An MBE and Modeling Study of Pulsed Growth on Ge(001)

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ABSTRACT

Ge molecular beam epitaxy (MBE) and kinetic Monte Carlo (KMC) simulations are used to study time-varying processing parameters and their effect on surface morphology. We focus here on Ge growth on highly-oriented Ge(001) substrates with reflection high-energy electron diffraction (RHEED) as a real-time sensor. KMC simulations are used as the physical model, and physical parameters are determined from growth under pulsed flux. A reduced version of the simulations is generated, and temperature trajectories are computed that minimize surface roughness subject to experimental constraints.

INTRODUCTION

The processing history during thin film deposition strongly influences the final properties of a film. Time-varying conditions may be beneficial [4], but it is not practical to try all possibilities in experiment. If a systematic optimization could be applied to a mathematical model of the physics, optimal time-dependent processing conditions could be computed. We model the interplay among nucleation, coarsening, and coalescence of islands with a cubic lattice KMC simulation, using RHEED data during submonolayer growth and subsequent recovery to infer the diffusion and detachment rates. A low-dimensional differential equation is then generated that captures the behavior seen in the KMC simulations. See [2] for more details on the experiments, the KMC model, and the model reduction.

EXPERIMENTAL

Germanium films were deposited on highly-oriented Ge(001) wafers, specified by Eagle-Picher as $0.05°\pm0.02°$. The wafers were prepared by sonicating in acetone and methanol, UV-ozone exposure, and a dip in 5% HF. A typical base pressure was 1×10^{-10} torr, with a growth pressure of 5×10^{-9} torr. After the growth of a buffer layer at 550°C, the RHEED pattern consisted of the Ewald sphere, indicating a smooth clean surface. The temperature was then lowered into the range of 230–305°C, after which submonolayer doses were deposited at rates of 0.05–0.8 Å/s. Between each submonolayer dose, the temperature was raised to 550°C for buffer layer growth at 1 Å/s. RHEED was used as a real-time diagnostic. The intensity of the spectral spot was monitored using a photodiode, with an off-Bragg angle of incidence of 5° and an azimuthal angle of 3° from the (110) direction.

Figure 1 shows the normalized intensity of the spectral spot during growth and subsequent recovery. Typical intensity data is shown in Figure 1(a), in which the intensity
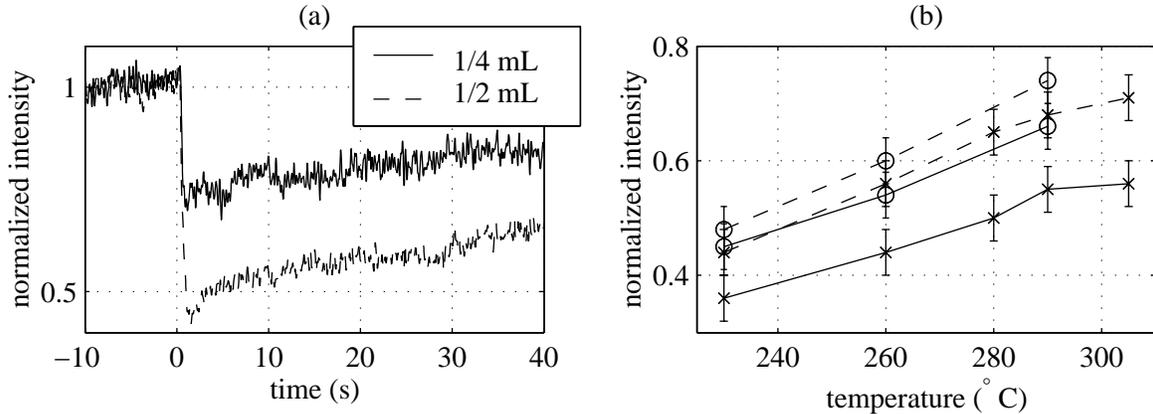
Figure 1: Normalized intensity of RHEED spectral spot. (a) During deposition at 0.8 Å/s and 290°C. (b) Immediately after the deposition of 1/2 mL ('x's) and after a further 40 s of annealing ('o's), at 0.4 Å/s (solid line) and 0.05 Å/s (dashed line).

drops during growth and recovers after the shutter is closed. Figure 1(b) shows the results of a parameter study, in which the deposition rate and growth temperature are varied. Only the intensity immediately following 1/2 mL deposition, and after 40 s of recovery, is plotted.

KINETIC MONTE CARLO SIMULATIONS

Monte Carlo simulations [3] are used as a model to describe the island nucleation, coarsening, and coalescence behavior characterizing the surface morphology of Ge(001). A 1.4 Å cubic lattice, solid-on-solid assumption, and periodic boundary conditions are used, and time is incremented as in [1]. Adsorption and surface diffusion are included, with the adsorption rate equal to the incoming flux, and the diffusion rate dependent on the number of side bonds i, such that $k_{\mathrm{dif},i} = \nu \exp((E_{\mathrm{dif},0} + \Delta E)/(k_b T))$. A standard value of 10^{13} s^{-1} is used for the vibrational frequency ν, while the appropriate values of $E_{\mathrm{dif},0}$ and ΔE are explored in simulation, as shown in Figure 2. The simulation conditions match those of the data in Figure 1(b). In all cases, 1/2 mL have been deposited. Therefore, when the temperature is fixed, we consider surfaces with equal RHEED intensity to have the same island density, and also consider surfaces with equal step density to have the same island density. Thus, the simulations are considered to match the data if the simulated step density after growth at 0.4 Å/s followed by 40 s of recovery is equal to that of the step density immediately following growth at 0.05 Å/s. The simulations of Figure 2(a) satisfy this criterion with $\Delta E = 0.20$ eV, while those in (b) with $\Delta E = 0.25$ eV do not. At a lower value of $\Delta E = 0.15$ eV, compact islands are not observed in this temperature range. The results are less sensitive to $E_{\mathrm{dif},0}$, so we use a value of $E_{\mathrm{dif},0}$=0.65 eV reported previously [5]. As another check, we performed additional simulations for comparison to island densities also reported in [5]. For a fixed value of $\Delta E = 0.20$ eV, the best fit was obtained using $E_{\mathrm{dif},0}$=0.65 eV, as compared to 0.60 and 0.70 eV, while at $\Delta E = 0.25$ eV, $E_{\mathrm{dif},0}$=0.60 eV provided the best comparison. The parameter values most consistent with the available
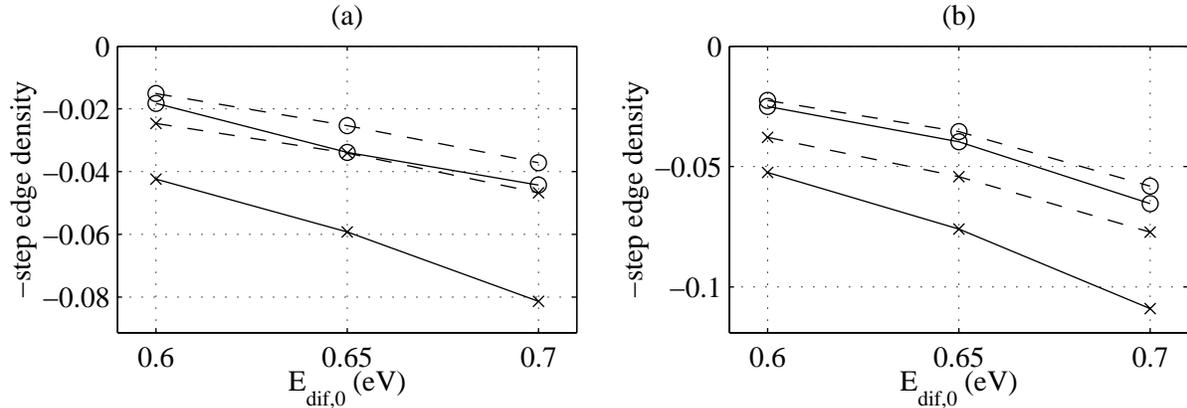
Figure 2: KMC simulations at T = 230 °C with (a) $\Delta E = 0.20$ eV, (b) $\Delta E = 0.25$ eV. Step edge density after the deposition of 1/2 mL ('x's) and after further 40 s of annealing ('o's), for 0.4 Å/s (solid line) and 0.05 Å/s (dashed line).

data are therefore $E_{\text{dif,0}}$=0.65±0.05 eV, and $\Delta E = 0.20$±0.05 eV. The nominal values are used in the subsequent simulations.

The experiments were performed at a sufficiently high temperature to ensure a straightforward interpretation of the specular spot intensity. In this temperature range, pulsing the flux in MBE using a shutter was not observed to alter the surface morphology in experiment or in simulation [2]. We now explore the effects of flux and temperature pulsing in growth at lower temperatures, using KMC simulations, with root-mean-square roughness used to characterize surface morphology. Figure 3(a) is a study of pulsed flux, with a temperature of 150°C and a mean growth rate of 1.4 Å/s. The flux is delivered in 5 ms pulses, reminiscent of pulsed laser deposition [6]. At instantaneous fluxes accessible in MBE, no difference is observed relative to continuous growth, but when extreme pulses are used the surface roughens. A different strategy is shown in Figure 3(b). A continuous flux of 1.4 Å/s is used, and a comparison is made between growth at a constant temperature of 150°C, and a strategy in which the temperature is lowered to 75°C during the first 20% of each layer to induce enhanced island nucleation, after which it is raised to 150°C. The increased island density delays the onset of secondary nucleation, yielding a smoother interface at the end of each monolayer [4]. Thus, pulsed growth may lead to rougher or smoother surfaces relative to growth at constant conditions.

REDUCED-ORDER MODEL

Time-varying growth conditions may lead to altered surface properties, but it is not practical to try every possible combination in experiment, or even in KMC simulation. An alternate approach is to apply an optimization algorithm to compute the best time-varying conditions using a model. However, the KMC simulations are computationally demanding, so that it is also not practical to perform the many simulations needed for an optimization algorithm. We reduce these computational demands by computing a reduced-order model (ROM) that captures the dynamics of the KMC simulation, using a method described in [2].
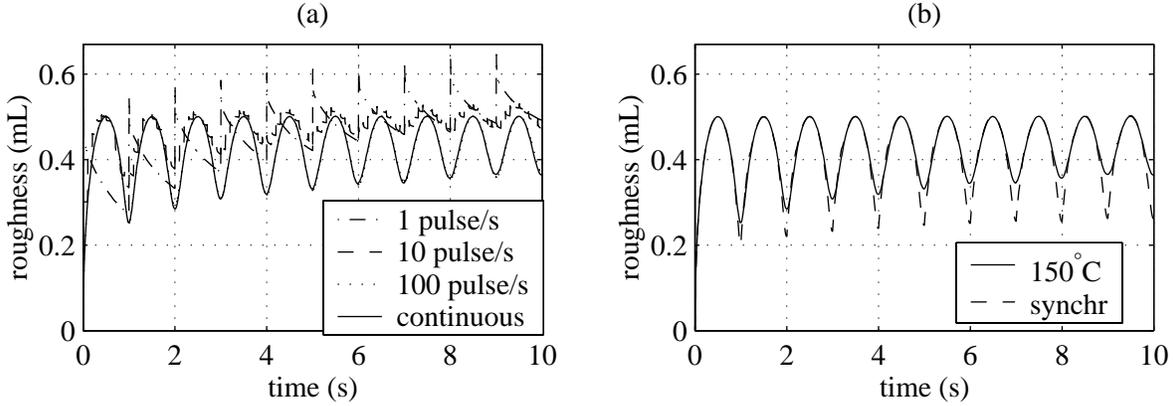
Figure 3: Kinetic Monte Carlo simulations of periodic growth conditions: (a) continuous temperature of 150°C, with a mean flux of 1.4 Å/s and various duty cycles; (b) continuous flux of 1.4 Å/s and either a continuous temperature of 150°C, or a synchronized temperature that is lowered to 75°C during the first 20% of each monolayer.
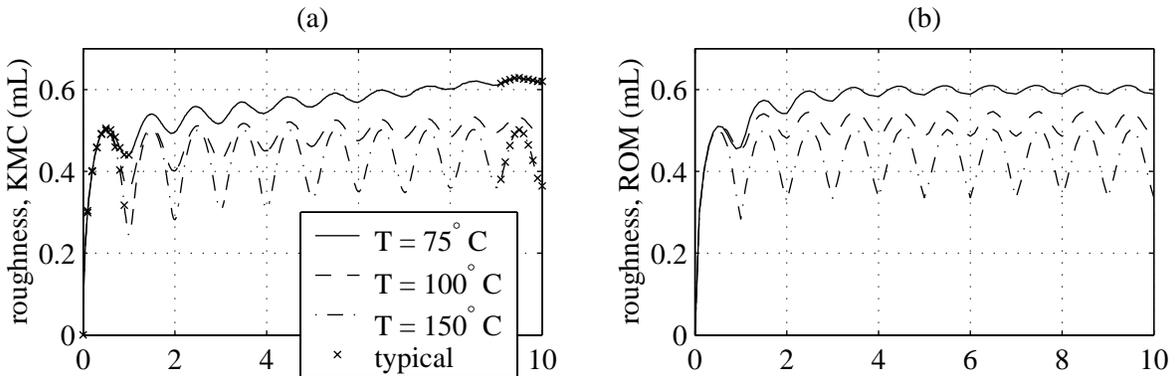

Figure 4: Comparison of RMS roughness for (a) KMC simulations and (b) reduced-order model. The 'x's denote points in the simulation when microscopic configurations were extracted to represent typical surfaces.

KMC simulation data is used to generate this model. First consider the three simulations shown in Figure 4(a). At the 40 points marks with 'x's, the surface configuration is saved. A total of 80 surfaces are prepared, by creating for each surface one surface with no adatoms, and one with a typical adatom density of 2.5×10^{-3} per site. KMC simulations are then performed beginning in each of the 80 configurations, at each of the three temperatures in Figure 4, for 0.4 s of growth. In all cases the flux is fixed at 1.4 Å/s. The KMC data is used to construct a reduced-order model, whose evolution under constant temperatures is plotted in Figure 4(b).

This model is now used to compute temperature profiles that minimize the roughness after two layers of growth, using Matlab's `fmincon` function. Three temperature profiles and the corresponding roughness evolution is shown in Figure 5. In all three cases, the objective is to minimize final roughness, while remaining in the range 75–150°C,
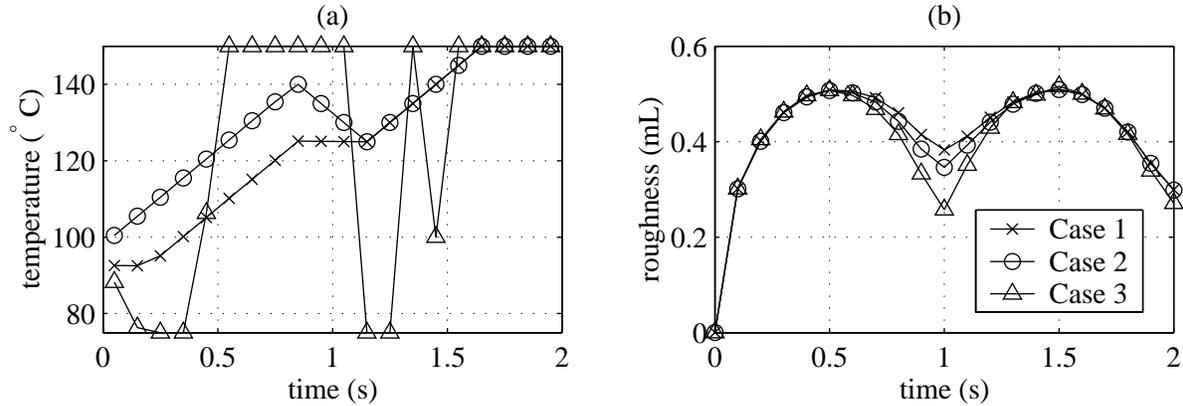
Figure 5: Optimal (a) temperature and (b) corresponding roughness computed using the reduced-order model, to minimize the final roughness. Case 1: maximum heating rate of 50 K/s and cooling rate of 0.5 K/s; Case 2: maximum heating and cooling rates of 50 K/s; Case 3: no constraints on temperature change.

but different constraints are imposed on the temperature. The first case is intended to represent the thermal environment of our MBE chamber, in which the maximum heating rate is estimated at 50 K/s in this temperature range, while the cooling rate of 0.5 K/s through radiation is much slower. In this case it is not possible to lower the temperature significantly over 2 s, so the best approach is to start with a low temperature to nucleate many islands, and then raise the temperature up to the maximum at the end. Note also that the temperature has plateaued around the initiation of the second layer, presumably so that more islands will be nucleated. In Case 2, the maximum cooling rate is raised to the value of the maximum heating rate. Again, it is desirable to minimize the temperature at the initiation of each layer, and also to have the maximum temperature at the end. In Case 3, no rate constraints are placed on the temperature, and the best strategy is to minimize the temperature at the beginning of a layer, and maximize it at the end.

DISCUSSION AND CONCLUSIONS

In this work we have performed MBE experiments to study the nucleation and coarsening of islands in Ge(001) homoepitaxy. Real-time RHEED measurements were used as the diagnostic for surface morphology, and were compared to KMC simulations to determine the activation energies for surface diffusion on a cubic lattice. The KMC simulations were then used to make predictions of growth strategies that were not accessible in our MBE system (high instantaneous flux) or that would have obfuscated the interpretation of the RHEED signal (temperature variation). The simulations predict that in low temperature growth, periodic growth conditions may produce either smoothening or roughening.

To study the effect of arbitrary time-varying growth conditions, a reduced-order model was generated using KMC simulation data. Temperature profiles that minimize surface roughness were then computed using an optimization algorithm, which includes the thermal response of the MBE heater assembly. The reduced model enabled the application of

an optimization algorithm, which was not practical using the full KMC simulation, and also enabled coupling between the microscopic dynamics of surface morphology and the macroscopic temperature dynamics of the MBE chamber.

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