Influence of GaAs substrate misorientation on gallium and arsenic evaporation rates

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Abstract. The dependence of the Ga and As evaporation rates on GaAs(111)A substrate misorientation was analyzed using Monte Carlo simulation. The gallium and arsenic desorption rates are proportional to the step density of vicinal substrates at congruent (layer-by-layer) evaporation. With incongruent evaporation (gallium droplet formation on the surface), the arsenic desorption rate weakly depends on the substrate misorientation and the gallium desorption rate is independent of it.

1. Introduction

The substrate surface misorientation is a deviation from the singular surface by some angle. The interest in misoriented GaAs substrates is due to their use for heterogrowth of III–V and II–VI layers. Misorientation of the growth surface from the singular one leads to a decrease in the distance between the steps, thereby decreasing the probability of two-dimensional nucleation on the terraces, and, consequently, decreasing the density of antisite defects [1]. It was previously demonstrated that the surface misorientation changes the kinetics of growth and evaporation processes. The influence of the misorientation angle on the lateral crystal growth was demonstrated in [2]. It was experimentally shown, that the GaAs(001) growth rate in the [110] direction decreases with increasing terrace width [2]. Using a simple adsorption/desorption rate model, an increase in the mean time from the adsorption at the surface to the arrival at the step with the decreasing misorientation angle was demonstrated [2]. This leads to a rise in the probability of particle desorption and, as a consequence, to a decrease in the crystal growth rate. Since the crystal growth rate changes with variation of the step density, it is necessary to adjust the growth conditions in accordance with the substrate misorientation angle.

The substrate evaporation rate also depends on the surface misorientation. Tersoff et al. considered the influence of surface misorientation on the GaAs(001) substrate desorption rate during Langmuir evaporation (evaporation in vacuum) [3]. This work predicts the dependence of the congruent evaporation temperature $T_c$ on the local substrate morphology. The $T_c$ value separates the temperature regions of congruent and incongruent evaporation of III-V semiconductors. During congruent evaporation, the components of groups III and V evaporate with the same rate. In the case of incongruent evaporation, the group V component evaporates more intensively and group III particles accumulate on the surface and form droplets. The dependence of $T_c$ on the surface morphology means that the congruent evaporation temperature should depend on the surface misorientation angle. An analytical model, in which the arsenic evaporation is controlled by step density, while evaporation of Ga is not, was proposed in [3].
The effect of the terrace width on the crystal desorption characteristics due to atomic processes occurring on the surface has not yet been analyzed in detail. It is impossible to adequately explain the change in the crystal evaporation rate with variation of the misorientation angle without considering the atom interaction on the surface. Previously, using Monte Carlo simulation, the \( T_e \) dependences on the GaAs substrate terrace width \( L \) for (111)A and (111)B were obtained and discussed [4]. It was found that the \( T_e \) value increases and reaches saturation as the terrace widths increase, which is associated with the relationship between the gallium diffusion length before evaporation and the distance between steps. In the present work, the \( T_e(L) \) dependence for the (111)A substrate was obtained for a wider terrace width range. In this paper, we consider the effect of the terrace width on the gallium and arsenic desorption rates during GaAs(111)A Langmuir evaporation. It is shown that the desorption rate of both components in the congruent evaporation regime is proportional to the step density, and the gallium and arsenic desorption during the incongruent evaporation is influenced by gallium droplets.

2. Monte Carlo model and simulation results

The simulations were carried out using the SilSim3D program package [5]. The simulation space is a set of sites in a diamond-like lattice. Each site can be vacant or occupied by only one particle. For simulation of nonequilibrium GaAs(111)A annealing, a 4-component system is considered. It consists of gallium in solid and liquid states (Ga(s), Ga(l)) and arsenic in atomic and molecular forms (As, As\(_2\)). The arsenic molecule, as all other particles in the model, occupies only one lattice site. The atomic events in the model are Ga(s), Ga(l), As, As\(_2\). As diffusion; Ga(s), Ga(l), As\(_2\) desorption; the As\(_2\) formation and decay; gallium melting; GaAs dissolution in liquid gallium; GaAs crystallization; As diffusion in liquid gallium. The probability of each event is calculated as: \( P = A \cdot \exp(-E_{act}/kT) \), where \( A \) is the pre-exponential factor, \( E_{act} \) is the activation energy of the event, \( k \) is the Boltzmann constant, \( T \) is the temperature. The \( A \) and \( E_{act} \) values are the input model parameters. The technique of the model parameter choice is described in [6 Supplementary material].

The GaAs(111)A substrates with a distance between steps from 3 to 120 nm (a misorientation angle from 5.2° to 0.1°) are considered. The annealing temperature range is chosen from 700 to 1000 K and covers the regions of both congruent and incongruent evaporation for substrates with different terrace widths. The experimental congruent evaporation temperature of GaAs(111)A is \( \sim 930–950 \) K [8, 9]. Earlier, using Monte Carlo simulation, it was shown that the congruent evaporation temperature \( T_e \) decreases when the terrace width \( L \) is decreased, and at \( L = 20 \) nm the \( T_e \) value is 920 K [4]. In this work, the terrace width range is expanded downward, which leads to even lower \( T_e \) values. The dependence of the congruent evaporation temperature on the distance between vicinal steps is shown in figure 1. The accuracy of \( T_e \) determination is 5 K. It is shown that the \( T_e \) value decreases by 200 K with decreasing distance between the steps from 120 nm to 3 nm. Such a significant decrease in \( T_e \) is due to an increase in the step density on the vicinal surface. The steps are a source of gallium and arsenic atoms on the surface. An increase in the step density results in a rise in the surface gallium concentration and, therefore, a rise in the probability of gallium droplet formation on the surface.

The fragments of the model GaAs(111)A surfaces with different terrace widths after annealing at the same temperature are shown in figure 2. It is seen that there are no gallium droplets on the surface with large \( L \) (\( L = 120 \) nm) (figure 2(a)), while there is one mobile droplet on the surface with \( L = 40 \) nm (figure 2(b)), and there are two immobile droplets on the surface with low \( L \) (\( L = 7 \) nm) (figure 2(c)). The reason for the difference in the surface morphologies is a varying relationship between the annealing temperature \( T = 960 \) K and the \( T_e \) values of substrates with various misorientation angles. The \( T_e \) value for the surface with a terrace width of 120 nm is 40 K higher than the annealing temperature. So, this surface is characterized by congruent (layer-by-layer) evaporation. For the surface with a terrace width of 40 nm, the relationship between temperatures changes: the annealing temperature is 10 K higher than \( T_e \). Under these conditions, the difference between the rates
of gallium and arsenic evaporation is small ($V_{des}^{Ga}(960K) = 0.8 \cdot 10^{-5} \text{cm}^{-2} \text{s}^{-1}$, $V_{des}^{As}(960K) = 1.3 \cdot 10^{-5} \text{cm}^{-2} \text{s}^{-1}$), and excessive gallium on the surface is sufficient to form only one gallium droplet. The droplet is moving along the surface. The direction of the droplet motion is determined by the dissolution anisotropy of lateral facets of the droplet-substrate interface. More details about the motion of the gallium droplet during nonequilibrium annealing can be found in [7]. The annealing temperature on the surface with $L = 7$ nm is more than 100 K higher than the $T_c$ value, and the difference between the rates of gallium and arsenic evaporation is about two orders of magnitude ($V_{des}^{Ga}(960K) = 4.3 \cdot 10^{-4} \text{cm}^{-2} \text{s}^{-1}$, $V_{des}^{As}(960K) = 8.0 \cdot 10^{-6} \text{cm}^{-2} \text{s}^{-1}$). In this case, a large amount of excess gallium is present on the surface. As a result, the size and number of gallium droplets on this surface is larger than those on surfaces with less misorientation. Gallium drops etch the substrate, while remaining motionless, since the driving force for droplet motion is the tendency to achieve the equilibrium arsenic concentration in liquid gallium. On vicinal surfaces with low terrace width, the required arsenic concentration in liquid gallium is achieved mainly by diffusion collection of arsenic from the vicinal steps.

Figure 1. The dependence of the congruent evaporation temperature on the GaAs(111)A terrace width.

The dependences of the gallium and arsenic desorption rates on the step density at different annealing temperatures are shown in figure 3 in log-log scale. The bold lines are the region of congruent evaporation, and the dotted lines are the region of incongruent evaporation. The dependences corresponding to congruent evaporation are approximated by the equation $V_{des} = V_0 L^{-1}$, that is, the Ga and As desorption rates are determined by the step density. In the case of incongruent evaporation ($T > T_c$), the character of the $V_{des}(L)$ dependences for gallium and arsenic is different. The gallium desorption rate is independent of the step density, and the arsenic desorption rate weakly depends on it. At $T > T_c$, gallium droplets are formed on the GaAs substrate surface. For smaller $L$, the droplet formation occurs at lower $T_c$. The presence of gallium droplets on the surface noticeably

Figure 2. Top views of model GaAs(111)A surfaces with terrace widths of (a) 120 nm, (b) 40 nm, (c) 7 nm after annealing at $T = 960$ K during 0.5 s.
increases the total gallium adatom concentration on the surface, which is schematically shown in the inset of figure 3(a). Therefore, the main contribution to the Ga desorption is determined by the Ga atom detachment not from the step, but from the droplet. Gallium droplets also affect the arsenic evaporation, since liquid gallium increases the As evaporation rate from the GaAs surface [7]. The surface area, from which arsenic mainly evaporates, is determined by the droplet surface, the substrate area adjacent to the droplet and the edges of vicinal surface steps (figure 3(b) inset). Due to the short arsenic diffusion length, the role of the steps in the arsenic evaporation process is dominant as long as the droplet diameter is small in comparison with the substrate surface area.

![Figure 3](image-url)

**Figure 3.** Dependences of the Ga (a) and As (b) evaporation rates on the step density of the GaAs(111)A surface. The bold lines correspond to congruent evaporation; the dotted lines, incongruent evaporation. The inserts show the schemes of desorption of (a) Ga and (b) As atoms from the terrace containing a Ga droplet. The arrows indicate the direction of particle movement.

Our results on the evaporation rate of GaAs components partially correspond to the similar results obtained in [3]. Tersoff considered the annealing temperature range $T = T_c + 30$, which covers only incongruent evaporation of GaAs(001). In particular, the gallium evaporation is independent of the step density, but only in the range of incongruent evaporation. The arsenic evaporation is indeed proportional to the step density, but only in the range of congruent evaporation. After the gallium droplet formation on the surface, the arsenic desorption rate is no longer determined by the simple equation $V_{des} = V_0 L^{-1}$, because Ga droplets, dissolving the GaAs crystal, supply additional arsenic to the substrate surface and contribute to evaporating arsenic. With increasing temperature, when most of the surface becomes covered with liquid gallium, the arsenic evaporation rate from the liquid gallium surface significantly increases, thereby, reducing the step role in the arsenic evaporation. At high temperatures, when the entire surface is covered with liquid gallium, the evaporation rates of both Ga and As are independent of $L$ (not shown in figure 3).

3. Conclusions
The influence of GaAs(111)A substrate misorientation on the gallium and arsenic desorption rates was analyzed using Monte Carlo simulation. The congruent evaporation temperatures and the gallium and arsenic desorption rates were determined for vicinal substrates with a distance between steps from 3 to 120 nm. The congruent evaporation temperature for the GaAs(111)A surface decreases by 200 K when the misorientation angle increases from 0.1° to 5.2°. It is found that the gallium and arsenic evaporation rates are proportional to the step density in the congruent evaporation regime. With incongruent evaporation, the gallium evaporation rate becomes independent of the step density, and
the arsenic evaporation rate exhibits a weak dependence on the step density. This is explained by the ratio of the number of gallium and arsenic atoms supplied by steps or gallium drops onto the substrate surface, and participating in evaporation.

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