Optimization of conditions for thermal smoothing GaAs surfaces

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Abstract. GaAs thermal smoothing by annealing in conditions which are close to equilibrium between the surface and vapors of As and Ga was earlier proved to be effective for the step-terraced surface formation on epi-ready substrates with a small root-mean-square roughness \(R_q \leq 0.15\,\text{nm}\). In the present study, this technique is further developed in order to reduce the annealing duration and to smooth GaAs samples with a larger initial roughness. To this end, we proposed a two-stage anneal with the first high-temperature stage aimed at smoothing "coarse" relief features and the second stage focused on "fine" smoothing at a lower temperature. The optimal temperatures and durations of two-stage annealing are found by Monte Carlo simulations and adjusted after experimentation. It is proved that the temperature and duration of the first high-temperature stage are restricted by the surface roughening, which occurs due to deviations from equilibrium conditions.

1. Introduction

Atomically flat semiconductor surfaces are needed for fundamental surface science, fabrication of nanoscale structures and device applications. Smooth surfaces with a small root-mean-square (rms) roughness (comparable to or even smaller than inter-atomic distances) can be obtained by chemomechanical polishing (CMP) [1]. However, a surface prepared by CMP is disordered on a microscopic scale due to the mechanical impact during polishing. Annealing at elevated temperatures can effectively reduce this disorder and yield regular step-terraced surfaces with atomically flat terraces separated by steps of monatomic height. Almost perfect step-terraced silicon surfaces are obtained by annealing in vacuum [2,3,4]. For III-V semiconductors, the application of vacuum annealing is hindered by the evaporation of a more volatile V component. To overcome this difficulty and obtain step-terraced GaAs surfaces, annealing in MBE or MOCVD setups under As-contained vapors was used in papers [5,6]. A more efficient and cost-effective technique for GaAs smoothing was proposed in [7]. This technique consists of annealing GaAs substrates in a quartz tube of a liquid phase epitaxy (LPE) setup. The conditions close to equilibrium between the surface and vapors of As and Ga were provided by the presence of a saturated Ga-As melt. This technique proved to be effective for the GaAs step-terraced surface formation on epi-ready substrates with a relatively small root-mean-square roughness \(R_q \leq 0.15\,\text{nm}\). For such substrates, the step-terraced morphology was formed during about one-hour anneals in the temperature range of 600°C-650°C. The full length of monatomic steps was used for the quantitative characterization of the step-terraced morphology formation. The experimental kinetics of the step length was compared to Monte Carlo simulations within the Kossel crystal model.
This comparison yielded the microscopic parameters of the model, namely, the activation energy for surface diffusion, the lateral bond energy, and the adatom desorption energy.

In paper [7] the opportunity to obtain step-terraced GaAs surfaces was proved only for substrates with a sufficiently small initial roughness ($R_q \leq 0.15$ nm). However, there is a need to smooth the surfaces of substrates and epitaxial films with a larger initial roughness. Obviously, smoothing rough surfaces requires higher temperatures and longer annealing times. However, the annealing temperature and duration are restricted by the surface roughening which occurs, supposedly, due to deviations from equilibrium conditions [10,11]. Here we propose to use the two-stage annealing to overcome this difficulty. The first stage should be performed at a high temperature in order to provide an effective mass transfer. The temperature and duration of this stage should be sufficiently high for flattening "coarse" relief features but, on the other hand, not too high in order to prevent the development of thermal roughening. The second low-temperature stage is aimed at "fine" smoothing of the small-scale roughness, including the roughness that is formed at the first stage. The goal of this study is to find the optimal parameters of two-stage annealing both experimentally and using Monte Carlo simulations.

2. Experiment

The anneals were performed in a quartz tube of an LPE setup under a flow of pure molecular hydrogen. The GaAs sample was put in a quasi-closed graphite cassette with a saturated Ga-As melt to provide As and Ga vapors. Before annealing, the surface oxides were removed in HCl-isopropanol solution [12]. 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 were described earlier [7]. The Monte Carlo simulations of the surface smoothing and step-terrace morphology formation were performed on the Kossel crystal in the standard solid-on-solid (SOS) model [8]. In this model, the complicated processes of III and V components mass transfer and the formation of GaAs unit cells are replaced by a random walk and attachment/detachment of one kind of "atoms" without taking into account the actual atomic structure of the crystal unit cell and surface reconstructions.

3. Results and discussion

As the first step, we tried to smooth a relatively "rough" epi-ready GaAs(001) substrate with $R_q \approx 0.2$ nm in the conditions similar to those used in [7]. Figure 1 shows the AFM images obtained after anneals at $T = 625 ^\circ C$ for various durations. Unlike the previous annealing experiments on smoother substrates [7], here, after a one-hour anneal, the surface is far from a regular step-terraced one. It is seen in the 5×5 μm$^2$ image in figure 1(a) that the surface relief is nonuniform and contains scratch-like trenches of up to ~ 50 – 100 nm in width and ~ 1 – 2 nm (~ 3 – 6 monolayers, ML) in depth. In the 1×1 μm$^2$ image (see figure 1(b)) one can see the nucleation of jagged atomic steps with a large concentration of islands and dips on terraces. With increasing anneal duration, the step-terraced morphology matures and is clearly seen after an 8-hour anneal, although the steps remain jagged, and some traces of scratches are still visible.

An empirical search for optimal conditions for two-stage anneals is labor-intensive and time-consuming because of a large number of unknown parameters (two annealing temperatures and two durations). Therefore, we performed Monte Carlo simulations to determine the optimal parameters of the two-stage anneals. The dimensionless step length $l_s = L_S/L_0$ was used for quantitative characterization of the step-terraced morphology formation [7,8]. Here $L_S$ is the full length of monatomic steps on a certain area, and $L_0$ is the length of straight monatomic steps on the ideal vicinal surface corresponding to this area. The step length proved to be a more adequate parameter than the rms roughness for the description of the surface morphology evolution of initially smooth substrates. The simulated kinetics of the step length for various annealing temperatures is shown in figure 2(a). It is seen that, after the initial steep decrease, the step length kinetics slows down and saturates at the equilibrium value $l_s$. The values of the equilibrium step length were determined from the inflection points of the kinetics (marked by arrows in figure 2(a)) and are shown by crosses versus annealing duration in figure 2(b). In the temperature range of 525 °C – 725 °C, the equilibrium step length
increases by 20% with increasing temperature due to thermal fluctuations. The temperature increase of 100 °C speeds up the smoothing kinetics by one or two orders of magnitude. It is also seen that, according to the simulations, the use of two-stage anneals can substantially reduce the total duration required to reach a certain step length. In particular, $l_s = 1.2$ can be obtained by a 4000-min one-stage anneal at 525 °C, as compared to the 20-min two-stage anneal at 725 °C followed by the second stage at 525 °C.

**Figure 1.** Smoothing kinetics of the "rough" substrate. The AFM images of 5×5 μm² and 1×1 μm² (top and bottom rows, respectively) obtained after the anneals at 625 °C, and successively increasing durations: 1 hour (a, b); 2 hours (c, d); 4 hours (e, f); 8 hours (g, h). White oval lines denote the "scratches" on the surface.

**Figure 2.** Monte Carlo simulation of surface smoothing by one-stage and two-stage anneals. (a) Step length kinetics under one-stage anneals at 725 °C (red curve #1), 625 °C (green, #2) and 525 °C (dark blue, #3). The second stage of the two-stage anneal at 725 °C and 525 °C is shown by the black curve #4. The inflection points of the kinetics $l^\text{eq}$, which corresponds reaching the equilibrium step length $l^\text{eq}_s$, are indicated by the arrows. (b) The equilibrium step length $l^\text{eq}_s$ as a function of the moments of time $t^\text{eq}$ for the one-stage and two-stage anneals at various temperatures. Two temperatures are given near the points corresponding to the two-stage anneals.
Thus, according to the simulations, the first stage of thermal smoothing should be carried out at the highest possible temperature. The experimental realization of this idea is complicated by the changeover from surface smoothing to surface roughening, which occurs at high temperatures [7,10,11]. This roughening consists in the destruction of the step-terraced morphology and the formation of islands (in the case of deviation towards sublimations) or pits (deviation towards growth). These islands (or pits) are, presumably, the surface spots at which the sublimation or growth, respectively, are suppressed, so their height (or depth) increases with respect to the overall surface level [10,11]. One should not allow the development of roughness, which can be smoothed only by CMP. Therefore, the upper limits for the temperature and duration of the first high-temperature stage are restricted by the roughening process. To find these limits, we performed one-hour anneals of a step-terraced GaAs(001) surface at successively increasing temperatures. The results are shown in figure 3. It is seen from figure 3(a, d) that the anneal at 700 °C led to the twists in the step shape, which occasionally caused the local step to merge into double steps. The temperature increase up to 750 °C led to the formation of elongated "finger-like" steps and the formation of islands with a height of 1 – 3 ML (figure 3(b, e)). At 775 °C, further step bunching and the formation of higher islands were observed (figure 3(c, f)). The formation of multilayer islands is supposedly due to the step flowing around some spots at which the sublimation is inhibited [10,11].

Figure 3. AFM images taken after one-hour anneals at (a) 700 °C (a); (b) 750 °C; (c) 775 °C. The respective z-y cross-sections along the white lines in panels (a-c) are shown in figures (d-f).

The analysis of the simulation (figure 2) and experimental (figure 3) results allowed us to choose the temperature $T = 725$ °C for the first stage of the two-stage anneal. On the one hand, this temperature is sufficiently high for the effective smoothing of the roughness with $R_q \sim 0.2$ nm and, on the other hand, not high enough to cause thermal roughening. To determine an optimal duration of the first stage, we performed anneals at 725°C for various durations (not shown). It was found that small durations of about 1 min, followed by a quick cooling down to 500 °C within 1–3 minutes, were insufficient to form a well-defined step-terraced morphology (a large concentration of monatomic islands that did not incorporate into vicinal steps was observed on terraces). However, at durations of
~ 30 min, pronounced step bunching was observed. Therefore, durations of ≤ 15 min should be chosen for the first stage of the two-stage smoothing experiments.

The results of the two-stage and one-stage smoothing experiments are presented in figure 4. It is seen from figure 4 (c, d) that the one-stage anneal at 625 °C did not form a well-defined step-terraced morphology. In distinction, the two-stage anneal (15 min at 725 °C plus one hour at 625 °C) yielded a much more perfect step-terraced surface (figure 4(e, f)). Interestingly, the two-stage anneal with reduced durations (1 min at 725 °C followed by a slow cooling down to 500 °C within ~ 15 min) yielded essentially the same well-defined step-terraced surface (figures 4(g, h)). The only difference is the presence of a small concentration of monatomic islands on the terraces after the latter two-stage anneal (figure 4(g)).

![Figure 4. The AFM images of 5×5 μm² (top row) and 1×1 μm² (bottom row) measured on the initial GaAs(001) substrate surface (images (a, b), after one-hour anneal at 625 °C (c, d), after two-stage anneal (15 min at 725 °C plus one-hour at 625 °C) and after another two-stage anneal (one min at 725 °C with a subsequent slow cooling down to 500 °C within ~ 15 min (g, h).]

4. Summary

Thus, it was proved both by Monte Carlo simulations and experimentally that the efficiency of thermal smoothing GaAs substrates can be improved using the two-stage anneals. This means that the substrates with a larger initial surface roughness can be brought to the step-terraced morphology and the smoothing durations can be considerably reduced. The surface roughening, which occurs at high temperatures due to deviations from equilibrium conditions, should be taken into account and it restricts the temperature and duration of the first high-temperature stage of thermal smoothing.

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