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Ab inito thermodynamics and statistics of semiconductor growth, and self-assembly of quantum dots

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Recent developments in methodology allow us to extend the *ab initio* (*i.e.*, starting from the self-consistent electronic structure) approach to poly-atomic complexes with 10,000 and more atoms, time-scales of seconds, and involved statistics (*e.g.*, *ab initio* molecular dynamics with 10,000 and more trajectories). In this contribution we will

- sketch recent density-functional theory based hybrid methods, which bridge the length and time scales from those of electron orbitals to meso- and macroscopic proportions,
- present results for crystal growth and the self-assembly of nano-scale structures.

I. INTRODUCTION

Molecular modeling with the goal to develop new materials or improving materials' properties (*e.g.* of surfaces, interfaces, or doping profiles) typically employ empirical methods together with *effective* parameters, which have little (if any) physical meaning. Thus, such simulations, though useful, are done *without (microscopic) understanding*, and are not predictive. As a consequence, for different conditions (temperature, partial pressures) the employed parameters may change in an unclear manner.

What has hindered the development and use of *predictive* methods, *e.g.* for diffusion and growth, is the significant lack of understanding of the underlying microscopic processes. This confession refers to the fact that quantitative numbers for diffusion energy barriers and pre-factors are unknown and even in a qualitative sense we note that it is grossly unknown how atoms adsorb, move, and interact with each other at surfaces.

Whereas *the ruling microscopic processes* operate in the length and time domains of 0.1 - 10 Å and 10^{-15} - 10^{-13} seconds, properties of interest (*e.g.* the growth morphology) exhibit proportions of $> 5,000$ atoms and they develop over a time of $> 10^{-2}$ seconds. Thus, we are challenged by the need to bridge the length and the time scales by many orders of magnitude. In fact, this also implies that concentrating on a few atomistic simulations will not give relevant information: Proper handling of the statistics is as important as is the accurate evaluation of the microscopic processes.

In this contribution we discuss methods and strategies to meet the above mentioned challenge. We emphasize the need to evaluate the microscopic properties by density-functional theory (DFT) and show how the obtained information can be combined with methods from thermodynamics and statistics. This bridges the time and length scales, provides *predictive* molecular modeling of growth, and it also provides *understanding.* As a specific example we will mention recent work on the growth of GaAs, and briefly discuss the formation of InAs quantum dots on GaAs(001).

II. SURFACE STOICHIOMETRY AND STRUCTURE

The stoichiometry and structure of a surface of a compound material is largely affected by the environment, because a surface will exchange atoms with its surroundings. Thus, if thermal and chemical equilibrium is achieved, the atomic surface geometry and composition is determined by the minimum of the Gibbs free energy of the system with respect to its dependence on the chemical potentials of the components present in the material and the environment. For a compound semiconductor, as for example GaAs or InAs, the As partial pressure is the most important factor in the analysis, as well as temperature.

For GaAs(001) under As rich (but not too rich) conditions the so-called $\beta 2$ structure with a (2×4) periodicity is the stable surface geometry. This was indeed predicted by theory since long (see for example Ref. [2] and references therein), but the experimental verification only succeeded last year. [1] A top view of this geometry (from the combined STM and DFT analysis) is shown in Fig. 1. This study also demonstrates clearly that STM studies the electronic structure and not simply images atomic positions.

A systematic discussion of the surface stoichiometries, atomic geometries, and surface energies of all low-index surfaces of GaAs, InAs, GaP, and InP can be found in Refs. [2,3].

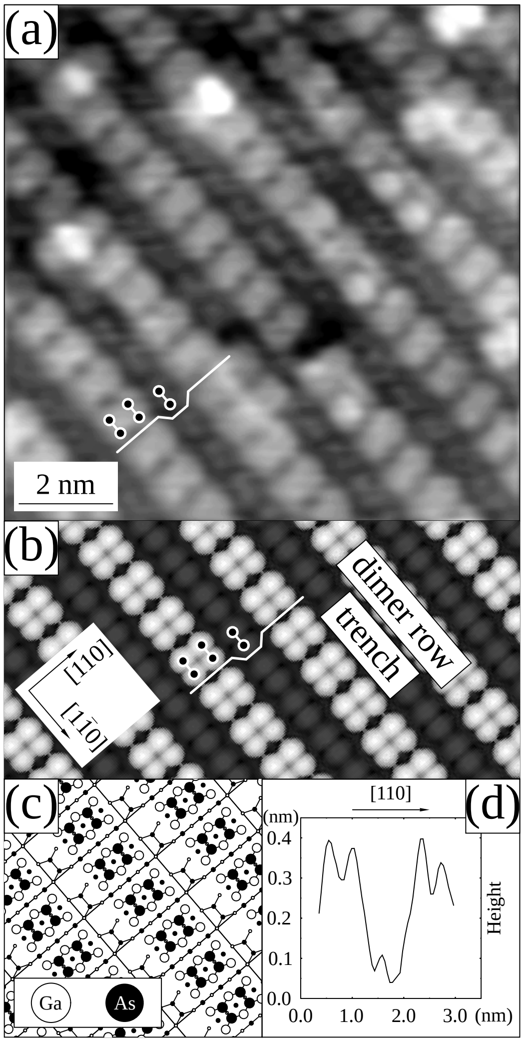

FIG. 1. STM data (a) and DFT-based STM simulation (b) of the $\beta 2$ structure of GaAs (see Ref. [1]). Panel (c) displays the atomic geometry found in the calculation, and panel (d) shows the STM topography along the [110] direction. We see rows of two neighboring As dimers (bright regions in a and b) separated by trenches. At the trench bottom there are also dimerized As atoms.

III. DIFFUSION AND GROWTH OF GAAS

This Section summarizes some general ideas and briefly describes results of a recent *ab initio* kinetic Monte Carlo simulation of growth of GaAs.

Crystal growth happens on a time scale of seconds, and the length of kinetically controlled island shapes can well be of the order of > 10 nanometers. This situation cannot be handled by brute-force molecular dynamics calculations, but instead it is necessary to combine the DFT calculations of the various microscopic diffusion processes with a statistical treatment of the long-term island formation and growth. The proper statistical approach is the kinetic Monte Carlo (kMC) method, which so far was typically employed together with empirical or semi-empirical parameters. Thus, so far the approach was not "predictive" and the microscopic meaning of the parameters typically ill defined. Only for homoepitaxy of metals a kMC calculation with *ab initio* determined input parameters was recently performed by Ruggerone *et al.*. [4]

The key idea behind the kinetic description of growth is that the underlying atomistic processes, such as diffusion or desorption, are described by rates. Once the rates are known, the various processes and their interplay can be handled by standard methods from statistical physics. The rate of a microscopic process j that occurs during growth usually has the form

$$\Gamma^{(j)} = \frac{k_{\rm B}T}{h} \exp(-\Delta F^{(j)}/k_{\rm B}T) \quad , \tag{1}$$

where $\Delta F^{(j)}$ is the difference in the Helmholtz free energy between the maximum (saddle point) and the minimum (equilibrium site) of the potential-energy curve along the reaction path of the process j. T is the temperature, $k_{\rm B}$ the Boltzmann constant, and h the Planck constant. The free energy of activation $\Delta F^{(j)}$ needed by the system to move from the initial position to the saddle point is given by

$$\Delta F^{(j)} = \Delta E_{\rm d}^{(j)} - T\Delta S_{\rm vib}^{(j)} \quad . \tag{2}$$

Here $\Delta E_{\rm d}^{(j)}$ is the differences of the total energy (static and vibrational) of the system with the particle at the minimum and at the saddle point, and $\Delta S_{\rm vib}^{(j)}$ is the analogous difference in the vibrational entropy. The rate of the process j can be cast as follows:

$$\Gamma^{(j)} = \Gamma_0^{(j)} \exp(-\Delta E_{\rm d}^{(j)}/k_{\rm B}T) \quad , \tag{3}$$

where $\Gamma_0^{(j)} = (k_{\rm B}T/h)\exp(\Delta S_{\rm vib}^{(j)}/k_{\rm B})$ is called the attempt frequency. The two basic quantities in Eq. (3), $\Gamma_0^{(j)}$ and $\Delta E_{\rm d}^{(j)}$, can be obtained from the potential-energy surface (PES), which is the potential energy experienced by the diffusing adatom (*e.g.* Ga), or molecule (*e.g.* As_2),

$$E^{\rm PES}(X_{\rm ad}, Y_{\rm ad}) = \min_{Z_{\rm ad},\{\mathbf{R}_I\}} E^{\rm tot}(X_{\rm ad}, Y_{\rm ad}, Z_{\rm ad}, \{\mathbf{R}_I\}) \quad , \tag{4}$$

where $E^{\rm tot}(X_{\rm ad}, Y_{\rm ad}, Z_{\rm ad}, \{\mathbf{R}_I\})$ is the ground-state energy of the many-electron system (also referred as the total energy) at the atomic configuration $(X_{\rm ad}, Y_{\rm ad}, Z_{\rm ad}, \{\mathbf{R}_I\})$. According to Eq. (4) the potential-energy surface is the minimum of the total energy with respect to the z-coordinate of the adatom $Z_{\rm ad}$ and all coordinates of the substrate atoms $\{\mathbf{R}_I\}$. Assuming that vibrational effects can be neglected, the minima of the potential-energy surface represent stable and metastable sites of the adatom. Note that this potential-energy surface refers to slow motion of nuclei and assumes that for any atomic configuration the electrons are in their respective ground state. Thus, it is assumed that the dynamics of the electrons and of the nuclei are decoupled. This is the Born-Oppenheimer approximation that for not too high temperatures is usually well justified.

Growth of GaAs, when using molecular beam epitaxy, typically starts with the $\beta 2$ reconstruction (see Fig. 1 above). Kley *et al.* performed systematic DFT studies of the potential-energy surface of a diffusing Ga adatom. [5] They found that the Ga diffusion is anisotropic, and that two sheets of potential-energy surfaces exist: On one sheet Ga adatoms diffuse quite efficiently, in particular in the trenches, along the $[1\bar{1}0]$ direction. However, a Ga adatom may also break the bonds of an As-dimer in the trench (a process, which is hindered by an energy barrier) and assume a nearly planar geometry with these two As atoms. [5] In this geometry the Ga adatom is essentially fixed.

DFT studies for the potential-energy surface of As_2 molecules on the $\beta 2$ surface were recently performed by Kratzer *et al.* [6–8]. These results (and more [9]) then form the basis of a subsequent kMC simulation. The results show, for example, that the "critical nucleus" of island formation and growth is zero (*i.e.*, the smallest stable island is one Ga atom in the trench plus an As addimer. Such small critical nucleus is quite unusual and will have interesting consequences for the island formation at this surface (see Ref. [9]). Kratzer *et al.* [9] find in their *ab initio* kMC study that, in contrast to previous simulations which only employed very few empirical parameters, it is necessary to include the interplay of about 30 different atomistic processes.

We conclude this Section with a warning. An *ab initio* kMC simulation of homoepitaxial growth of a compound semiconductor is a significantly more complicated task than a growth simulation of a metal (*e.g.*, for the growth of GaAs two species are present (one raining down as a molecule), and various complicated surface reconstructions may evolve when the growth proceeds). Still, even for an *ab initio* kMC simulation of homoepitaxial growth of a metal [4] the risk exists that an important microscopic process may be overlooked. Indeed, the earlier work suffered from such a problem (see [10]). Thus, DFT-based growth simulations should be treated with much respect and caution. We just see the early beginning of this approach.

IV. EQUILIBRIUM SHAPE OF QUANTUM DOTS: INAS ON GAAS

Whereas Section III emphasized the importance of adatom kinetics and the statistical nature of growth, sometimes a restriction to thermal equilibrium may be sufficient. Of course, thermal equilibrium is also contained in a kinetic modeling, but the costs for such situation were unnecessarily expensive. This Section now assumes that thermal equilibrium is achieved, or, as we will emphasize, that the system may be trapped in a *constrained* thermal equilibrium state.

Quantum dots are small three-dimensional islands of a smaller-bandgap semiconductor which are enclosed in a wider-bandgap semiconductor matrix. Provided the bands of the quantum dot and of the host are appropriately aligned, the valence and conduction bands produce a confinement potential for the holes in the valence band and the electrons in the conduction band.

The recombination spectrum of a single quantum dot consists of a single sharp line. The main problem, which presents a significant challenge for the application of quantum dots for LEDs and lasers, is that many dots (*i.e.* $> 10^6$) are needed, in order to obtain a high light intensity. And all dots should be nearly identical, so that they all emit at the same wave length. Thus, in a quantum dot LED the width of the line is determined by the composition, size, and shape fluctuations of the ensemble of quantum dots.

The required length scale of the dots dimension is dictated by the condition that the energy separation of the quantized electronic levels should be about 0.1-0.2 eV, so that they are not populated at room temperature. And the dots have to be sufficiently large that at least one bound level exists; for too small islands this is not the case. For GaInAs these quantization conditions imply that the required length of quantum dots is between 50 and 200 Å, which means that we are dealing with objects which contain between 5,000 and 50,000 atoms. How can one produce such small objects with the required uniformity in composition, size, and shape?

Already in 1985 it had been observed that such dots form by itself when InAs is deposited on GaAs. However, at that time it was not believed that the needed uniformity in size and shape can be obtained. Only since 1993 several groups have shown that a range of growth parameters exist at which quantum dots assemble themselves with the desired and tunable size and a rather narrow size distribution, and in research laboratories LEDs and lasers have been already built with such quantum dots.

Although one is able to produce such quantum dots, the mechanism giving rise to their self-assembly is still not understood, and in fact, the discussion is quite controversial. We therefore performed DFT calculations of the equilibrium structure in order to compare these results with results from growth experiments. [11] The motivation is that, if the experimental shapes disagree with the equilibrium geometry, it should be concluded that kinetics rule the self-assembly of the quantum dot and not equilibrium thermodynamics. Of course, the experimental quantum dot shapes (and composition) depend on the growth conditions, but the calculations show that in some experiments the quantum dots indeed conform with the properties predicted by the constrained thermodynamic equilibrium theory.

Part of the concept behind our calculations is shown in Fig. 2. Using InAs deposited on GaAs(001) as an example, we compare the total energy of an InAs film (thickness θ_0), see top of Fig. 2, with the energy of quantum dots, at a given density, and a thinner film (bottom of Fig. 2). Obviously, the total amount of material in both situations must be the same. In these calculations the surface energies of the various side facets of the quantum dot, and the surface and interface energies of the wetting layer (also as function of the wetting layer thickness) were calculated by density-functional theory. The strain relaxation of the quantum dot, in the wetting layer and the substrate, and the elastic energy were calculated by continuum elasticity theory, employing a finite-element approach. For dots containing more than 5,000 atoms this is indeed appropriate. The calculational details are described elsewhere (see Refs. [12,13] and references therein).

Some words about the constraint, namely the quantum dot density, are in order. Though we employ (equilibrium) thermodynamics, we assume that the process of the quantum dot growth happens in three phases: a nucleation phase, which mainly determines the island density n, a second phase where the islands grow mostly on expense of the wetting layer, sometimes, depending on the growth conditions, followed by a third phase characterized by Ostwald ripening. As long as the wetting layer acts as a source for material, existing nuclei will grow rapidly. Hereby the island density n remains constant [14] during the growth. We treat it as an input to our model noting that it may be determined separately by a theory of the growth kinetics. [15,16]

The results of this study reveal that an optimum island size exists for a given coverage and island density, and this indeed explains the narrow size distribution of quantum dots observed in some experiments. Closely linked to this optimum islands size is the thickness of the wetting layer. Figure 3 shows these results as function of the island density and the amount of deposited material. It is found that only about 10-30% of the total deposited material is assembled into islands, depending on the nominal coverage and the island density. Furthermore, the results show that there always exists a wetting layer thicker than 1 ML after the formation of three-dimensional islands has set in (see Fig. 3). This is apparently in agreement with recent results of a cross-sectional scanning-tunneling microscopy investigation. [17]

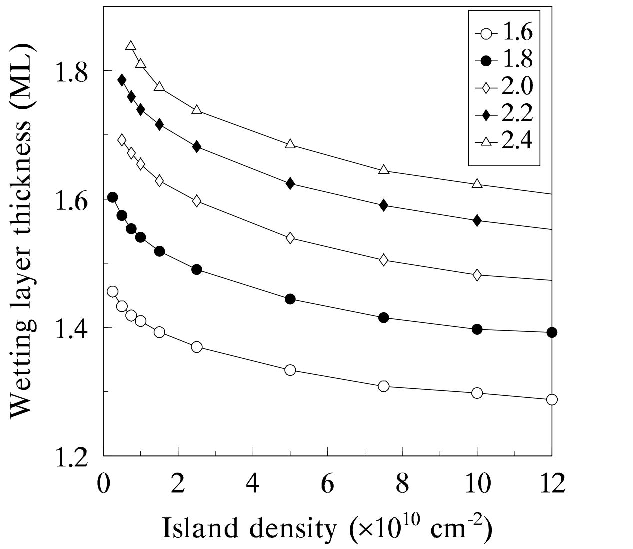

FIG. 3. Dependence of the wetting layer thickness on the island density and the nominal coverage.

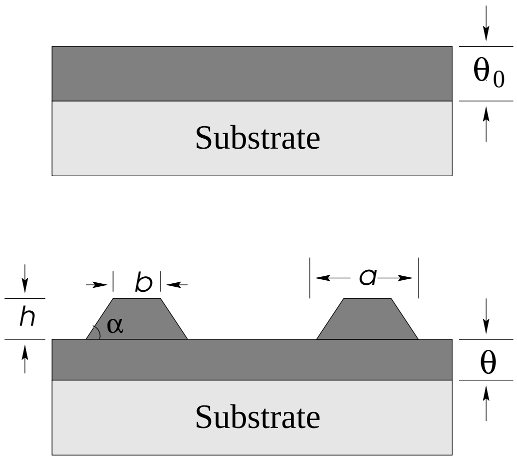

FIG. 2. Schematic illustration of the formation of coherent islands on the substrate surface. θ_0 is the nominal coverage (i.e., the total amount of deposited material) and θ is wetting layer thickness. α is the tilt angle of island facets. The square island base corresponds to the [110] and [$\bar{1}$10] directions and the bottom face and top face are a^2 and b^2, respectively. h is the island height.

The island shape (*e.g.*, aspect ratio: h/a, cf. Fig. 2) is found to depend only on the island size. Results for the equilibrium shape of InAs quantum dots on GaAs(001) and their dependence on size and As partial pressure have been published by Moll *et al.* [2], and for InP quantum dots on GaP(001) Liu *et al.* [3] have performed a corresponding analysis.

Despite the noted results for the constrained equilibrium (given island density), we also note that larger islands in conjunction with a lower island density are more stable, which means that the islands will undergo ripening, but this will happen on considerably longer time scales, and thus can be avoided in actual growth experiments.

V. SUMMARY

Figure 4 summarizes the basic concepts discussed in this paper. The top emphasizes that materials' properties are ruled by the nature of chemical binding, *i.e.*, by the electronic structure. This determines the total energy of poly-atomic systems. The total energy as a

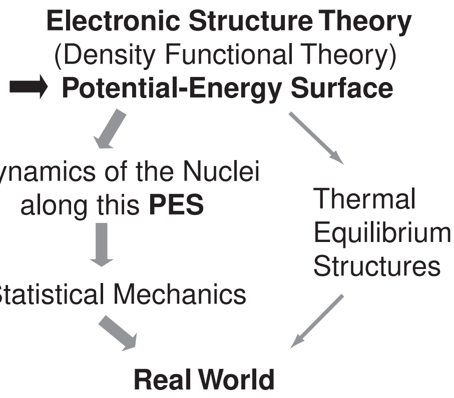

FIG. 4. Schematic summary of the thermal-equilibrium approach (right) and of the more general kinetic description (left).

function of the atomic coordinates represents the high-dimensional potential-energy surface. The right part of Fig. 4 shows the traditional approach which "only" concentrates on minima of the potential-energy surface, as these determine the thermal equilibrium properties of materials. This is part, though only a little part, of the "real world". Sections II and IV of this paper had taken this view. The approach sketched on the left side follows the route taken by nature (and in Section III). It realizes that the knowledge of the potential-energy surface is not the final step, but the basis of the full description. In addition to the potential-energy surface we need to consider the dynamics of the nuclei, *e.g.* how atoms diffuse on a surface, and what happens when two (or more) adatoms meet. However, in order to understand growth and island size distributions, we have to describe very long times, many atoms, and many islands. This requires the use of statistical mechanics.

Each of these three levels (electronic structure theory, dynamics of the nuclei, statistics) is of similar complexity, and each of them is of similar importance. Only if a careful job is done on all these three levels, one may make contact with the real world, *i.e.*, only then one will learn about crystal growth, formation of adsorbate islands, and self-assembly of quantum dots, for example.

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