Thermal roughening of GaAs surface by dislocation-induced step-flow sublimation

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Abstract. The thermal roughening of epitaxial GaAs film surface is studied under anneals at temperatures 700-775 °C in the presence of a saturated Ga-As melt. Surface roughening consists in the formation of spiral “inverted pyramids” on the initially flat surface due to the step-flow sublimation induced by screw dislocations. The observed roughening indicates that, despite the presence of As and Ga vapors provided by the melt, the annealing conditions are shifted from equilibrium towards sublimation.

1. Introduction

Atomically flat semiconductor surfaces are needed for fundamental surface science, device applications and reproducible fabrication of nanoscale structures [1, 2]. Close to ideal ones, silicon surfaces with atomically flat terraces separated by steps of monatomic height were obtained by annealing chemo-mechanically polished Si substrates in vacuum [3, 4]. The application of this method to III-V semiconductors is problematic because, due to a high evaporation rate of the volatile V component, it is difficult to find the vacuum annealing temperature range, in which the surface diffusion is sufficiently effective for surface smoothing, while the sublimation is still negligible [5]. To avoid the surface morphology deterioration due to depletion with arsenic, GaAs thermal smoothing, which yields GaAs step-terraced surfaces, can be performed under overpressure of arsenic-containing vapors in the MBE or MOCVD growth chambers [6, 7].

Thermal smoothing experiments in the growth chambers of MBE or MOCVD set-ups are expensive and time-consuming. A more efficient technique of GaAs surface thermal smoothing was proposed and developed in Refs. [8-12]. This technique consists in annealing GaAs substrates in the conditions close to equilibrium with Ga and As vapors, provided by the presence of the saturated Ga-As melt. So far, this smoothing technique has been demonstrated only for chemo-mechanically polished epi-ready GaAs substrates with a small root mean square roughness $\rho \leq 0.15$ nm. To apply this method to substrates or epitaxial films with a larger surface roughness and to speed up the smoothing process, one should increase the annealing temperature. However, at an increased temperature $T \geq 700$ °C, GaAs surface smoothing is gradually changed to surface roughening, which reveals itself in step meandering, the formation of deep pits and complete destruction of step-terraced morphology [8]. This roughening may be due to the thermodynamic roughening transition [13, 14], or to kinetic instabilities caused by deviations from equilibrium at high temperatures. On a step-terraced surface, the deviations from equilibrium towards growth or sublimation can be detected by the atomic step motion towards lower of higher lying terraces, respectively. Various origins of atomic steps are possible at a crystal surface. Misorientation of the vicinal crystal surface from a singular face may result in a regular set of straight equidistant atomic steps, which separate terraces with the width determined by the misorientation angle. However, the step motion under step-flow growth or sublimation on an ideal vicinal surface does not change the character of the homogenous step-terrace relief. Therefore, it is difficult to determine the direction and velocity of the step motion by studying the morphology of step-terraced vicinal surfaces because of the problems connected with localization of the same area on the sample with a submicron accuracy in *ex situ* AFM measurements.

A screw dislocation ending at a crystal surface provides an alternative source of a monatomic step. The steps induced by screw dislocations result in the formation of spiral pyramid hills on the surfaces of epitaxially grown films, as it was proposed and theoretically described in the classical paper by Burton, Cabrera and Frank [15] and studied experimentally by means of liquid phase epitaxy on mesa-structured GaAs(001) substrates [16]. In distinction, under sublimation, spiral dips ("inverted pyramids") are formed due to the flow of the atomic steps induced by screw dislocation endings [17]. Thus, unlike vicinal steps, screw dislocation steps lead to the surface morphology that unambiguously indicates the deviation from equilibrium towards growth or sublimation. The present study is aimed at clarifying the reasons for GaAs roughening at high temperatures by observation of the spiral structures induced by screw dislocations under annealing epitaxial GaAs films.

2. Experimental

GaAs films were grown by liquid phase epitaxy (LPE) on conventional flat GaAs(001) substrates and on the substrates with preliminarily prepared lithographic square mesa structures similar to those used in [16, 18]. The size of the mesas ranged from 0.2×0.2 mm^2 to 1×1 mm^2. The morphology of the films grown on flat substrates was usually non-uniform. The surface of such films contained relatively wide ($\sim 2-5$ μm) flat terraces with randomly spaced vicinal monatomic steps and high step bunches (up to ~ 40 monolayers), which separated the terraces [18]. The morphology of the films grown on mesa structured substrates was more uniform. Depending on the growth conditions (presumably, on the growth termination conditions, which could not be well-controlled in the LPE set-up), the mesa as-grown surfaces contained spiral pyramid hills [16], or inverted pyramid pits induced by screw dislocations [18]. These morphologies correspond to the dislocation-controlled crystal growth or dissolution, respectively, at the last stage of LPE growth. We also obtained mesa-structured epitaxial film surfaces, containing atomically flat terraces and screw dislocation endings, which induced nearly straight monatomic steps. In the present study these latter mesa-structured films with straight dislocation-induced steps were used in the annealing experiments. The mean concentration of dislocation endings was about 5×10^4 cm^{-2}. The anneals were performed under the molecular hydrogen flow, in a quartz tube of the LPE set-up. The GaAs sample was put in a quasi-closed graphite cassette, which contained the saturated Ga-As melt in order to provide As and Ga vapors. Before annealing the surface oxides were removed in the HCl-isopropanol solution [18]. The morphology of the initial and annealed GaAs surfaces was studied *ex situ* by atomic force microscopy (AFM). The details of the anneals and AFM measurements are described in [8].

3. Results and Discussion

To elucidate the reasons of high-temperature GaAs surface roughening, one hour anneals of the samples cut from the same GaAs epitaxial film were performed at various temperatures. The results are shown in figure 1. The as-grown surface (figure 1a) contains wide (up to ~ 7 μm) atomically flat terraces separated by atomic steps, which are preferentially oriented in the same direction. Marked by the white dashed circles in figures 1a and 1b are the emergence points of "screw dislocations", which are not necessarily "pure screw", but have their Burgers vector component, perpendicular to the surface [15, 16]. The emergence point can be identified by the dislocation-induced step of monatomic height $h \approx 0.3$ nm, which corresponds to the GaAs period in the [001] direction.

Annealing at $T = 700$ °C (figure 1b) did not lead to substantial changes in the surface morphology. Annealing at higher temperature $T = 750$ °C (figure 1c) led to the step displacement by ~ 3 μm with respect to the dislocation ending point. The steps moved towards the higher lying terraces. Consequently, the annealing conditions correspond to crystal sublimation rather than growth. Near the point of dislocation emergence, the step twists into a spiral and forms a distinct spiral pit ("inverted pyramid" hollow), which also corresponds to the step motion towards the higher lying terrace and, thus, to the step-flow sublimation. The increase of the annealing temperature up to 775 °C caused a further spiral spinup (figure 1d). This process is reverse to the dislocation-controlled step-flow crystal growth described in [15]. While the dislocation-controlled step-flow growth was observed experimentally on the surfaces of many crystals, including GaAs [16], we report here on the observation of the dislocation-controlled step-flow sublimation on the GaAs surface.

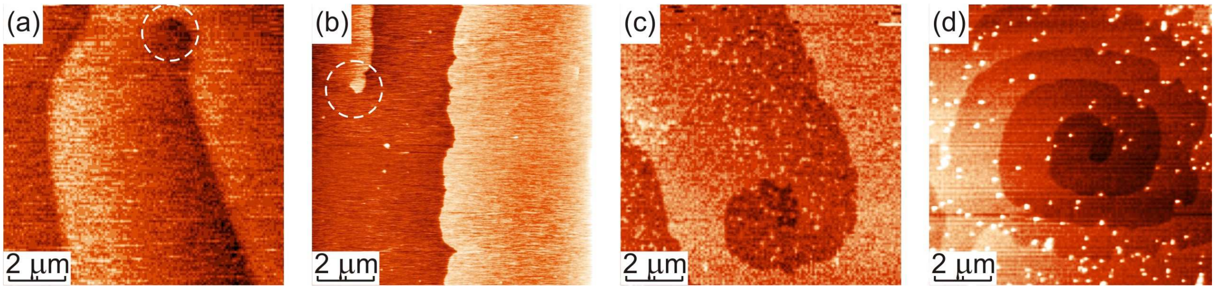

Figure 1. 10×10 μm^2 AFM images of the surface of an epitaxial GaAs film with screw dislocation exits before annealing (a) and after one-hour anneals at T = 700°C (b), 750°C (c) and 775°C (d).

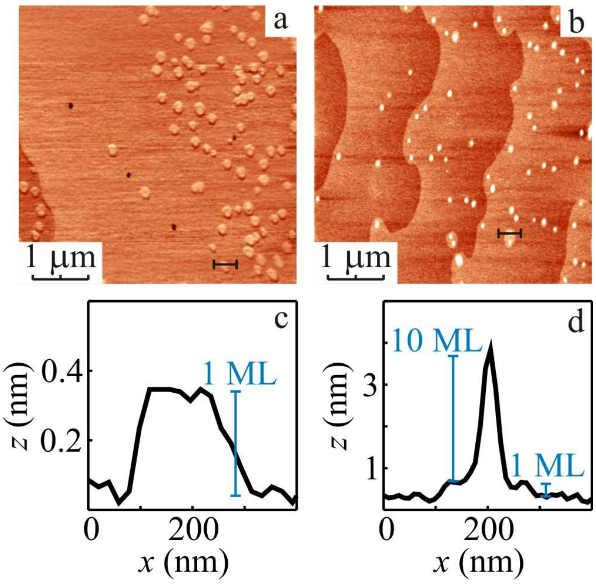

Figure 2. (a, b): Zoomed images of terraces with islands after anneals at T = 750°C (a) and 775°C (b). (c, d): *z-x* cross sections of selected islands measured along the black segments shown in figures 2a and 2b, respectively.

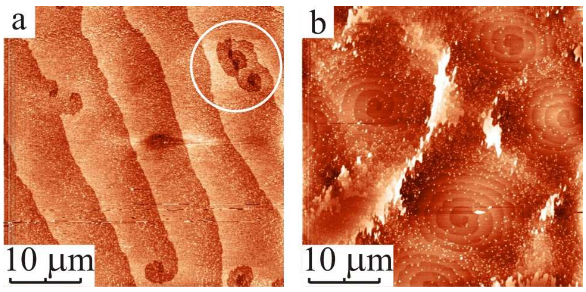

Figure 3. Intersection of spiral structures originating from various points of screw dislocation emergence after annealing at T = 750 °C (a) and 775 °C (b). Indicated by the white circle in (a) is a pair of closely spaced spiral structures.

It is seen from figures 1c and 1d that the spiral step motion is accompanied by the formation of islands on terraces. To consider these islands in more detail, zoomed images of the surface relief after anneals at T = 750 °C and 775 °C are shown in figures 2a and 2b, respectively, together with the *z-x* cross-sections of typical islands (figures 2c, d). The island lateral sizes are in the range of ~ 100 – 500 nm in diameter. It is seen from figures 2a, and 2c that annealing at T = 750 °C leads to the formation of the islands one or two monolayers (ML) high. At higher temperature T = 775 °C, multilayer islands are formed being from ~ 3 ML to 10 ML high. A possible reason for the formation of these islands is the existence of defect- or contamination-induced surface spots at which the sublimation is inhibited [19]. Under the motion towards higher lying terraces, the steps flow around such spots, leaving the islands behind. Each time a monatomic step passes through the spot, the island height increases by one monolayer with respect to the terrace level. Thus, the formation of a multilayer island at $T = 775$ °C corresponds to the multiple step passages through the island, in accordance with the observed multiple spiral turns (figure 2b). This suggestion is confirmed by the non-uniform monatomic island distribution over the terraces after annealing at $T = 750$ °C (figures 1c and 2a). Indeed, it is clearly seen from figures 1c and 2a that the monatomic islands are observed only on the part of the terrace that has been already passed by the moving dislocation-induced step. It should be also noted that the concentration of the multilayer islands (figure 2b) is smaller than that of the monatomic islands (figure 2a). A possible reason for this fact is that a part of monatomic islands evaporated during high-temperature annealing.

Another peculiarity of the GaAs thermal surface roughening is the intersection of spiral structures at high annealing temperatures. Shown in figure 3 are the 40×40 μm^2 AFM images of the surface relief, which demonstrate this intersection. Very few nucleation centers of the spiral structures are seen after annealing at $T = 750$ °C, with only one pair of closely spaced intersecting spiral structures indicated by the white circle in figure 3a. In distinction, as it is seen from figure 3b, after annealing at 775 °C, the whole surface area consists of mature deep spiral pits separated by high (~ 10 ML or higher) ridges. It is evident that the spiral spin-up is blocked by adjacent spiral structures. Both right-hand and left-hand spirals are observed in figure 3b, indicating different sings of the screw dislocation Burgers vectors.

It should be noted that spiral structure jamming and the respective step motion deceleration hinder the comparison of the experimental morphology with the theory [15] and a correct determination of the parameters, in particular, the undersaturation. However, we can estimate the deviation of the annealing condition from the equilibrium by means of the measured displacement of the dislocation-induced step linear segment after one-hour annealing at $T = 750$ °C. The linear segment step velocity v_∞ and relative Ga vapor supersaturation σ can be expressed as follows [15]:

$$v_\infty = 2\lambda_S \frac{j - j_0}{n_0} , \tag{1}$$

$$\sigma = \frac{j - j_0}{j_0} = \frac{P - P_0}{P_0} , \tag{2}$$

where λ_S is the Ga adatom diffusion length, n_0 is the surface atomic concentration, j and P, j_0 and P_0 are the actual (non-equilibrium) and equilibrium (denoted by subscript 0) atomic flows and pressures, respectively. From measured step velocity $v_\infty = 3.5$ μm/hour and known values $P_0 = 1.3\times10^{-8}$ bar at $T = 750$ °C [20, 21] and $n_0 = 2.5\times10^{15}$ cm^2, we obtain $\sigma = -0.02$. The negative value of σ corresponds to undersaturation of the vapor pressure and, thus, to crystal sublimation.

4. Summary

In conclusion, the surface morphology evolution of epitaxial GaAs films grown on mesa structured substrates is studied under annealing in the presence of the saturated Ga-As melt at temperatures up to 775 °C. Surface roughening is observed at high annealing temperatures T ≥ 750 °C. This roughening consists in the formation of spiral "inverted pyramid" pits on the initially flat surface due to the step-flow sublimation induced by screw dislocations. This observation indicates that, despite the presence of As and Ga vapors provided by the melt, the annealing conditions are shifted from the equilibrium towards sublimation. The observed spiral step spin-up is accompanied by the formation of islands on the terraces. A possible reason for the island formation is that steps flow around the surface spots at which the sublimation is inhibited: each time the step passes through the spot, the island height increases by one monolayer with respect to the terrace level. The velocities of sublimation and relative undersaturation are estimated from the measured step displacement after annealing at $T = 750$ °C. Annealing at higher temperature $T = 775$ resulted in a peculiar "vortex"-like morphology, which consists in deep spiral pits covering the major part of the surface area. To the best of our knowledge, such vortex-like morphology was not observed earlier at semiconductor surfaces.

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