm{surf-In}} + 0.85D^{\mathrm{surf-Ga}}) \times 0.5 + 0.5D^{\mathrm{surf-As}} \\ &\approx 1.87 \times 10^{-7}\ \mathrm{m^2/s}. \end{aligned} \tag{4}$$

The thermal activation energy provides the probability for the surface adatoms diffusing from one island to another, while the driving force is not the activation energy, it should be regarded as the surface free energy $\Delta G$, the free energy per atom $\Delta G/N$ has been reported of being about 0.026 eV for a one-layer-island of 39.9% coverage.[20] The parameter $N$ is the number of adatoms deposited on the sample and it can be described as

$$N = \theta L^2 d, \tag{5}$$

where $\theta$ is the island coverage, $L^2$ is the lattice site number of single $In_{0.15}Ga_{0.85}As$ layer on the substrate, $d$ is the number of layers ($d = 16$ layers for this experiment). The size of the substrate we used is 1 cm×1 cm, so $L^2$ can be calculated accordingly as about $6.25 \times 10^{14}$.

From the above discussion, the formula of the average diffusion speed $v$ can be given as[11]

$$v \approx \kappa\left(\frac{D}{RT\lambda}\right)\Delta G. \tag{6}$$

We substituted all the required parameters into the formula and derived the value to be 0.065 nm/s.

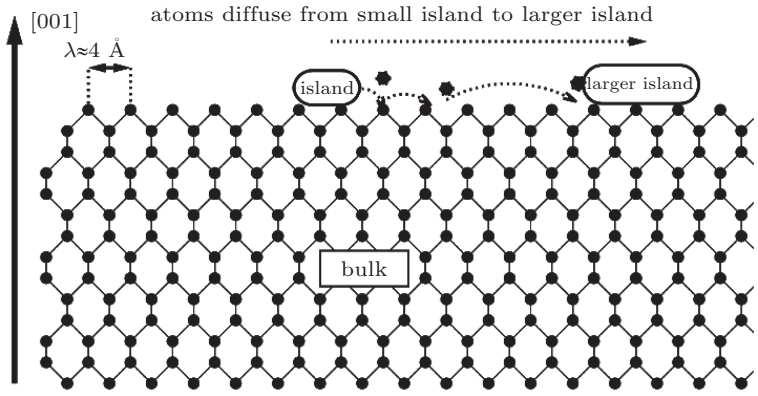



**Fig. 4.** Diagram of adatoms diffusing on the bulk-terminated surface in the [001] direction. The unit hopping distance $\lambda$ is the space between two nearest top atoms.

Before annealing, the small islands on the surface are distributed evenly in one single layer. During the annealing process, the islands join together to form flat terraces after the Ostwald ripening. In order to closely investigate the diffusion behavior of the adatoms in $In_{0.15}Ga_{0.85}As$ film, we select two STM images that contain only two layers from Fig. 2(a) and Fig. 2(c) with the size of 200 nm×200 nm. The magnified images are illustrated in Fig. 5. The outlines of the single-layer islands and the terraces are drawn with gray-level lines, while black solid circles represent the mass center of single-layer islands. In Fig. 5(a), the mass center of islands before annealing is at the center of the STM image. During the ripening process, the mass center diffuses across the white solid line in Fig. 5(a). The diffusion direction of adatoms is along the $[1\bar{1}0]$ direction, which is similar to that in GaAs (001)-surface during annealing.[21] Therefore, approximately half of them need to travel across the white solid line. We suppose the total diffusion distance is the diagonal length of the image; when annealing time reaches 15 min, as shown in Fig. 5(b), the mass center has moved one quarter of the length of the diagonal. Figure 5 depicts the mass center moving from Fig. 5(a) to Fig. 5(b) along the dashed arrow line, so its effective diffusion distance is one-quarter of the total diffusion distance, or the single-layer terrace width.




**Fig. 5.** 200 nm×200 nm STM images of $In_{0.15}Ga_{0.85}As$ islands diffusing and converging on the terrace. (a) $In_{0.15}Ga_{0.85}As$ islands without annealing, the boundary islands need to move across the solid white line and the dashed arrow shows their diffusion direction. (b) $In_{0.15}Ga_{0.85}As$ terrace formed by annealing for 15 min. The black solid circles in panels (a) and (b) represent the mass center of all islands.

There are six terraces in the 1000 nm×1000 nm STM image of the $In_{0.15}Ga_{0.85}As$ film before annealing. The diagonal length of the image is about 1414 nm, so one-quarter of a single terrace width is about 59 nm if we assume that the terrace evenly divides the diagonal in the image, as calculated by the following formula

$$L_{\text{eff}} = 1414/(4\times 6) = 59 \text{ nm}. \quad (7)$$

Since the average diffusion speed has been calculated to be 0.061 nm/s, the theoretical necessary annealing time can be determined as

$$t = 59/0.065 = 908 \text{ s} = 15.1 \text{ min}. \quad (8)$$

As mentioned above, there are still 6.3% islands after annealing for 15 minutes in the morphology of the $In_{0.15}Ga_{0.85}As$ film sample. Actually, we obtained an annealing time constant of 17.3 min by fitting the islands coverage data points in Fig. 3. This demonstrates the $In_{0.15}Ga_{0.85}As$ film needs an annealing time longer than 15 min to obtain a perfectly flat surface. And here, the thermodynamic calculation result indicates the necessary annealing time is 15.1 min. The relative error between the two methods is about 13%. Considering the errors introduced in the estimation of the thermodynamic model, the agreement reveals that the theoretical model we proposed is feasible.

## 4. Conclusions

In the present paper, a group of STM images of an $In_{0.15}Ga_{0.85}As$ surface with different annealing times are employed to explore development of the surface morphology. The results indicate that after annealing for 15 minutes, the surface becomes flat. We analyze the ripening process using a half-terrace diffusion model based on thermodynamic theory. The effective diffusion speed and distance of the $In_{0.15}Ga_{0.85}As$ adatoms are derived to be 0.065 nm/s and 59 nm, respectively, based on which the optimal annealing time for obtaining a perfectly flat surface is calculated to be 15.1 min. The theoretical value agrees quite well with the experimental result, which suggests the half-terrace diffusion model we propose will be helpful in predicting annealing time for films.

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