Thermodynamic and kinetic roughening: Monte Carlo simulation and experiment on GaAs

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Abstract. GaAs thermal smoothing at temperatures $T \leq 650$°C in the conditions close to equilibrium yields surfaces with atomically smooth terraces separated by steps of monatomic height. At higher temperatures $T \geq 700$°C, surface smoothing is changed to roughening. In the present paper, possible reasons of surface roughening at elevated temperatures are studied by means of Monte Carlo simulation and compared with the experimental results on GaAs. It is proved that the thermodynamic roughening transition, which consists in spontaneous generation of atomic steps due to decrease in the step line tension down to zero, cannot explain the experiment because it should occur at temperatures $T \sim 1800$ - 2000°C, i.e. much higher than in the experiment. Kinetic instabilities caused by deviations from equilibrium towards growth or sublimation are shown to cause GaAs roughening at elevated temperatures. The microscopic mechanisms of kinetic-driven roughening are discussed.

1. Introduction

Fundamental surface science, nanostructures fabrication and device applications require high-quality, atomically flat crystal surfaces [1-5]. A technique for GaAs surface smoothing by allowing mass transport at elevated temperatures was developed in [6,7]. To avoid surface depletion with arsenic, the anneals were performed in conditions close to equilibrium between the surface and Ga and As vapors, when neither growth nor sublimation takes place. This technique yields GaAs(001) surfaces with atomically smooth terraces separated by steps of monatomic height (figure 1(a-c)).

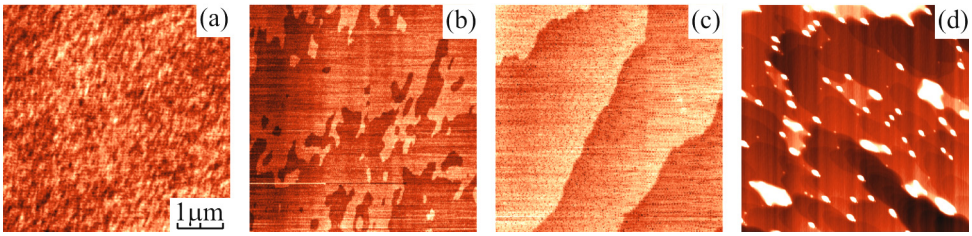

Figure 1. AFM images of an epi-ready GaAs substrate before (a) and after anneals for 2 h at 575°C (b), 650°C (c) and 775°C (d) [6].

Increasing the annealing temperature speeds up surface mass transport and, thus, facilitates the smoothing process. However, at temperatures $T \geq 700$°C, GaAs surface smoothing is replaced by roughening which consists in the formation of step bunches, multilayer islands and pits, and

destruction of step-terraced morphology (figure 1(d)) [6]. This roughening restricts the annealing temperature and, thus, the maximal initial surface roughness that can be smoothed within a reasonable time. In principle, surface roughening can be caused by the thermodynamic roughening transition, when the step line tension decreases down to zero due to the entropy term in the surface free energy and spontaneous step generation becomes energetically favorable [8,9]. The roughening temperature, however, is typically close to or above the crystal melting point [8-10]. Alternatively, surface roughening can be caused by kinetic instabilities which, in their turn, may arise due to deviations of annealing conditions from equilibrium towards growth or sublimation. This paper is aimed at elucidating the reason of GaAs surface roughening at elevated temperatures by means of Monte Carlo simulation of thermodynamic and kinetic roughening.

2. Method

Initial step-terraced GaAs(001) surfaces used in this experiments were obtained by means of annealing "epi-ready" substrates at $T = 600 – 650$°C in the conditions close to equilibrium between the surface and Ga and As vapors, when atomic fluxes to the surface and from the surface are equilibrated so neither surface sublimation, nor growth occurs [6,7]. The equilibrium conditions were provided in a quasi-closed container by the presence of the saturated Ga-As melt. The anneals at higher temperatures $T = 700 – 775$°C were performed in the same container. The morphology of the initial and annealed GaAs surfaces was studied *ex situ* by atomic force microscopy (AFM).

Monte Carlo simulations of surface roughening were performed in a one-component model on the Kossel crystal. GaAs(001) surface smoothing and step-terraced morphology formation were previously described by this method [11,12]. The model parameters, which include the diffusion activation energy $E_d = 1.3 \pm 0.05$ eV, the lateral bond energy $E_b = 0.32 \pm 0.02$ eV and the adatom desorption energy $E_{des} = 2.1 \pm 0.05$ eV, were obtained earlier from the description of the experimental GaAs smoothing kinetics by Monte Carlo simulation. The same parameters were used in the present study for the surface roughening simulation.

3. Results and discussion

3.1. Thermodynamic roughening transition

At the first stage of the present study, we performed Monte Carlo simulation of the thermodynamic roughening transition on the initially flat Kossel crystal surface. Simulation of anneals at $T \leq 800$°C did not lead to substantial surface roughness which could explain the experiment. Notable surface roughening occurred at much higher temperatures $T \geq 1700$°C. Shown in figure 2(a-c) are the simulated surface images corresponding to various temperatures and an annealing time of 0.01 s.

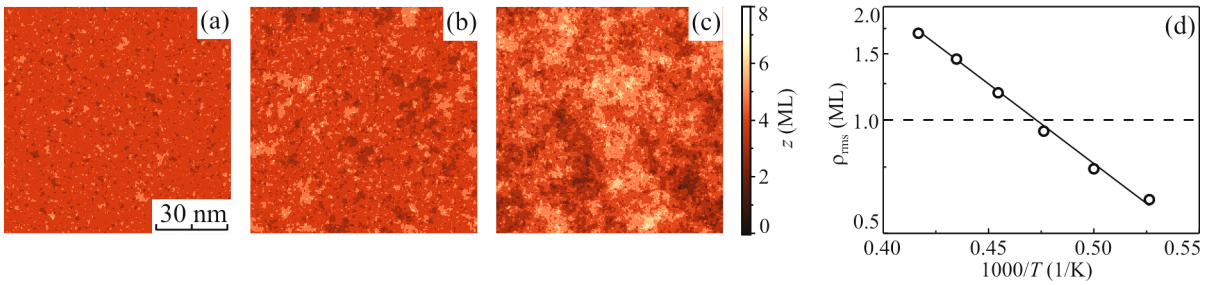

Figure 2. Simulated images of the initially flat surface after annealing for 0.01 s at 1725°C (a), 1925°C (b), 2125°C (c) and the rms roughness of the annealed surface as a function of inverse temperature (d). Dashed line in (d) shows monatomic step height. Solid line is the Arrhenius law approximation.

The roughening simulations are much more time-consuming than smoothing simulations performed in [11,12] due to increased temperature. Therefore, the annealing time in the simulation is limited by restricted computational resources. With increasing the temperature, the transition from a "smooth" surface (figure 2(a)) to an entirely disordered "rough" surface with undulations of about ± 8 ML (figure 2(c)) takes place. An estimated roughening transition temperature of the GaAs(001) surface is about $T_r \approx 1900$°C. The question remains: how to characterize quantitatively the transition from the smooth to the rough surface?

The simplest and straightforward characteristic of a rough surface is root mean square (rms) roughness. The Arrhenius plot of the rms roughness ρ_{rms} of the simulated surfaces is shown in figure 2(d). It is seen that ρ_{rms} is described by the Arrhenius dependence on the temperature with an activation energy of 2.6 E_b. The obtained activation energy value shows that a surface atom has to break 2 or 3 lateral bonds (2.6 on the average) to become an adatom. The activation dependence has no visible bend point or other features which could be considered as a roughening transition temperature. Assuming that the roughening transition corresponds to $\rho_{rms} = 1$ ML, we obtain the roughening temperature $T_r \approx 1825$°C.

A more strict criterion for surface roughening is asymptotic behavior of the surface height correlation function $G(\rho) = \langle (h_i - h_{i+\rho})^2 \rangle_i$, where h_i is the surface height at point i, ρ is an arbitrary vector in the surface plane [8,9]. If the function diverges with increasing ρ, the surface is rough. If $G(\rho)$ remains finite at large ρ, the surface is considered as smooth, although there are islands and pits. The height correlation functions calculated for the simulated surfaces are plotted in figure 3(a) in a semi-logarithmic scale. It is seen that the asymptotic behavior of the height correlation function is not clear enough due to limited annealing time and, possibly, due to the finite size of the model surface area. Still, the roughening transition temperature estimated from figure 3(d) is about $T_r \approx 2000$°C.

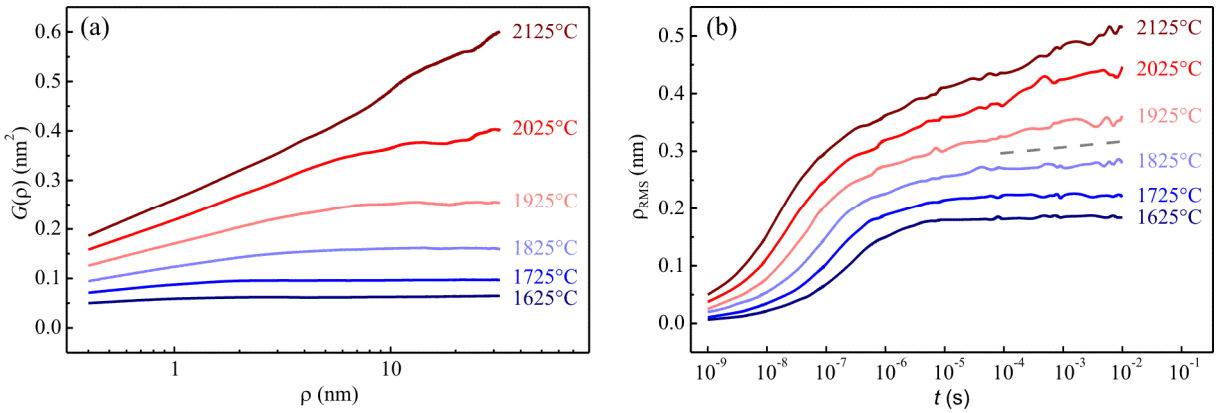

Figure 3. Surface height correlation function $G(\rho)$ (a) and kinetics of root mean square roughness (b) calculated at various annealing temperatures. The dashed line in (b) separates the "smooth" and "rough" surfaces.

To discriminate between smooth and rough surfaces more clearly, the rms roughness kinetics can be used. Figure 3(b) shows this kinetics for the simulated surfaces annealed at various temperatures. It is seen that, within the simulation accuracy, $\rho_{rms}(t)$ saturates for $T \leq 1825$°C (the surfaces remained smooth) and keeps increasing for $T \geq 1925$°C (the surfaces became rough). One can speculate that smooth surfaces reached thermodynamic equilibrium during the simulation, while above the roughening transition the equilibrium morphology is not reached, and the surface roughness continues to build up with increasing annealing time. The roughening transition temperature estimated from the kinetics is $T_r = 1925 \pm 50$ °C.

The estimated value of the thermodynamic roughening transition temperature T_r is much higher than the temperatures at which the experimental GaAs surface roughening is observed; T_r is even

higher than the GaAs melting point $T_m = 1240°$. As the equilibrium surface roughness is determined by the competition between the step line tension and step thermal fluctuations [8,9], one needs to decrease the lateral bond energy by the factor of 2, down to $E_b = 0.16$ eV in order to fit the experimental roughening by the simulation, which seems unreasonable. Therefore, the experimentally observed GaAs surface roughening is likely due to kinetic instabilities which are considered in the next section.

3.2. Kinetic roughening

To prove that GaAs surface disordering at elevated temperatures is due to kinetic factors, an additional experiment was performed. Two GaAs samples with step-terrace morphology were annealed simultaneously with one of them being covered by another GaAs slab in order to form a narrow slit ("capillary") between two adjacent GaAs surfaces [6]. Shown in figure 4 are the initial step-terraced surface (preliminary obtained by annealing at $T = 650°C$) and the surfaces of the two samples after annealing at $T = 775°C$. It is seen that, as a result of the high-temperature anneal, multilayer high islands (white dots in figure 4(b)) and multilayer deep pits (black dots in figure 4(c)) have been formed on the open and covered surfaces, respectively. The qualitative difference in morphology between the open and covered samples proves that the disordering is due to kinetic instabilities caused by deviations of annealing conditions from equilibrium towards sublimation (for the open sample) or growth (for the covered one), because one would expect a universal morphology of the disordered surface for the thermodynamic roughening.

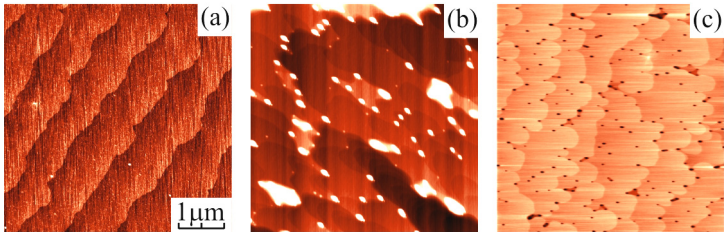

Figure 4. Surface roughening under different annealing conditions. AFM images of the initial step-terraced surface (a), and of the open (b) and covered (c) samples after annealing at $T = 775°C$.

The formation of multilayer islands and pits can be explained by monoatomic step flow around defect- or contamination-induced surface spots at which the sublimation and growth are inhibited. This explanation is confirmed by Monte Carlo simulation of steps interaction with a single defect spot. Shown in figure 5 is the simulated sublimation of a step-terraced surface with one spot in the center at which the sublimation is forbidden. After approaching the spot (figure 5(a)), a monatomic step is stopped by the spot. The step flows around the spot and, thus, forms an inlet (figure 5(b)). The inlet becomes longer and thinner (figure 5(c)), and, eventually, the step detaches from the spot (figure 5(d)). It is seen from figure 5(d) that the next step approaches the spot. Each time a monatomic step passes through the spot, the spot height is increased by one monolayer (ML) with respect to the terrace level. Thus, the islands of multilayer height are formed on the surface under sublimation.

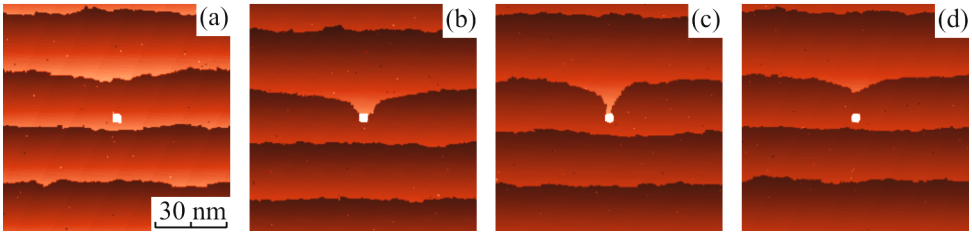

Figure 5. Consequent stages of simulated step flow through a defect-induced spot during sublimation.

4. Conclusions

In summary, possible reasons of GaAs surface roughening, which was observed experimentally at elevated annealing temperatures $T \geq 700$°C, are studied by Monte Carlo simulations. According to the simulations with model parameters obtained from the description of surface smoothing at lower temperatures $T \leq 650$°C, the thermodynamic roughening transition can not explain the experiment because it should occur at too high temperatures $T > 1800$°C. It is proved both experimentally and by means of Monte Carlo simulations that GaAs surface roughening is due to kinetic instabilities caused by deviations from equilibrium towards surface growth or sublimation. In particular, the formation of multilayer islands and pits on terraces are explained by steps flowing round some defect-induced surface spots at which the sublimation and growth are inhibited.

Acknowledgements

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