

## Atomistic Modeling of III-V Semiconductors: Thermodynamic Equilibrium and Growth Kinetics

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### ABSTRACT

Growth kinetics and thermodynamic equilibrium can both be determining factors at different stages of III-V semiconductor heteroepitaxy. We study their interplay, employing kinetic Monte Carlo simulations for the InAs(001) surface. The simulation contains atomistic details of both species, including the stability of different reconstructions and their kinetics. The behavior of the surface in thermodynamic equilibrium, including different reconstructions, is determined exclusively by extensive total energy calculations employing *ab initio* density functional theory. The continuous phase transition between the  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$ , predicted by theory, is confirmed by experiment. At full layer coverage, a recovery of the stable reconstruction is observed. The different time scales associated with As<sub>2</sub> and In are discussed with respect to equilibrium and kinetics.

### INTRODUCTION

Recent improvements in heteroepitaxy of III-V semiconductors enable nearly atomically flat interfaces between different layers. The reduction in width of some device layers down to a few atomic lattice constants on the other hand increases the effect of variations on the atomic scale. The complex behavior of III-V semiconductor surfaces makes investigation of atomic mechanisms challenging. Although many new insights into static surfaces, particularly concerning reconstructions, have been gained over the past few years, [1-4] the understanding of kinetics on the atomic scale is still in its infancy, even despite recent progress [5-7]. Because direct observation of microscopic processes is experimentally very difficult one relies on either *in situ* techniques like reflection high energy electron diffraction (RHEED) or photo emission (PE) that need additional interpretation to conclude microscopic morphology, or *ex situ* characterization with techniques like atomic resolution scanning tunneling microscopy (STM), where the surface is processed before it is investigated. The challenge for theoretical investigation is the determination of the large number of possible surface processes and their complex interplay. Although total energy calculations employing *ab initio* density functional theory (DFT) allow studying single processes with high accuracy [7,8], a full quantum mechanical treatment over long time scales or larger cells is not possible. These arguments suggest that computer simulations based on a combination of theory and experiment, for model construction and verification respectively, might be necessary to gain understanding in the complex dynamics of III-V semiconductors.

In this paper, we describe a new methodology that combines thermodynamic equilibrium and growth kinetics within one unified model, based on extensive DFT calculations and supported by experimental results. The achievable accuracy is demonstrated using the example of a kinetic Monte Carlo (KMC) simulation for the InAs(001) surface. Theoretical results predict a continuous transition between the  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$ . Simulated and experimental results

agree quantitatively in the temperature dependence of the As-dimer density, directly related to this phase transition. Extending the results we reported elsewhere [9] for submonolayer deposition, we report simulation results for higher coverage exceeding one monolayer (ML) deposition. We discuss the possible use of our simulation results for surface and interface engineering.

## AB INITIO DENSITY FUNCTIONAL CALCULATIONS

Atomic and electronic structure of the InAs(001) surface is studied employing *ab initio* density functional theory using the FHI98MD program package [10]. Total surface energies are calculated by modeling them in a slab geometry with periodic boundary conditions. The bottom of the slab is passivated with pseudohydrogen. Slab and vacuum thickness are converged with respect to the total energy at a length equivalent to 8 atomic layers. The local density approximation (LDA) as well as generalized gradient approximation (GGA) is used for the exchange correlation functional. Wavefunctions are expanded in plane waves up to the converged energy of  $E_{cut}=12$  Ry. The k-point summation is carried out with a Monkhost-Pack k-point set equivalent to 8x8 k-points per 1x1 unit cell.

## KINETIC MONTE CARLO SIMULATION

The surface structure of InAs, including its bulk zincblende, structure is described in the simulation as follows. The simulation is carried out on a square lattice with unit vectors in the [110] and [-110] direction. Each site represents a (1x1) unit cell of the InAs(001) surface, and is characterized by its state. Allowed states are In that can have a [110], [-1-10], or no in-plane bond, and As that can have a [-110], [1-10], or no bond. The state of a site can be changed by processes describing adsorption, desorption, and diffusion on the surface. The state of site  $i$  and its neighborhood determines the local surface energy. The total surface energy is given by summing the local energy contributions of all sites.

The definition of a total surface energy in the model allows a direct mapping to total energies calculated by DFT. The parameter determination of the model energy utilizes more than 40 total energies, including those of different surface reconstructions, In adatom configurations on those reconstructions, and different As-dimer adsorption energies. By comparing energies from this model to an independent set of DFT calculations, we can test convergence with respect to interaction length, number of parameters, and parameter values. We find that energies are sufficiently converged, including interactions up to next nearest neighbor sites together with many body interactions involving up to six sites. Importantly, we find that the accuracy achieved with the model is comparable to the accuracy of the DFT calculations. A few remaining kinetic parameters (the prefactor for In and As processes, and the transition energy for In diffusion) were determined by comparing simulation results to specifically designed experiments [9]. A complete description of our KMC model will be published elsewhere.

After describing the experimental setup in the next section, we then compare simulation results for temperature dependent As-dimer densities in equilibrium with experiment. Growth kinetics is investigated for submonolayer deposition [9] and, presented here, multilayer deposition.

## EXPERIMENTS

InAs(001) surfaces are prepared on undoped InAs buffer layers using conventional MBE techniques. The magnitude of the As-flux from the valved EPI As<sub>2</sub> source is measured by the

uptake method [11]. RHEED and PE are used as *in situ* sensors. Surfaces are annealed (In-flux  $F(\text{In}) = 0$  ML/s) under fixed As-flux of  $F(\text{As}) = 0.083$  ML/s at different temperatures. After achieving a steady-state annealing condition as shown by RHEED and PE the surfaces were quenched by simultaneously closing the valve and As-shutter, cutting the power to the substrate heater, and rotating the sample towards the cryopanel. The sample was transferred under UHV to the analysis chamber with an Omicron LS full-wafer STM and imaged after cooling to room temperature.

## THERMODYNAMIC EQUILIBRIUM

We simulate the temperature dependence of annealed InAs(001) surfaces that is under zero In-flux. The initial surface is setup as a perfectly flat  $\beta 2(2 \times 4)$  reconstructed surface. We monitor the As-density during the simulation for different temperatures using otherwise identical conditions. The As-density is determined within the simulation by counting sites that have an As state and no higher neighboring sites. Therefore the ideal  $\alpha 2(2 \times 4)$  has a top As-density of 0.25 atoms per (1x1) whereas  $\beta 2(2 \times 4)$  0.5 atoms per (1x1).

The time dependence of the As-density is plotted in Fig. 1 for temperatures between 380°C and 440°C at an As flux of 0.083 ML/s.

The higher the temperature the faster the reduction and the lower the As-density. But even at higher temperatures equilibration needs a few seconds. The simulated surface morphologies after

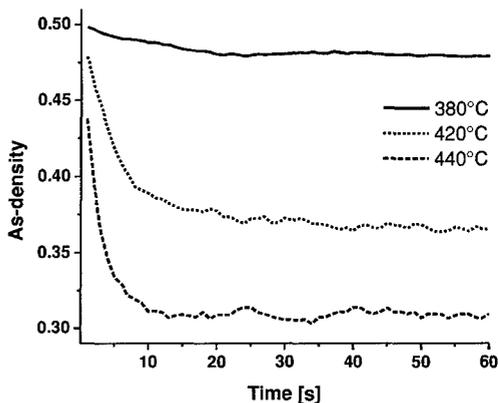


Figure 1 Simulated time dependence of As-density starting from a perfect  $\beta 2(2 \times 4)$  reconstructed surface at various temperatures.

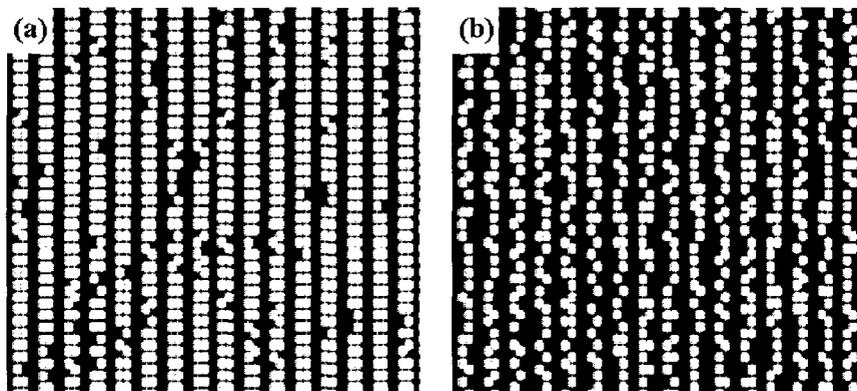


Figure 2 Simulated annealed InAs(001) surface in thermodynamic equilibrium. Parameters: As-flux  $F(\text{As}) = 0.083$  ML/s, (a)  $T = 380^\circ\text{C}$  (b)  $T = 440^\circ\text{C}$ .

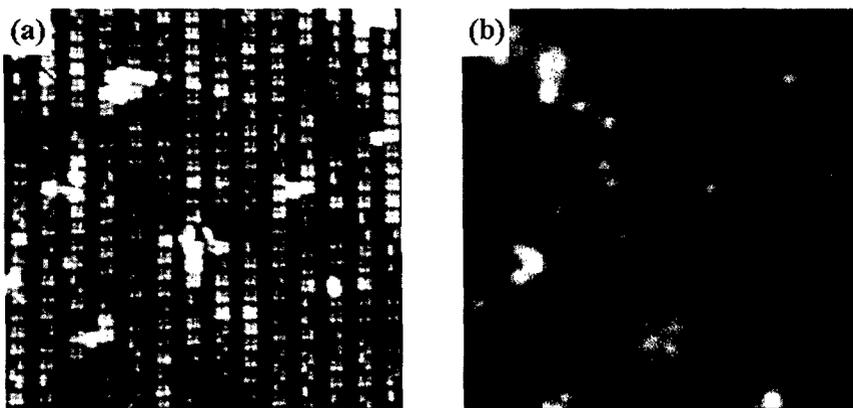


Figure 3 Annealed InAs(001) surface in experiment investigated by scanning tunneling microscopy. Conditions are identical to simulation (see Fig. 1):  $F(\text{As}) = 0.083 \text{ ML/s}$ , (a)  $T = 380^\circ\text{C}$  (b)  $T = 440^\circ\text{C}$ .

100 min annealing time are plotted in Fig. 2 for two different temperatures. In both situations the surface consists mainly of  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  unit cells. Additionally there are staggered dimers i.e. dimers that are phase-shifted along the dimer rows by one lattice constant. Experimental results for surfaces annealed under identical conditions are presented in Fig. 3.

## GROWTH KINETICS

We present simulation results for homoepitaxial growth of InAs(001). The initial surface has the  $\beta 2(2 \times 4)$ -reconstruction. The growth simulation is carried out with parameters given in caption of Fig. 4. The growth rate is determined by the In-flux equal to  $0.5 \text{ ML/s}$ . The average As-incorporation is identical balanced by adsorption and desorption. Fig. 4 presents the surface morphology after (a) half a ML and after (b) a full ML of deposition during growth. Whereas the  $\beta 2(2 \times 4)$ -reconstruction nearly disappears after  $0.5 \text{ ML}$ , at ML completion patches of reconstructed unit cells become visible again. Note that these simulations should not be directly compared to existing STM pictures because we have not included the quenching process. We monitor changes in surface morphology by determining the density of certain local structures. As an example we plot the As-density during growth in Fig. 5. We find an oscillatory behavior connected to the ML coverage. The As-density has its minimum close to  $1/2 \text{ ML}$  at  $1 \text{ s}$  and its maximum at ML completion at  $2 \text{ s}$ .

## DISCUSSION

The  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  reconstructions are stable for InAs(001), as shown experimentally and theoretically [1,4]. Due to lack of interaction between neighboring  $(2 \times 4)$  cells, a continuous transition between both reconstructions is observed. Here we demonstrate the possibility of utilizing the substrate temperature to determine the exact As-density within the limits given by  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$ . The resulting simulated surface morphologies (see Fig. 2) agree quantitatively with the experiment (Fig. 3). The As-density as a function of the substrate temperature is identical in simulation and experiment. The time to equilibrate the InAs(001) surface, is under typical growth conditions, at least a few seconds and exceeds typical growth rates.

Starting from a  $\beta 2(2 \times 4)$  reconstructed surface, initially deposited In atoms form dimers and later smaller clusters on the As-dimer rows, leading to the reduction of the surface As-density

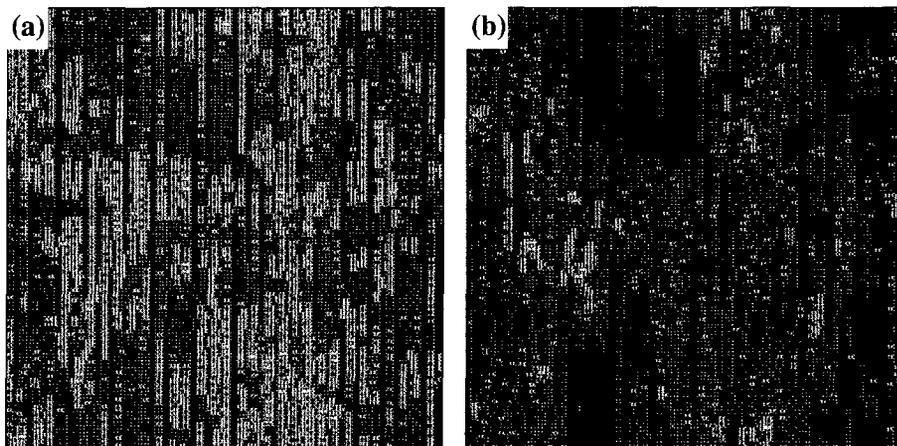


Figure 4 Surface morphologies after deposition of (a) 0.5 ML and (b) 1.0 ML (lower layer is omitted for clarity). Growth parameters  $F(\text{In}) = 0.5 \text{ ML/s}$ ,  $F(\text{As}) = 2.5 \text{ ML/s}$ ,  $T = 380^\circ\text{C}$ .

shown in Fig. 5. At later stages, more In clusters form and additional In adatoms filling the reconstruction trench. This opens adsorption sites for the simultaneously incoming As-flux. The minimum of exposed surface As-dimers is found to be close to the half ML. Related changes in local surface electronic structure could give rise to oscillations observed by *in situ* characterization techniques.

As we have demonstrated, equilibration times exceed typical growth rates. Therefore, we conclude that typical InAs(001) growth does not take place close to thermodynamic equilibrium. However, time scales associated with the dynamics of In-atoms are several orders of magnitude shorter and hence allow a partial equilibration of the In subsystem between As adsorption/desorption processes. This interplay between equilibration and non-equilibrium can be utilized for interface design. Thermodynamic equilibrium provides the possibility to continuously adjust the As-density and influence details of the initial surface. By changing the As-density, the surface kinetics and therefore the non-equilibrium behavior is directly affected.

The KMC model we present here allows investigation of detailed dynamics on the atomic scale that is difficult to achieve by experimental means. The agreement with experimental results

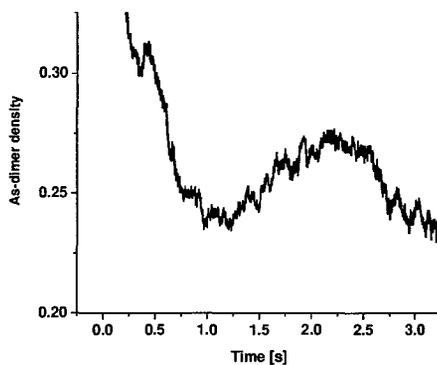


Figure 5 Time development of the As-density during growth. Identical simulation as presented in Fig. 4.

in thermodynamic equilibrium and submonolayer deposition [9] and the parameter determination by *ab initio* DFT calculations was necessary to achieve this kind of predictive capability. Modeling of *in situ* growth sensors like RHEED and PE can take advantage of the detailed microscopic information given by the KMC simulation.

## SUMMARY

Simulations and experiments are presented that investigate the thermodynamic equilibrium and growth kinetics of the InAs(001) surface. We employed *ab initio* DFT based KMC simulation to study surface dynamics on the atomic scale. Theoretical and experimental results, together with simulations, suggest a unique continuous phase transition between the stable  $\alpha 2(2 \times 4)$  and  $\beta 2(2 \times 4)$  reconstruction. Different time scales of the As-dimers and In-atoms lead to important consequences for understanding growth of InAs(001). Equilibration times for As-dimers exceed typical growth rates. Growing surfaces are therefore globally in non-equilibrium. However, the high mobility of In-atoms compared to the slower kinetics of As processes leads to partial equilibration of the In subsystem between successive As dimer deposition events.

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