An application of half-terrace model to surface ripening of non-bulk GaAs layers*

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In order to predict the actual quantity of non-bulk GaAs layers after long-time homoepitaxy on GaAs (001) by theoretical calculation, a half-terrace diffusion model based on thermodynamics is used to calculate the ripening time of GaAs layers to form a flat morphology in annealing. To verify the accuracy of the calculation, real space scanning tunneling microscopy images of GaAs surface after different annealing times are obtained and the roughness of the GaAs surface is measured. The results suggest that the half terrace model is an accurate method with a relative error of about 4.1%.

Keywords: scanning tunneling microscopy, III–V semiconductors, annealing, diffusion in nanoscale solids

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1. Introduction

The ripening process is widespread in the heat treatment process, and it has been tested extensively.[1–4] In the surface morphology transition during annealing, the ripening process has been used to analyze the physical mechanism and experimental results, both theoretically and experimentally.[5–7] The ripening process of surface islands is driven by the Gibbs free energy of the surface. The value of the Gibbs free energy of the system decreases when it transits from nonequilibrium state to equilibrium state. On the condition that two-dimensional (2D) islands form in different sizes by the same adatoms with a constant total quantity, the Gibbs surface free energies would be different if average diameters of the 2D islands are different. The larger islands have lower Gibbs free surface energy than the smaller ones, which means the state of larger islands is more stable than that of smaller islands. This is the reason why adatoms detach from smaller islands and then attach to the larger ones in the ripening process. In the microscopic view, what lies in the ripening process is that the adatoms detach from smaller islands and then diffuse on the surface, finally attaching to the larger islands.

A GaAs (001) surface is an ideal medium to study the transitions of surface morphology.[8–11] The ripening process of 2D GaAs islands has been found and analyzed.[12,13] Thermodynamic theory could be employed to explore the evolution of micro-structures.[14,16–20] According to the theory, diffusion behavior of surface adatoms during the annealing could be predicted by two statistic parameters: migration ratio and driving force. Previous research on the ripening process based on thermodynamics has mainly focused on the theoretical calculation of time-depending size increasing of 2D islands on a single terrace of approximately infinite width, few researchers have related the length of adatom diffusion and diffusion speed in the prediction of the morphology evolution of islands on the step-shaped surface.

We have recently proposed a half-terrace diffusion model based on thermodynamic theory to predict the annealing time required for islands on the step-shaped surface to reach the flat terrace morphology.[21] According to the model, in the ripening process of $In_{0.15}Ga_{0.85}As$ 2D islands, the average diffusion speed and diffusion length per adatom could be estimated. Considering the simple linear function between speed and length, the annealing time for the surface to turn into a flat surface can be calculated. In that paper, because the growth of InGaAs on GaAs can be regarded as a heteroepitaxy procedure, all InGaAs adatoms deposited on the sample were considered to be involved in the ripening process due to the lattice mismatch. The result of the half-terrace diffusion model applied to InGaAs island ripening process appears to be feasible. However, it may not be strictly accurate to believe that all adatoms contribute to the ripening, especially when the growth process is homoepitaxy. In the ripening process of homoepitaxy films, most adatoms can be regarded as bulk layers, hence the lattice mismatch can be omitted. Only the non-bulk adatoms diffuse on the surface and attach to bigger islands to form flat terraces. The purpose of the half-terrace diffusion model is to predict the relatively accurate annealing time that the ripening process needs. The half-terrace diffusion model provides a concise picture to analyze the dynamic diffusion of the surface adatoms and to understand the physical mechanism involved. In this article, we apply the model to the GaAs/GaAs homoepitaxy growth to reckon the quantity of non-bulk GaAs

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layers associated with the ripening process in order to authenticate the universality of that model.

2. Experiment

Experiments were carried out by an MBE–STM combined system. The epitaxial growth is processed in an ultrahigh vacuum (10^{-7} Pa) chamber which contains solid-source evaporation cells with automated shutters or valve. The MBE chamber is connected to a surface analysis chamber in ultrahigh vacuum. A scanning tunneling microscopy (STM) system is integrated with the surface analysis STM chamber. GaAs (001) substrate is Si-doped n+ "epi-ready" product, and the oxide layers of the new substrate were removed by heating them at 550 °C.

After the oxide layers were removed, an approximately 170-nm GaAs layer was deposited on the substrate at 545 °C under an As_4 beam equivalent pressure (BEP) of 1.07×10^{-3} Pa. During epitaxial growth, high-energy electron diffraction (RHEED) was employed to monitor the surface morphology. At the same time, the RHEED oscillation curve was recorded to calculate the growth rate. The oscillation data showed the growth rate to be 0.335 monolayer/second (ML/s) in this experiment.

The deoxidation and growth processes described above were repeated on four GaAs (001) substrates. After the growth, the four samples were annealed at 560 °C under As_4 BEP of 1.07×10^{-3} Pa. for different time periods: 0 min, 5 min, 15 min, and 40 min. When the annealing process ended, the samples were cooled down to room temperature and transferred to the STM chamber for analysis of the real space surface images.

3. Results and discussion

In Ref. [21], where the half-terrace diffusion model is proposed, the annealing time for surface islands to complete the ripening process by forming flat terrace morphology can be predicted. The average diffusion length per adatom is estimated by calculating diagonal length of the STM images and counting the number of the terraces, which approximately equals 59 nm. The driving force for the ripening process is surface free energy, and surface free energy per adatom of 2D islands with different island coverages has been theoretically calculated by Xiang *et al*.[22] The number of adatoms included in our ripening experiment can be measured to be 6.25×10^{14} according to the method used in Ref. [21].

STM images of GaAs single-layer islands with different annealing times at 560 °C are presented in Figs. 1(a)–1(d). As the STM images reveal, single-layer GaAs islands go through a typical ripening process as the annealing time is extended. Figure 1(a) shows the surface morphologies of GaAs islands when the growth process is just finished. As figure 1(a) shows, the islands are distributed evenly on the terrace prior to the annealing process. This distribution of the GaAs islands explains why the mass center of single-layer islands on the same terrace could be regarded as in the half of the total diffusion. The three other STM images of GaAs surface, figures 1(b)–1(d), exhibit that the average diameter of surface islands increases as annealing time increases. When the annealing time comes to 40 min, as shown in Fig. 1(d), the islands merge to form flat terraces. The transition process of surface morphology from evenly distributed 2D islands to flat terrace is a typical ripening process, as shown in Fig. 1. The real space STM images show that the number of non-bulk GaAs layers remains unchanged during ripening, which implies that the surface adatoms only diffuse on one single-layer without hopping over to the upper layer or down to the lower one. The progress of the ripening process for any single layer is approximately the same. Based on these points, the motion of surface adatoms on one specific layer could be employed to estimate the general situation of the ripening process.

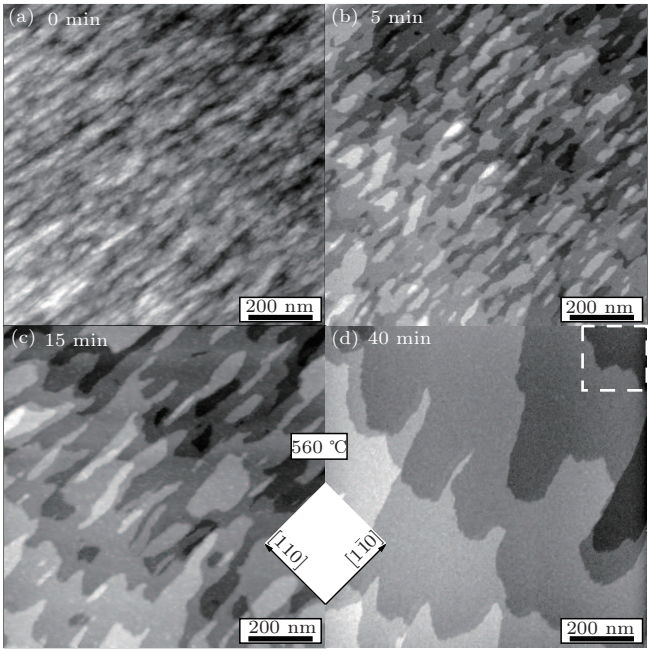


Fig. 1. STM images of GaAs single-layer islands with different annealing times at 560 °C, As_4 BEP = 1.06×10^{-3} Pa. (a) Without annealing, (b) annealing time 5 min, (c) annealing time 15 min, (d) annealing time 40 min.

In order to obtain the time of actual annealing that the GaAs islands undergo, the coverage of GaAs islands that are annealed for 0 min, 5 min, and 15min are analyzed. The statistical values are acquired by selecting 10 image clips of 100 nm $\times$100 nm from each STM image, analyzing island coverage of each image clips, and averaging ten results by mean value calculation. After the statistics, the data were fitted by exponential decay function, as shown in Fig. 2. With this method, the function can be used to predict how island coverage of

GaAs surface decays as annealing time increases. The decay time constant of the function is 33.3 min, which should be a relatively accurate time of annealing that the GaAs islands experience prior to the formation of flat terraces.

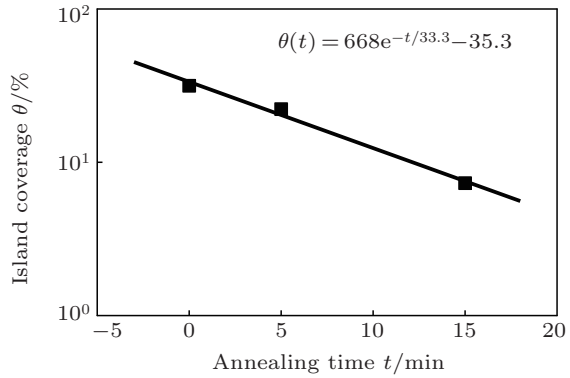


Fig. 2. GaAs island coverage as a function of annealing time. The data points are fitted to an exponential decay function.

By applying the half-terrace diffusion model[21] to the ripening of GaAs single-layer islands (because the average diffusion length is estimated to be 59 nm and ripening time constant has been fitted to be 33.3 min), the average diffusion speed v of adatoms could be calculated to be

$$v = 59 \text{ nm}/1998 \text{ s} = 0.0295 \text{ nm/s}. \quad (1)$$

Ripening proceeds during the annealing when growth procedure has been completed. A reasonable hypothesis is that the total number of surface adatoms remains unchanged during the ripening because they are protected by steady As_4 flux and kept at a constant temperature. Approximately, the surface adatoms neither exchange with bulk atoms nor escape from the sample. The microscopic image of the ripening process can be illustrated as surface adatom diffusion. Adatom diffusion relies on two kinds of energies: activation energy and surface free energy. According to thermodynamic theory, diffusion speed v is related to migration ratio M and surface free energy ΔG by the following formula:

$$v = M \times \Delta G. \quad (2)$$

The surface free energy determines how the GaAs surface morphology will be in the final stable state. The activation energy mainly affects the translation speed of the surface morphology from 2D islands to flat terrace, as Figure 3 illustrates.

The activation energy is supplied by the thermal energy that stems from substrate heater. The migration ratio can be adapted to characterize the activation energy

$$M \approx \kappa \left(\frac{D}{RT\lambda} \right), \quad (3)$$

with

$$D \approx 7 \times 10^{-6} \exp \left[-\frac{56}{R} \left(\frac{T_m}{T} \right) \right], \quad (4)$$

where M is the migration ratio of surface diffusion adatom, κ the adaption coefficient with a value of 0.5×10^{-4}, D the diffusion coefficient, R the Mole gas constant, which equals 8.314 J/mol·K, λ the unit moving length of surface adatoms, which equals 0.4 nm, T_m the melting temperature of elemental adatoms, and T the temperature of the GaAs substrate with a value of 723.16 K in our experiment.

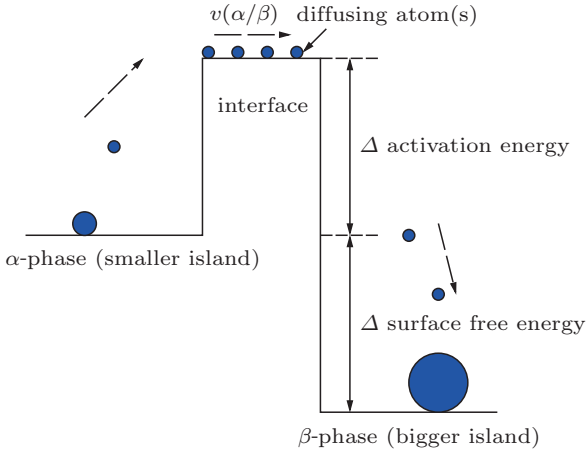


Fig. 3. (color online) Diagram of adatom activation energy and surface free energy in the ripening process. Dashed arrows indicate the diffusion directions of surface adatoms.

The other factor influencing the diffusion speed is surface free energy. To quantify the surface energy, there is a simple idea that each single adatom is thought to make the same contribution to the ripening process. Then, the total surface free energy can be calculated by multiplying the surface energy per adatom with the number of adatoms, which is expressed as

$$\Delta G = 0.027 \text{ (eV)} \cdot N = 0.027 \text{ (eV)} \cdot \theta \cdot L^2 \cdot d, \quad (5)$$

where ΔG is the surface free energy, contributed by N adatoms in the ripening process, θ the island coverage (31.56% for this experiment), L^2 the lattice site number of a single layer (its value should be 6.25×10^{14} for the 1 cm×1 cm GaAs substrate), and d is the number of non-bulk layers.

From the above discussion, non-bulk GaAs layers which contribute to the ripening process can be quantified according to the half-terrace diffusion theory expression given below,[20,22] as follows:

$$d = \frac{v}{(0.027 \text{ eV}) \cdot M\theta L^2}. \quad (6)$$

In the above formula, the average diffusion speed v, migration ratio M of surface diffusion adatom, island coverage θ, and the lattice site number L^2 are all calculated. By substituting these calculation values into Eq. (6), the number of non-bulk layers, d, can be obtained to be approximately 6.25. The result shows that in the ripening, the adatoms in the outmost 6.25 layers can be regarded as the virtual parts that transmit from small islands to large terraces.

To verify the results calculated by the half-terrace diffusion model, the actual height of the non-bulk GaAs layers is measured by investigating the roughness of the GaAs surface without annealing. The roughness data are obtained by analyzing the absolute height of the middle position in the STM image. The selected measurement points are illustrated with a solid white line in Fig. 4(a), and the values of heights which the white line sweeps across are shown in Fig. 4(b). The height difference of the surface is 1.716 nm, which is calculated by using the maximum height minus the minimum height. The height of GaAs monolayer is 0.282 nm, so there are six layers of GaAs islands that constitute the non-bulk part. The relative error could be calculated to be 4.1%, approximately. The error primarily derives from the linear approximation for the functional relationship between annealing time and the diffusion distance, which leads to a diffusion speed constant. The processing of the STM images may also introduce measuring error.

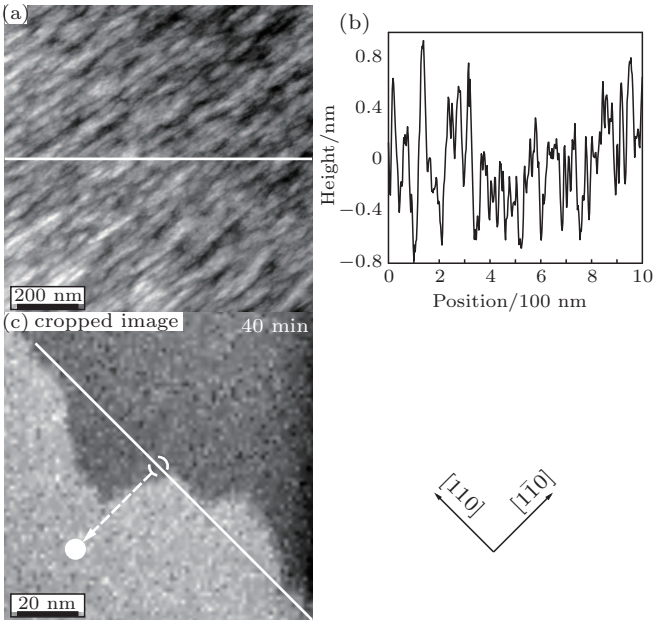


Fig. 4. (a) 1000 nm×1000 nm STM image of as-grown GaAs. (b) Height profile of non-bulk GaAs layers. (c) Cropped 100 nm×100 nm images from Fig. 1, (d) ideal movement of the 2D islands mass center.

The result suggests that the half-terrace diffusion model based on thermodynamic theory could be universally used to analyze the ripening process of the island structure on a relatively macroscopic scale. This analysis can also be conducted through using macroscopic physical quantity. In a strict sense, the diffusion of surface adatoms should be a complicated anisotropic process, although this process could be simplified into an isotropic issue by our half-terrace diffusion model. In the model, the diffusion process can be analyzed by using phenomenological physical quantities. It reveals that what lies in the intricate diffusion process is a relatively simple nature and that the half-terrace diffusion model is an applicable theory in discussing ripening phenomenon.

4. Conclusion

In this paper, the number of non-bulk GaAs layers during ripening is calculated by the half-terrace diffusion phenomenological model. By applying the model, the physical mechanism of ripening process is analyzed. The anisotropic diffusion of surface adatoms could be simplified by the mass center method. The real space images of GaAs surface under a series of annealing times are obtained by STM, the number of non-bulk GaAs layers is achieved by measuring the height difference of the GaAs surface STM image. The theoretical values and the actual values are in agreement with each other within a relatively small error. The error is most likely to be due to simplifying the variable motion of the mass center of surface adatoms into a uniform motion. It would be useful to quantify non-bulk surface layers because, to a great extent, the optoelectronic properties of the sample are determined by the surface layers. As the results suggest, the half-terrace diffusion model can be helpful in calculating the number of layers playing a part in the ripening process and in understanding the ripening of a step-shaped surface.

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