SimGrow 2015

CECAM/Psi-k/HERALD Workshop
Simulation of chemistry-driven growth phenomena for metastable materials

Schloss Rauischholzhausen/Germany, 08.–11. November 2015

Program

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Location

The conference will take place in Schloss Rauischholzhausen, a 19th century building owned by the University of Gießen in the vicinity of the old university town of Marburg. The closest international airport is Frankfurt/Main, from where a hourly train connection to Marburg exists. Marburg main station is located at the railroad line Frankfurt–Kassel and is regularly reached by regional and intercity trains (see www.bahn.de for schedules).

There will be a shuttle bus from Marburg main station to the conference location. It is also possible to take a taxi (taxi stand close to the train staion or call SparCar (+49 6421 999988) and they will pick you up).

By car, Rauischholzhausen can be reached coming from Gießen in the south and coming from Kassel in the north following the B3 direction Marburg and leaving at the exit Fronhausen/Ebsdorfergrund. Following the Landstraße L 3048 direction Kirchhain, Rauischholzhausen is reached after approx. 17 km. In Rauischholzhausen, follow the main road (Wittelsberger Straße), then change to Alte Schulstraße until you reach the Schloss. The best parking lot is at the "Höinger Straße" (see map).

The entrance to the castle is located under the arch.

Emergency contact: Ralf Tonner (+49 1578 7399727) and Karsten Reuter (+49 152 8801498).

Internet access

Wireless internet access is provided via *eduroam* and the local network (User name: wlan-rhh, Password: 0815gastrhh).

Excursion & conference dinner

The excursion on Tuesday will lead to Marburg. We will meet at 2:00 pm in front of the castle in Rauischholzhausen and take a bus to the town for a guided tour through the picturesque historical center. The tour will end at the "Weinlädle" (Schloßtreppe 1, 35037 Marburg) with some mulled wine. For the conference dinner, we will return to the castle where we should arrive around 5:45 pm.

Sunday, 08.11.2015

14:15–17:00	Registration
17:00–18:00	Welcome reception
Session 1	CVD I Chair: Ralf Tonner
18:00–18:45	Kerstin Volz (U Marburg) *Metastable III/V semiconductors: growth & structure formation*
18:45–21:00	Dinner

Monday, 09.11.2015

Session 2	ALD I Chair: Mikko Ritala
8:30–9:15	Erwin Kessels (TU Eindhoven) *Atomic layer deposition of Al_2O_3: new insights from sum-frequency generation studies*
9:15–10:00	Simon Elliott (Tyndall National Institute) *Building atomic-level information into growth simulations for atomic layer deposition*
10:00–10:30	Coffee break
Session 3	DFT I Chair: Chris van de Walle
10:30–11:15	Christian Carbogno (FHI Berlin) *Thermodynamic Equilibrium and Non-equilibrium Properties from First Principles*
11:15–11:35	Nicolas Salles (LAAS-CNRS, Toulouse) *Coupling Activation Relaxation Technique to first principles calculations: a new way to understand the growth of silica on silicon*
11:35–11:55	Andreas Stegmüller (U Marburg) *A density functional study on elementary processes during epitaxy growth and GaP-Si interface formation*
11:55–12:15	Jan Oliver Oelerich (U Marburg) *Bond-Counting KMC Simulation of Growth Kinetics of Compound Semiconductors*
12:15–14:00	Lunch

Session 4	CVD II Chair: Kerstin Volz
14:00–14:45	Henrik Pedersen (U Linköping) *Modelling Chemical Vapor Deposition*
14:45–15:05	Mira Todorova (MPI Düsseldorf) *Growth of a protective oxide layer in electrochemical environment*
15:05–15:25	Chiara Panosetti (TU München) *Get real! Towards structure prediction of complex systems with efficient global optimization in an ab initio thermodynamics framework.*
15:25–15:45	Alessandro Fortunelli (CNR ICOMM, Pisa) *A computational protocol for simulating silicon carbide (SiC) CVD/CVI growth via precursor thermal decomposition*
15:45–16:15	Coffee break
Session 5	KMC I Chair: Peter Kratzer
16:15–17:00	Kristen Fichthorn (Penn State U) *Growth and Assembly of Nanoscale Materials: Insights from Simulation*
17:00–17:45	Talat Rahman (U Central Florida) *Self Learning Kinetic Monte Carlo Method and its application to adatom-island diffusion and coarsening*
18:00–19:30	Dinner
19:30–21:00	Poster session

Tuesday, 10.11.2015

Session 6	ALD II Chair: Simon Elliott
8:30–9:15	Mikko Ritala (University of Helsinki) *In situ studies on reaction mechanisms in atomic layer deposition processes*
9:15–10:00	Mahdi Shirazi (U Antwerpen) *Cooperation between adsorbates provides a facilitative environment for atomic layer deposition reactions*
10:00–10:30	Coffee break

Session 7	Meso/Continuum Chair: Karsten Reuter
10:30–11:15	Ingo Steinbach (U Bochum) *Phase-Field simulation of non-equilibrium processes at the mesoscopic scale*
11:15–12:00	Francesco Montalenti (U Milano) *Towards a realistic, continuum modeling of heteroepitaxial growth: elastic relaxation, surface-energy minimization, misfit dislocations, and intermixing*
12:00–14:00	Lunch
14:15–18:00	Social activity
18:00–21:00	Conference dinner

Wednesday, 11.11.2015

Session 9	KMC II/MD Chair: Wolfgang Stolz
8:30–9:15	Peter Kratzer (U Duisburg-Essen) *First-principles studies of atomic-scale kinetic processes in metastable wurtzite GaAs*
9:15–10:00	Wolfram Miller (IKZ Berlin) *Epitaxial Growth of oxide layers - contributions of DFT and KMC calculations for understanding the kinetics*
10:00–10:30	Coffee break
Session 10	DFT II Chair: Jörg Neugebauer
10:30–11:15	Alexey Timoshkin (U St. Petersburg) *Gas-phase association reactions in 13-15 CVD*
11:15–12:00	Chris Van de Walle (UC Santa Barbara) *Electronic structure and stability of charged complex oxide surfaces*
12:00–12:30	Concluding remarks
12:30	Departure

Poster titles

1. Christoffer Heath Turner
   Computational Identification of Synthesis Conditions for Metal Nanoparticle Growth
2. Martin Stöhr
   DFTB+vdW^{surf} *– Efficient simulation of organic/inorganic interfaces*
3. Paul Rotter
   Molecules on Rails: Coupling of Diffusion and Orientation for Pentacene on an Organic Surface
4. Phil Rosenow
   Towards an ab initio description of the electronic structure of epitaxially grown ternary and quarternary III/V semiconductors
5. Josua Pecher
   Adsorption and surface dynamics of organic molecules on Si(001) for growing internal interfaces – a theoretical investigation
6. Sherri Hadian
   Grain boundary migration and surface growth: Two sides of the same coin
7. Liverios Lymperakis
   Grown of III-Nitride surfaces: Surface thermodynamics and kinetics
8. Anne Hemeryck
   A focus on interface formation during sputtering deposition of Al/CuO Nanolaminated materials: a DFT - Kinetic Monte Carlo Approach
9. Lukas Nattermann
   MOVPE growth of dilute Bi containing III/Vs for optoelectronic applications
10. Lennart Duschek
    Influence of lattice bending due to elastic relaxation of thin TEM samples on HAADS intensities
11. Nikolay Zaitsev
    The ordered overlayers of NTCDA molecules on Ag(111) surface: DFT-vdW calculations

Metastable III/V semiconductors:
Growth and structure formation

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Philipps-Universität Marburg, Marburg, Germany

III/V semiconductors with cubic zinc-blende crystal structure become metastable when they are alloyed with atoms, which have a significantly larger or smaller covalent radius than the atoms of the host lattice. Examples are Nitrogen-containing, Boron-containing or Bismuth-containing III/Vs. These materials are not only fundamentally interesting, as their growth requires extreme non-equilibrium conditions, but also the alloying and/or the growth conditions might lead to structural characteristics different from stable materials. Furthermore, the band structure formation of these materials is very characteristic and novel fields of applications can be opened up. For instance, dilute nitrides and borides are used in high efficient solar cells on GaAs or Ge substrates or in lasers and solar cells on Si substrates. Dilute bismides have potential application in laser diodes on GaAs substrates for telecommunication applications exhibiting fewer losses than the conventionally used (GaIn)(PAs) lasers on InP substrates.

The contribution will summarize the current understanding in MOVPE growth of these extreme materials. Several structural characteristics the materials have due to their metastability will be highlighted and discussed.

Atomic layer deposition of Al_2O_3: new insights from sum-frequency generation

W.M.M. (Erwin) Kessels and V. Vandalon

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Atomic layer deposition (ALD) is the method of choice to deposit thin films with sub-nanometer sensitivity and with an excellent step-coverage or conformality on 3D-structured materials with high-aspect ratio structures. In this presentation the surface chemistry during ALD of Al_2O_3 – by far the most used and studied ALD material – is revisited on the basis of broadband sum-frequency generation (BB-SFG) experiments. BB-SFG is a nonlinear optical technique that is excellently suited for *in-situ* studies of the surface chemistry governing ALD because of its inherent interface selectivity, submonolayer sensitivity, and short acquisition times. In contrast to BB-SFG, conventional absorption spectroscopy, based on differential measurements, monitors only changes on the surface. On the other hand, due to its surface selectivity, BB-SFG reveals information about both persistent and changing surface groups. Therefore, with this technique, open questions have been addressed to obtain a more complete picture of the ALD surface chemistry. Aspects that will be addressed in this presentation are:

- What are the reaction kinetics during the $Al(CH_3)_3$ and H_2O exposure steps?
- What are the sticking probabilities of $Al(CH_3)_3$ and H_2O during the ALD process
- What's the origin of the decrease in growth per cycle (GPC) of Al_2O_3 at low temperatures?
- What about so-called "cooperative" effects during ALD surface reactions?
- What about the initial growth during ALD on substrate materials?

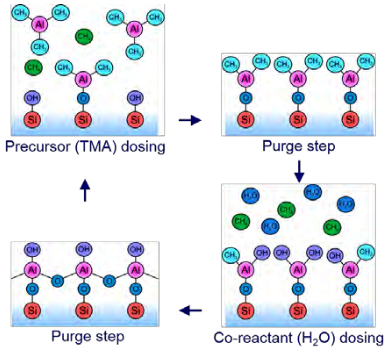

Fig. 1: Cycle for ALD of Al_2O_3 from $Al(CH_3)_3$ (trimethylaluminum, TMA) and H_2O. The precursor and co-reactant dosing steps are alternated by purge steps. Every cycle results in an increase of thickness (1 Å at 250 °C) such that the targeted film thickness can be reached by repeating the right number of cycles.

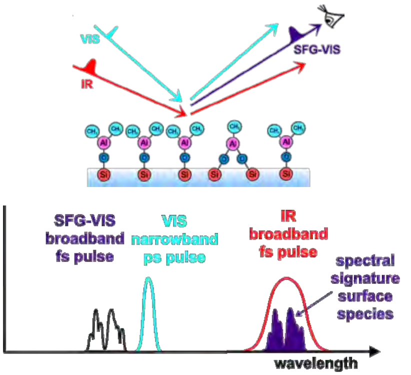

Fig. 2: Broadband sum-frequency generation (BB-SFG) on surfaces: (top) schematic illustration of the technique applied to an amorphous Al_2O_3 surface; (bottom) schematic showing that a wide spectral coverage in the IR can be obtained within one laser shot and with femtosecond time-resolution.

Building atomic-level information into growth simulations for atomic layer deposition

Simon D. Elliott

Tyndall National Institute, Ireland

One of the most exciting areas of research into material processing is atomic layer deposition (ALD), a variant of chemical vapour deposition that delivers unparalleled control of film thickness and conformality at the nanometre-scale. ALD has allowed the semiconductor industry to overcome roadblocks in memory and transistor development, and now ALD is being applied to solar cells, LEDs, catalysts, sensors and packaging.

ALD is research-intensive insofar as new chemicals and process parameters are required for each new material. It is therefore crucial to understand as much as possible about the growth process, through both experiment and simulation. Understanding is needed at multiple length scales (atomic-scale reactions, nanoscale roughness, micron-scale features, mm-scale gas flow) and time scales (reaction kinetics from picosecond to microsecond, second-long gas pulsing). Such multi-scale problems present a considerable challenge to simulation. However, as will be shown in this presentation, atomic-scale simulations of ALD chemistry can give insight into key macroscopic features of the ALD process, such as precursor design and film growth rate. We discuss the success of the atomic-scale approaches, recent work towards multi-scale simulation and future challenges for the simulation of materials growth.

Accurate Thermal Conductivities from First Principles

Christian Carbogno*

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Heat dispersion plays a decisive role in many scientific and industrial applications, because it determines the actual thermodynamic conditions at the microscopic level, e.g., during crystal growth. *Ab initio molecular dynamics* (aiMD) is the computational technique to investigate and understand the dynamics of solids at high temperatures, at which perturbative harmonic approximations break down. Determining accurate thermal transport coefficients from aiMD has however so far remained elusive both due to conceptual and numerical challenges. In this work, we overcome these limitations by employing the Green-Kubo formalism[1]: We evaluate the auto-correlation function of the heat flux by aiMD simulations of the thermodynamic equilibrium. In this talk, we discuss the fundamental theory underlying a first-principles definition of the heat flux using the virial theorem. We demonstrate and validate our approach by inspecting silicon, the thermal conductivity of which is particularly challenging to converge[2]. Furthermore, we use this framework to investigate the thermal conductivity of ZrO_2, which is known for its high degree of anharmonicity and most important role for thermal barrier systems. Our calculations shed light on the heat resistance mechanism active in this material, which eventually allows us to discuss how the thermal conductivity can be controlled by doping and co-doping[3].

(*) This work has been performed in collaboration with M. Scheffler (Fritz-Haber-Institute), R. Ramprasad (Univ. of Connecticut), C. G. Levi and C. G. Van de Walle (Univ. of California Santa Barbara).

[1] R. Kubo, M. Yokota, S. Nakajima, J. Phys. Soc. Jpn. 12, 1203 (1957).

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Modelling Chemical Vapor Deposition

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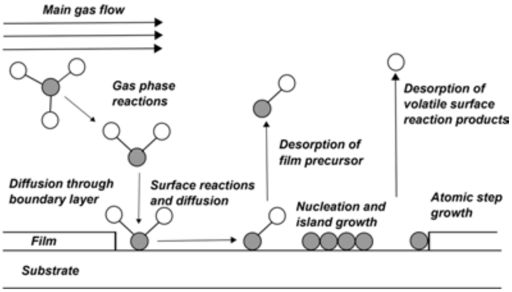
Chemical vapor deposition (CVD) is a family of processes where a thin film of some material is deposited onto a surface via the chemical reactions of gaseous molecules that contain the atoms needed for the film material. CVD is used for a great number of application ranging from hard coatings on the cutting tools used to make our cars to the high precision microelectronics in our smart phones and computers. The chemical reactions in CVD take place on the surface and in many cases also in the gas phase.[1] To better understand the chemistry in CVD, quantum chemical modeling is an invaluable tool for providing atomic-scale detail on surface and gas phase chemistry.[2, 3] But to understand the CVD process, the distribution of chemical species in the reaction chamber must also be modelled by gas flow dynamics and thermochemical modelling.[4] Multiscale modelling, both on the length scale and time scale, is thus needed to fully map the CVD process. For a complete understanding this modelling must also be connected to experiments. This talk will introduce CVD to the non-expert and, from an experimentalist's point of view, discuss the use of quantum chemistry, thermochemistry and gas flow dynamics needed in CVD modeling and the level of understanding accessible when the modeling is connected to experiments.[5, 6]



Schematic summary of the most important chemical reactions involved in thin film synthesis by CVD. All reactions are not desired for all types of CVD – but all must be understood. From ref (1).

References:

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Growth and Assembly of Nanoscale Materials: Insights from Simulation

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ABSTRACT

Achieving the controlled synthesis of colloidal nanomaterials with selected shapes and sizes is an important goal for a variety of applications that can exploit their unique properties (e.g., optical, catalytic, magnetic, etc.). In the past decade, a number of promising solution-phase synthesis techniques have been developed to fabricate various nanostructures. A deep, fundamental understanding of the phenomena that promote selective growth and assembly in these syntheses would enable tight control of nanostructure morphologies in next-generation techniques. I will discuss our efforts to understand how colloidal nanostructures assume selective shapes during their synthesis. To highlight one of our research directions, I will discuss our efforts to understand the workings of PVP, a structure-directing molecule that facilitates the formation of selective Ag nanoparticle shapes. In these studies, we use first-principles density-functional theory, molecular dynamics (MD) simulations, and continuum theory to predict PVP-induced Ag nanocrystal shapes in the 10-100 nm size range. [1-5]

References

[1] W. Al-Saidi, H. Feng, and K. A. Fichthorn, "Adsorption of polyvinylpyrrolidone on Ag surfaces: Insight into a structure-directing agent", Nano Letters, **2012**, 12, 997-1001.

[2] W. A. Saidi, H. Feng, and K. A. Fichthorn, "The binding of PVP to Ag surfaces: Insight into a structure-directing agent from dispersion-corrected density-functional theory," J. Phys. Chem. C, **2013**, 117, 1163-1171.

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Self Learning Kinetic Monte Carlo Method and its application to adatom-island diffusion and coarsening *

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When complimented with accurate techniques for calculation of atomistic diffusion rates, the kinetic Monte Carlo (KMC) method can serve as an important tool for the simulation of temporal and spatial evolution of surface phenomena such as epitaxial growth, adatom-island diffusion, coarsening, and morphological transformations. To enhance its predictive capacity, we have developed a self-learning kinetic Monte Carlo (SLKMC) [1] method, in which the standard KMC is combined with automatic generation of a table of microscopic events, facilitated by a pattern recognition scheme. Each time the system encounters a new configuration, the algorithm initiates a procedure for saddle point search. Nontrivial paths are thus selected and the fully characterized transition path is permanently recorded in a database for future usage. Once the data base of all possible single and multiple atom processes is built, the system evolves automatically and efficiently by picking diffusion mechanisms of its choice. I will present application of the method to the diffusion and coalescence of 2-dimensional Cu, Ni and Ag adatom and vacancy clusters on the (111) surface of these three transition metal, covering both homo- and hetro-systems. Of interest are multiple atom processes revealed in the simulation whose presence may have been ignored otherwise. For adatom clusters varying in size from 2 to 100, I will discuss the dependence of the diffusion coefficient, effective energy barriers, and dominant mechanism (periphery atom or concerted-cluster motion), on cluster size. I will highlight the role played by specific diffusion processes and show that a crossover from collective island motion to periphery diffusion takes place at critical sizes which are specific to the metallic system in question. Comparison will be made of processes responsible for the diffusion of same-sized clusters in homo and hetero systems. Results will be compared with experiments, where available, and with those from KMC simulations based on a fixed catalogue of diffusion processes. I will also provide details of a recent extension of the techniques to three dimensions. Also, for the case of early stages of sub monolayer island coarsening, I will point to the kinetic stabilization of certain island sizes resulting from specifics of adatom detachment /attachment processes[2]. Finally, I will summarize our efforts at parallelizing the code and its application to examine large-scale phenomena.

[*] Work done in collaboration with O. Trushin, A. Kara, A. Karim, G. Nandipati and S. I. Shah and supported by US-NSF.

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In situ studies on reaction mechanisms in Atomic Layer Deposition processes

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Atomic Layer Deposition (ALD) is a chemical gas phase method for highly controlled thin film growth. The characteristic features of ALD are the alternate supply of the precursors and their saturative reactions with the surface species left by the other precursor. The saturative reactions make the film growth self-limiting which in turn gives ALD a number of features that make it superior compared to the competing techniques: conformality, large area uniformity, simple and accurate film thickness and composition control, and reproducibility. For these reasons ALD has found increasing use in the semiconductor industry and is also strongly emerging to other application areas.

The success of ALD is built on chemistry: the unique benefits of ALD can be exploited only when proper precursors undergoing saturative surface reactions can be identified for the materials of an interest. A thorough understanding of the surface reactions is therefore of an utmost importance for both controlling and optimizing the processes and for developing new ALD processes and precursors. In this presentation, in situ reaction mechanism studies on ALD processes are reviewed with representative examples about using quadrupole mass spectrometry (QMS) and quartz crystal microbalance (QCM). These two techniques have turned out to be the most useful in studying chemical reactions under the conditions prevailing in the common flow-type ALD reactors, i.e. a few mbar pressure, temperatures up to around 400 °C and cycle times of a few seconds.

Cooperation between adsorbates provides a facilitative environment for atomic layer deposition reactions

Mahdi Shirazi*[1], Erik Neyts[1], Annemie Bogaerts[1], Simon D. Elliott[2],

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[2]Tyndall National Institute, University College Cork, Lee Maltings, Cork, Ireland.

ABSTRACT: Atomic layer deposition (ALD) is a technique for producing conformal layers of nanometre-scale thickness, used commercially in non-planar electronics and increasingly in other high-tech industries. ALD depends on self-limiting surface chemistry but the mechanistic reasons for this are not understood in detail. Here we demonstrate, by first-principle calculations of growth of HfO2 from Hf(N(CH3)2)4–H2O and HfCl4–H2O and growth of Al2O3 from Al(CH3)3–H2O, that, for all these precursors, co-adsorption plays an important role in ALD. By this we mean that previously-inert adsorbed fragments can become reactive once sufficient numbers of molecules adsorb in their neighbourhood during either precursor pulse. Through the calculated activation energies, this 'cooperative' mechanism is shown to have a profound influence on proton transfer and ligand desorption, which are crucial steps in the ALD cycle. Depletion of reactive species and increasing coordination cause these reactions to self-limit during one precursor pulse, but to be re-activated via the cooperative effect in the next pulse.

Phase-Field simulation of non-equilibrium processes at the mesoscopic scale.

INGO STEINBACH

Ruhr University-Bochum, Interdisciplinary Centre for Advanced Materials Simulation

This lecture reviews the phase-field method that is generally applicable to homogeneous and heterogeneous systems at the mesoscopic scale. Reviewed first are general aspects about first- and second-order phase transitions that need to be considered to understand the theoretical background of a phase field. The mesoscopic model equations are defined by a coarse-graining procedure from a microscopic model in the continuum limit on the atomic scale. Special emphasis is given to the question of how to separate the interface and bulk contributions to the generalized thermodynamic functional, which forms the basis of all phase-field models. Numerical aspects of the discretization are discussed at the lower scale of applicability. Several examples are highlighted regarding coupled non-equilibrium transformations.

Towards a realistic, continuum modeling of heteroepitaxial growth: elastic relaxation, surface-energy minimization, misfit dislocations, and intermixing.

Francesco Montalenti

L-NESS and Dipartimento di Scienza dei Materiali, Via R. Cozzi 55, 20126 Milano (Italy).

Lattice-mismatched heteroepitaxial growth is nowadays a key step involved in the fabrication of a multitude of devices, mostly based on semiconductors. However, full control over the different, sometimes competing phenomena taking place during deposition [1] has yet to be reached. Simulations can be precious in limiting the growth-parameter space to be sampled in actual experiments when searching for the desired system morphology.

In this work we present a continuum approach able to tackle heteroepitaxy while matching typical experimental sizes and time scales. Starting from a suitable free-energy functional describing both elastic and surface energy , evolution is described based on a surface-diffusion model including an external flux. A convenient and general description of surface-energy anisotropy (allowing us to simulate faceting also in the “strong anisotropy” regime) is introduced [2] and several illustrative applications (see, e.g., [3]) to semiconductors are described, exploiting both Phase-Field and sharp-interface approaches. Successful comparison with experiments is demonstrated for qualitatively different systems.

We also discuss our attempt to simultaneously tackle elastic and plastic relaxation. In particular, we show how the stress field associated with an assigned distribution of misfit dislocations can be computed on the fly, its contribution to the surface chemical potential deeply influencing the growth mode.

It must be noted that for miscible systems, such as Ge/Si, the above set of phenomena is not yet sufficient to yield a realistic description of the growth process. At high growth temperatures, indeed, entropy of mixing can lead to significant surface exchanges between deposited and surface atoms. Tackling intermixing is possible, but it requires for a considerable extension of the formalism [4,5].

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First-principles studies of atomic-scale kinetic processes in metastable wurtzite GaAs

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While the III-V compound semiconductor gallium-arsenide (GaAs) normally occurs in the zincblende (ZB) crystal structure, the metastable wurtzite (WZ) form of GaAs has become available recently via the growth of nanowires. In both crystal structures, the atoms are four-fold coordinated. The common nearest-neighbour shell results in similar thermodynamic properties of point defects in both the ZB and the WZ material. However, as I will show in this talk, the kinetics of materials transport differs in both forms of GaAs.

Density functional theory is used to calculate the energy barriers for diffusion of atoms or vacancies. As one example of modified kinetics, we have recently studied the diffusion of As vacancies in GaAs [1]. Vacancy diffusion in ZB is found to be isotropic with an energy barrier of ~1.9 eV, but anisotropic in WZ GaAs: Diffusion in the basal plane is easier, with an energy barrier of 1.60 eV to 1.79 eV (depending on the charge state of the vacancy), whereas diffusion along the c-axis is more difficult (energy barriers of 2.07 eV to 2.44 eV).

Different kinetics in both phases also affects their surface chemistry: ZB GaAs(110) and WZ GaAs(11 −2 0) are stoichiometric surfaces with similar structural motives (buckled zig-zag chains of As and Ga atoms). Yet, their chemical reactivity towards the isoelectronic substitution of As by Sb is very different: Sb adatoms substitute more easily for surface As atoms at GaAs(110) compared to GaAs(11 −2 0) Again, this effect can be traced back to different energy barriers for the substitution reaction. Our theoretical results are in line with experimental STM studies[*] demonstrating the different substitution probabilities on a multi-phase GaAs nanowire sample. The substitution kinetics is relevant for modelling the growth of a GaSb shell around a GaAs nanowire core.

In summary, kinetic processes in metastable materials usually cannot be described by kinetic parameters gathered from samples in the conventional ground-state phase. DFT calculations are required to gain quantitative insight into the energy barriers governing the kinetic processes, while some qualitative trends might be rationalized already by considering in both phases the steric constraints for the process of interest.

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* work done in collaboration with Martin Hjort and Anders Mikkelsen, Lund University, Sweden

Epitaxial Growth of oxide layers - contributions of DFT and KMC calculations for understanding the kinetics

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During the last years oxide crystal layers have become of wide interest in different areas of application. Oxide layers are grown by molecular beam epitaxy (MBE), pulsed laser depostion (PLD), and metal organic chemical vapour deposition (MOCVD). The latter method is the most promising for industrial production but the most complicated from the point of chemistry. MBE often suffers by the requirement of low pressure atmosphere which results in a deficency of providing oxygen and thus might provoke a larger number of oxygen vacancies in the lattice.

Depending on the process parameters the growth will be a layer by layer growth or an island growth, oxygen vacancies will occur or metal atoms are missing or replaced. Furthermore, in the case of MOCVD automatically C, H, and in many cases O is provided by the organic chains of the precursor, which provides the metals for the oxide crystal. At that point density functional theory (DFT) calculations and in a further step kinetic Monte Carlo (kMC) simulations can help to understand the growth kinetics.

Exploiting the piezo- and ferroelectric properties for acoustic surface waves, sensors and non-volatile RAMs several kinds of perovskites are in focus of research to replace the commony used PZT ($PbZr_xTi_{1-x}O_3$). Some examples are discussed in the context of growth kinetics and surface structure both by experimental observations and DFT calculations. In addition, approaches for kinetic Monte Carlo simulations will presented to mimic the growth kinetics.

Another currently hot topic is Ga_2O_3 for transparent electronics and high power electronics. Results of homo-epitaxial growth by MOCVD will be presented. Certain questions arise from the experimental observations which could be addressed by DFT computations. Thanks to the fact that Ga_2O_3 is also of interest as a catalyst DFT calculations for some adsorbates have been performed. However, the computations have been limited to the view point of catalysis. Possible future directions of DFT calculations will be discussed.

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Gas-phase association reactions in 13-15 CVD

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Results of extensive quantum chemical computations of gas phase association processes operating at chemical vapor deposition (CVD) of binary 13-15 materials will be presented. It is shown that formation of relatively large $[RMNH]_n$ oligomers ($n \approx 50$-70, M=Al, Ga, In; R=H, CH_3) is thermodynamically favorable in the gas phase at elevated temperatures. The potential usefulness of such reactions for 13-15 nanoparticle formation is emphasized. Strong dependence of the electronic properties of needle-shaped $[RMNH]_n$ oligomers on the terminal groups will be demonstrated.

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Electronic structure and stability of charged complex oxide surfaces

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Charged surfaces occur in many systems and applications of practical interest. A prime example is the surface of semiconductors, which typically exhibits band bending in the near-surface region due to carriers from the bulk populating surface states. Describing the energetics through first-principles methods is key to understanding the surface physics and its role in devices. However, first-principles calculations of non-neutral surfaces present problems due to the divergent behavior of potential and energy. Introducing a uniform counter charge, which is the common approach in bulk, leads to spurious contributions to the energy. For bulk systems, rigorous methodology exists to remove these contributions [1]. For surfaces of semiconductors and insulators, we have built on the approach of Lozovoi *et al*. [2] for charged metal surfaces to take into account the spatially varying dielectric profile, in order to disentangle the spurious contributions.

We have applied the approach to charging of complex oxide surfaces, which has emerged as an important problem in the application of high-density two-dimensional electron gases (2DEGs) at the interface between two insulators, for instance $SrTiO_3$ (STO) and $LaAlO_3$ (LAO). The 2DEG density in this system has been observed to be much lower than the expected 3×10^{14} cm^{-2}, and sensitive to the proximity of the LAO surface. Carrier transfer from the interface to surface states on the thin LAO film results in a decrease in the 2DEG density [3]. The surface band structure indeed shows the presence of empty surface states to which 2DEG electrons can transfer [4].

Applying the methodology to treat surface charging allowed us to determine the stability of different surface terminations, including effects of charge transfer. By taking into account the formation of different surface defects, such as O vacancies, Al adatoms, or H adatoms, we have determined the 2DEG density at the interface as a function of LAO thickness for different surface terminations under various surface exposure conditions. The technologically relevant problem of surface charging in the LAO/STO system provides a proof of concept for the application of the methodology, as well as insight into the phenomenon of surface-interface interaction in this system.

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Coupling Activation Relaxation Technique to first principles calculations: a new way to understand the growth of silica on silicon

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The formation of the interface between amorphous silica and crystalline silicon through thermal oxidation has been studied extensively since the raise of silicon based Metal-Oxide-Semiconductor transistors in the 60's (see among others [1] for a review). Despite all these experimental and theoretical studies, the first steps of silicon oxidation are still badly understood and need more fundamental analysis [2] to get clues on interfacial layer. Beyond this technological interest, the formation of the SiO_2/Si interface is considered as a model system for the understanding the chemistry phenomena leading to growth of an amorphous oxide from a crystalline substrate.

In order to bring new insights on the intermediate configurations involved during interface formation, we used the Activation Relaxation Technique nouveau (ART nouveau) [3]. ART nouveau enables us to explore the PES (Potential Energy Surface) and to determine transition states, i.e. the different possible configurations and their corresponding energy barriers, by using the Lanczos algorithm. It has been already used to study thermal oxidation of silicon surface through an empirical potential [4] and *ab initio* calculation (SIESTA [5] and Big-GDT [6]) and demonstrates then its ability to help the simulation of the formation of heterogeneous interfaces. Here, to be able to describe more precisely the complex chemistry happening during the growth (such as spin transitions or charge transfers), we coupled ART nouveau to the first principles Density Functional Theory (DFT) code VASP [7]. This original method permits us to find new configurations explaining the crystalline/amorphous transition.

Moreover, to cover larger length and time scales and to get a broader view of the phenomena, all atomic configurations and reactions barriers found in the DFT+ART step are added to the Kinetic Monte Carlo Code OXCAD [8], especially designed to simulate thermal oxidation of silicon.

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A density functional study on elementary processes during epitaxy growth and GaP-Si interface formation

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In an attempt to understand epitaxy growth of III/V materials like gallium phosphide (GaP) on silicon Si(001) we investigated gas phase as well as surface chemical processes of triethylgallane (TEGa), tert-butylphosphine (TBP) and a number of other, recently developed chemical vapour deposition (CVD) precursors. For the GaP-Si system a combination of metal-organic vapour phase epitaxy (MOVPE) growth experiments and transmission electron microscopy revealed an unexpected interface morphology which was retraced by kinetic Monte Carlo growth simulation and density functional theory (DFT, PBE-D3) calculations. Kinetic growth effects (i.e. adatom diffusion) lead to intermixing and different stabilities favour higher index interface configurations over the (001) orientation. This leads to an intermixed interface morphology with triangular-shaped features which stretches over eight atomic layers along growth direction.[1] We will present absolute formation energies of various interface configurations and relate the stabilities found to arguments on chemical bonding.

For the two GaP precursors (TEGa, TBP) as well as the single-source precursors for boron carbide (triethylboron) and nitride-arsenide materials (1,1-dimethylhydrazine, 1,1-di-tert-butylarsanoamine) β-hydrogen elimination mechanisms represent the kinetically most efficient decomposition routes.[2,3,4] However, for group 15 compounds, the mechanism fundamentally differs from the hydride elimination known for metal compounds resulting in drastically increased decomposition barriers. We investigated the nature of the group 15 β-hydrogen elimination by DFT-based bonding analyses and found that the high barrier is caused by an inverse electron flow with respect to the metal hydride mechanism and a proton is transferred to the group 15 center.[5] The large barrier of tert-butyl pnictogenes can be decreased e.g. by designing ligands that facilitate β-silyl effects stabilizing the transition state of the elimination.[6]

Based on the understanding gained from gas phase studies, adsorbate decomposition mechanisms were investigated for the hydrogen-passivated Si(001) surface. While the prominent decomposition mechanisms remain important, the substrate inductively affects the barrier height of most eliminations. Kinetically limited gas phase reactions are thus more likely to proceed from precursor fragments adsorbed to the substrate in agreement with the defect-free, high-quality materials known from experiment.

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Bond-Counting KMC Simulation of Growth Kinetics of Compound Semiconductors

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Growth of III/V semiconductor compounds on Si substrates is currently in the focus of experimental and theoretical research because of its promising applications in functionalization of semiconductors. While surface structures and properties of the grown materials are experimentally well accessible, little is known about the formation and structural characteristics of the interfaces between the Si substrate and the III/V semiconductor compound. To gain insight into the intermediate stages of epitaxial growth and the interface properties, we developed a Kinetic Monte Carlo (KMC) computer simulation package implementing the bond-counting KMC method for the theoretical study of the kinetic characteristics of epitaxial growth. Two particular problems were addressed in the simulations. First, it was recently observed that growth of GaP on the Si-{001} surface leads to significant intermixing of the two materials at their interface. In our simulation we were able to identify the driving forces of the intermixing and accurately reproduce the experimentally observed features [1]. Second, melt-back etching of Ga droplets on the Si-{001} surface was simulated. In a recent experimental study it was shown that deposition of Ga onto a Si substrate leads to formation of metallic Ga droplets, etching large, pyramidally shaped structures into the bulk Si. We can reproduce this behaviour in the simulation and thereby study intermediate stages of the etching during the Ga deposition [2].

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Growth of a protective oxide layer in electrochemical environment

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The omnipresent oxidising environment we are living in makes it hard to believe that metals play such an important role in our society. Their utilisation in different areas of application is made possible by the spontaneous growth of thin oxide layers on the metal surface, which dramatically enhance a metal's corrosion resistance. Understanding passivity of metals and the modelling of oxide growth is therefore, not surprisingly, a central topic in corrosion science.

Using the example of the Zn/ZnO/H_2O interface we discuss how electronic-structure calculations can be used to identify the dominant point defects that control the growth and dissolution of the oxide barrier layer which forms when a metal comes into contact with a corrosive environment. Our recently developed approach, which is fully based on a grand-canonical description of both ions and electrons, and "translates" and unifies theoretical concepts from the field of semiconductor defect chemistry and electrochemistry [1] is instrumental in this context. By constructing point defect stability diagrams [2] for ZnO and water we detect the native point defects that dominate oxide growth in an electrochemical environment. Interestingly, most of the thus identified point defects have hitherto not been considered in empirical models of the ZnO growth [3]. These new defect types critically impact our understanding of oxide growth and provide new insight into strategies to develop alloys with higher corrosion resistance.

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Get real! Towards structure prediction of complex systems with efficient global optimization in an *ab initio* thermodynamics framework.

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Abstract

Continuous computational and methodological advances provide first-principles atomistic insight into ever larger and complex materials, intensifying the need for efficient geometry sampling techniques in high-dimensional configuration spaces. We adapt the basin hopping global geometry optimization scheme to employ automatically-generated collective curvilinear coordinates. Due to the physical correspondence of these coordinates with vibrations, this enhances the generation of chemically meaningful trial structures for covalently bound systems. In the application to hydrogenated Si clusters we concomitantly observe a significantly increased efficiency in identifying low-energy structures and a reduction of unphysical geometries when compared to the same number of typical random Cartesian trial moves. [1]. We further propose to combine this and the *ab initio* thermodynamics idea [2] in a grand-canonical global optimization framework, where the function to minimize is no longer the total energy, but rather the Gibbs free energy at several values of the chemical potential of the components of the target system in order to establish a chemically-motivated and fist-principle-based structure optimization tool for predictive-quality modelling of highly complex processes of nanotechnological relevance such as the direct formation of metal–silicon clusters at silicon surfaces.

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A computational protocol for simulating silicon carbide (SiC) CVD/CVI growth via precursor thermal decomposition

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The controlled growth of surface overlayers via Chemical Vapour Deposition (CVD) represents one of the main technological processes for surface treatment and coating. In CVD, the thermal decomposition of a precursor compound accumulates material deposit on the surface while gaseous by-products are eliminated by working under continuous flow. Many ceramic materials can be produced via CVD, such as silicon carbide (SiC) usually obtained by thermal degradation of methyltrichlorosilane (CH3SiCl3, MTS) according to the reaction scheme:

$$CH_3SiCl_{3(g)} \rightarrow SiC_{(s)} + 3\ HCl_{(g)}$$

An interesting variant of CVD is Chemical Vapour Infiltration (CVI), which is tailored to fine processes such as densification of a porous perform or synthesis of fiber-reinforced composites. While CVD and CVI processing techniques are already widely used in industrial settings to produce SiC and other materials for a variety of applications, current research focuses on increasing the control of final material parameters, such as microstructure, mechanical strength and resistance to wear and shock, chemical inertness, etc. Reduction of production costs is also a field of intense efforts, especially aimed at reducing the long manifacturing times of CVI processes. To achieve these goals, increasing use is made of theoretical modelling based on both continuum and atomistic approaches. Atomistic simulations would be particularly helpful to provide deeper insight into microscopic detail of the final materials. The extremely long CVI time scales however pose a real challenge for atomistic simulations, which typically cover up to milliseconds and are here required to extend their scope by many orders of magnitude to seconds or even days. New atomistic approaches going well beyond standard Molecular Dynamics (MD) simulations are required to cover the relevant time scale simultaneously retaining predictive accuracy needed to help scanning the vast parameter space of synthetic techniques thus singling out ideal growth conditions.

Here we explore an original approach to atomistic simulation of CVD/CVI which is able to solve the time scale issues of conventional modelling and we apply it to the specific example of the growth of SiC via MTS decomposition [1]. This approach avoids unrealistic thermodynamic equilibrium conditions often used in continuum methods and achieves the required acceleration in simulation times by assuming realistic steady-state conditions under constant flux of reactant molecules on a growing surface. Atomistic simulations employing a recently developed Reax force field are used to equilibrate the surface under the given experimental conditions while the local character of such a covalent bond system (SiC) is exploited in simplifying the evaluation of reaction rates at the gas/solid interface from tabulated values. We demonstrate that under such assumptions, a quasi-stationary state of growth is achieved in a very short time scale. Such a quasi-stationary state is also shown to be robust with respect to external parameters and is thus consistent with the initial assumptions. This opens the way to the detailed investigation of microscale growth phenomena which can hardly be investigated using experimental tools, but that yield a large influence on the final properties of the materials, Being able to predict final composition and atomistic structure of the material lays the basis for simulation of materials properties (such as friction), of great interest under both a scientific and an industrial point of view.

[1] Unpublished work, manuscript in preparation

Poster Presentation

Computational Identification of Synthesis Conditions for Metal Nanoparticle Growth

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Abstract

As commercial applications for nanomaterials and nanoparticles begin to emerge, and as demand for products grows, there is a critical need to understand the cause-effect relationships for guiding the synthesis of nanoparticles. While this represents a vast parameter space (various synthesis techniques, precursors, solvents, concentrations, temperature, time, etc.), we have reached a stage where there is now enough information available in the literature to begin transitioning to a more data-driven approach. In our work, we are using kinetic Monte Carlo (KMC) methods to make connections between experimental growth conditions and observed Au nanoparticle structures. By using this database of structures and growth conditions, the underlying kinetic rate parameters can be identified (such as surface adsorption/desorption rates, binding energies on different crystal faces, surface diffusion coefficients, etc.). This fundamental information can then be used in a predictive mode to identify the necessary synthesis conditions of desirable Au nanoparticle structures for targeted applications. Furthermore, the search for optimal conditions for nanoparticle growth can easily be adapted to genetic algorithm methods, in order to allow for efficient identification of optimal experimental conditions. Our initial results illustrating the diversity of KMC-generated nanoparticle structures and optimization methods will be presented, as well as benchmarks of our structures against experimental conditions.

DFTB+vdW^{surf} – Efficient simulation of organic/inorganic interfaces

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Simulation of chemistry-driven growth phenomena for metastable materials
CECAM/Psi-k/HERALD Workshop

First principles-based simulation can play a key-role in understanding and interpreting experimental observations in modern surface and nano science. Moreover, it can guide the design of nano-scale devices such as molecular machines. Unfortunately, size and configurational complexity of the systems under consideration still limit the applicability of computationally demanding *state-of-the-art* methods, i.e. Density Functional Theory (DFT). In recent years Density Functional Tight-Binding (DFTB), a tight binding formulation based on DFT, has shown to be successful in describing a variety of organic compounds at only a fraction of the computational cost of DFT. The goal of this work is to establish a DFTB-framework for organic molecules adsorbed on inorganic surfaces. In this context we present a systematic approach towards parametrization of DFTB interaction parameters. Being derived from DFT, DFTB also shares common shortcomings of current DFT approximations such as a missing treatment of dispersive interactions, which are inherent to surface-adsorbate interactions. We account for van der Waals interactions by the use of recently developed dispersion correction schemes proposed by Tkatschenko, Scheffler, and co-workers. A key-feature in this approach is the density-derived calculation of C_6 coefficients that accounts for the chemical environment of the atom. We adapt this scheme to the specifics of DFTB with the help of density partitioning and an adaptively confined basis set and investigate the general performance of this DFTB+vdW^{surf} approach for common benchmark systems in comparison to full dispersion-corrected DFT. Finally we exemply the usefulness of our method on the example of overlayer formation of Bisphenol A on Ag(111) in different phases.

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Molecules on Rails:
Coupling of Diffusion and Orientation for Pentacene on an Organic Surface

We advance the microscopic understanding of surface diffusion to comparatively large organic adsorbates on organic surfaces. A coplanar monolayer of pentacene chemisorbed on Cu(110) serves as a thermally stable, well-ordered organic model surface. The diffusion of additionally deposited pentacene was studied with the helium-3 spin-echo (HeSE) technique, which achieves both nanoteter spatial and picosecond time resolution, even at elevated temperatures. Information about individual diffusion processes, which is contained in the ensemble properties provided by HeSE, was extracted by comparison with Langevin computer simulations of admolecule trajectories. The necessary potential energy surface (PES) is based on molecular mechanics calculations. We explain the experimental data by admolecule rotation leading to unexpected diffusion dynamics: molecules freely diffuse along their long molecular axis parallel or perpendicular to the uniformly oriented surface molecules but may suddenly turn their orientation and thus their diffusion direction by 90°. The combination of those processes leads to apparent long jumps, which is further corroborated by an analytical model. The results provide the first direct observation and quantitative description of molecular scale admolecule diffusion in a complex organic system. Our findings enable the first experimental validation of a PES constructed from force field schemes and can serve as benchmark for future *ab initio* approaches.

Towards an *ab initio* description of the electronic structure of epitaxially grown ternary and quarternary III/V semiconductors

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Epitaxially grown semiconductor alloys of group 13 and 15 elements (III/V semiconductors) are promising materials for the integration of laser devices on silicon. Changing the composition of these materials allows to taylor their lattic constant and band gap to a given need. The computational description of alloys requires supercell constructions and subsequent unfolding to an effective band structure (EBS). The accuracy of density functional theory derived band gaps is limited by (a) the accuracy of available functionals and (b) by a lowering of the band gap due to an artificial interaction between translationally symmetric guest atoms because of the limited size of feasible supercells. The latter effect is stronger the more the guest atoms disturbs the host lattice.

We present some results on the way to an accurate *ab initio* computation of alloy band structures. With the modified Becke-Johnson exchange functional by Tran and Blaha in combination with LDA correlation (TB09), an affordable functional yielding accurate band gaps is available. The band gaps of alloy supercells without lattice relaxation match well with those obtained from established models. However, the issue of artificial interaction upon relaxation due to periodic boundary conditions persists for relaxed cells with a size that is affordable for routine computations, implying the well-known neccessity of using larger supercells.

Barring the issues described above, it is possible to extract *ab initio* derived band structure parameters in the framework of $\mathbf{k}\cdot\mathbf{p}$-theory, which will allow to predict the optical properties of quantum well superstructures.

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Adsorption and surface dynamics of organic molecules on Si(001) for growing internal interfaces - a theoretical investigation

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Organic/semiconductor interfaces play an important role in the development of new materials and devices. In particular, the use of cyclooctyne derivatives on the silicon(001) surface promises to be an ideal starting point for the construction of such interfaces. Adsorption structures and their thermodynamical aspects have been determined experimentally for unsubstituted cyclooctyne on Si(001),[1] while an analysis of the kinetic processes and the behaviour of cyclooctyne derivatives remains to be done.

We compare the adsorption dynamics of cyclooctyne and 5-Ethoxymethyl-5-methyl-cyclooctyne, a possible candidate for internal interface construction, to highlight differences caused by the substituent groups. Additionally, we investigate the reactivity of adsorbed structures, focussing on a $\mathrm{S_N}2$ type C-O bond cleavage mechanism at the latter molecule's ethoxymethyl side group which mirrors behaviour found for tetrahydrofuran[2] and diethylether[3] on Si(001). The calculated energy barrier turns out to be large enough that this unwanted reaction can be kinetically controlled under experimental conditions and the side group remains available for further functionalization.

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Grain boundary migration and surface growth: Two sides of the same coin

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Historically, theoretical concepts and mechanisms that describe surface growth and grain boundary migration have been developed completely independently and an exchange between the two research communities is virtually non-existent. Recent studies on grain boundary migration performed by us showed however that many concepts and atomistic mechanisms that are characteristics of surface growth apply also when grain boundaries move. The reason why these similarities have not been recognized earlier is that due to the very low experimental driving forces, which are typically 3-4 orders of magnitude lower than the difference in chemical potential (which act as driving force for surface growth) , long simulation times and large system sizes are required. Conventional simulations thus often used unphysically large driving forces and rather small simulation cells to speed up the simulations. Using physically converged simulations we find that mesoscale phenomena such as island and double kink nucleation become active, i.e., mechanisms that are well known in surface growth but have hitherto not been considered in describing the migration of grain boundaries. We discuss, how and for which aspects the well-established concepts of surface growth can be applied and for which aspects they fail.

Grown of III-Nitride surfaces: Surface thermodynamics and kinetics

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GaN and related group III-Nitrides are materials of choice for high temperature and high power microelectronic devices as well as for solid state lighting. However, in molecular beam epitaxy (MBE), the use of low pressures, the high melting temperatures of GaN, and the extremely large binding energy of the N_2 molecule make the growth of high quality films with smooth surface morphologies challenging.

In order to circumvent the aforementioned obstacles, plasma cells in MBE are often utilized to provide chemically active nitrogen species. This reduces the chemical potential of N species and allows the growth at considerably larger temperatures [1]. Moreover, self-surftactants [2] and/or antisurfactants [3] are utilized to influence surface kinetics: MBE takes advantage of the peculiarity of III-Nitride surfaces to stabilize excess metal on the surface, in the form of mono- or multi-layers, for growth under moderate to metal-rich conditions [2,4]. The latter is in contrast to conventional III-V semiconductors, and reduces considerably the adatom kinetic barriers. On the other hand antisurfactants such as Si, can be utilized within an epitaxial lateral overgrowth approach to block the growth of extended defects and reduce the dislocation density in the active region of the device [3].

In the present contribution we will discuss the general trends and mechanisms underlying the growth of the technologically important III-Nitrides surfaces and we will focus on the physics underlying the thermodynamics, kinetics, surfactants and anti-surfactants of III-Nitride.

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A focus on interface formation during sputtering deposition of Al/CuO Nanolaminated materials: a DFT - Kinetic Monte Carlo Approach

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Nanolaminated materials made of nanometer-thick layers are nowadays facing the technological challenge of mastering interfacial layers, inevitably formed during technological fabrication processes. At these dimensions, atomistic composition of the interfacial layers become preponderant and play a determining role on the macroscopic properties of designed materials.

Nanolaminated energetic materials, more precisely multilayered Al/CuO nanothermites, can be achieved through sputtering process. The interesting point of these materials is the intimacy of Al and CuO components, that can be customized to tailor macroscopic properties. Actually, it has been proven that interfacial layers impact final performances of achieved materials, such as stability, reactivity and energy release. In this field, master of interfaces during their fabrication is a major issue since it offers the new opportunity to increase and tune their final performances.

To push forward their nanoscale–controlled fabrication, predictive atomic scale modeling of the deposition process can help, by providing a fundamental description on how they are achieved. In our approach, we propose a model based on a kinetic Monte Carlo (KMC) method to simulate multilayered Al/CuO materials deposition, as PVD process, in order to get clues, depict and predict a realistic interfacial formation. Here, Density Functional Theory-based (DFT) calculations are first used to identify and characterize, kinetically and thermodynamically, atomic scale events, that are then used as input parameters to parameterize a KMC model. Presented results will include CuO chemistry on the Al surface, and the early stages of PVD deposition will be examined up to the complete passivation of the Al surface. This methodology offers the possibility to access to the exact structure of the material as a function of the manufacturing process and thus to access to the detailed composition, that depends on the conditions in which it was synthesized. We except to propose microscopic elements that could guide the technologist to improve processing and improve the properties of the operating material.

MOVPE growth of dilute Bi containing III/Vs for optoelectronic applications

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The incorporation of bismuth (Bi) in III/V semiconductors can play an important role in addressing the development of the new generation of highly efficient optoelectronic devices [1]. A major problem of most of the currently used telecom lasers is their low efficiency, which is around 20 % [2]. Cooling effort decreases the efficiency again by an order of magnitude. Bi leads to a strong reduction of the band gap by 80 meV per % Bi in GaAs and simultaneously shifts the spin orbit split off band to lower energies. Hence, loss processes could be suppressed for Bi fractions above 11 % Bi in GaAs [1], [3]–[5]. Furthermore, a decreased sensitivity of band gap energy to temperature has been observed which increases the efficiency of Bi containing devices additionally [6]. Nevertheless, the metal organic vapour phase epitaxy (MOVPE) growth of dilute Bi containing materials is challenging, as significant amounts of Bi are required. In previous studies it has been reported about a saturation level of the Bi incorporation in GaAs and that the saturation level depends on temperature and As/Ga ratio [7]–[10]. Indeed the Bi incorporation in high quality Ga(AsBi) using MOVPE is still limited to a Bi fraction of 7%.

The mechanisms of Bi incorporation in different III/V materials are of interest in this work. Incorporation mechanisms during the MOVPE growth of Ga(AsBi), Ga(PAsBi), Ga(NAsBi) and Ga(PBi) at low temperatures will be discussed and compared.

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Influence of lattice bending due to elastic relaxation of thin TEM samples on HAADF intensities

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Transmission electron microscopy as well as scanning transmission electron microscopy (S)TEM is the method of choice concerning atomic resolution analysis of semiconductor devices. Often it is not possible to interpret the acquired experimental images directly without additional information of the structure. This may be either structural information of the multi-quantum-well (MQW) architecture or detailed knowledge of composition. Often, experimental data is compared to theoretical simulated images in order to extract quantitave data like atom distribution and local displacements. Thereto, HAADF (high angle annular dark field) in STEM can be used.

The first step of simulating electron microscopy images is to build a model and geometry of the sample. Since the modelling of real prepared TEM samples is very complex and therefore hardly possible, several assumptions have to be made to simplify the structure. To decide which assumption is acceptable and does not affect the final result, the influence of this specific assumption has to be studied carefully. For this purpose modelled test-systems are a good way to determine the key factors of the effect without the limitations of experimental disturbances.

In compressively strained QW structures of thin TEM samples, a bulging of the QW region on the surface can be found, due to elastic relaxation of the material. The amount of this effect depends on the sample thickness *t*, the QW thickness *d* as well as on the strain between substrate and QW material.

First, this contribution focuses on the dependencies of the bulging on the parameters *d* and *t* for a given material combination. Furthermore the influence of this bulging effect in binary materials on simulated HAADF STEM images is investigated and quantified. This also gives a value for the error one makes when neglecting strain relaxation of the sample in quantitative analysis, especially at interfaces between materials.

Several GaAs QW structures embedded in GaP buffers were modelled varying *d* and *t* systematically. The structures were designed and relaxed with the software COMSOL Multiphysics[1] to take into account the strain and the elastic relaxation of the compressively grown structure, respectively. Afterwards STEM HAADF images of the relaxed TEM samples were simulated with the help of the STEMsim [2] code. For investigating what difference the influence of the bulging makes on the images, also reference simulations were performed without the elastic relaxation of the sample.

It could be shown that a modelled GaAs QW structure embedded in a GaP buffer shows a noticeably bulging. This effect has a significant influence on the intensities and positions of atom columns in HAADF image simulations. The study was performed for a binary compound GaAs/GaP in several configurations of the parameters *d* and *t*. This contribution shows, that the effect of bulging due to elastic relaxation of compressively grown samples can have a significant effect on HAADF intensities. If the STEM images are used for gathering very precise quantitative data, it is advisable to estimate the effect of the investigated material system carefully.

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The ordered overlayers of NTCDA molecules on Ag(111) surface: DFT-vdW calculations.

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The geometrical, vibrational and electronic structures of the ordered overlayers of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) molecules on Ag(111) are investigated on the basis of density functional theory (DFT) calculations. We performed the detailed comparative analysis of the equilibrium geometries of the compressed and relaxed phases of NTCDA/Ag(111) computed with the different vdW-approximations and representations of the basis functions. We found all optimized srtuctures are consistent to each other and they are in agreement with the available experimental measurements in case of the relaxed phase.

For all optimized structures we analysed the calculated interfacial electronic structure in order to reveal the factors acting on the formation of interface state (IS). The coverage and vertical separation between substrate and adsorbate are the most important factors which define the energy of IS. The increase of coverage and shortening of adsorption distance result in growth of IS energy, on the other hand increasing the coverage gives rise to diminution of substrate-adsorbate interaction and as consequence to a larger adsorption distance. Our calculation provides a good electronic structure description of the relaxed phase while the compressed phase is described poorly in compare with experiment.

So far as, the detailed infrared absorption spectroscopic data of NTCDA/Ag(111) with different coverage are available, the analysis of the vibrational properties and comparison of the IR spectra were done by means of frozen phonon calculation for all structures.

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Time	Sunday	Monday	Tuesday	Wednesday
8:30–9:15		Kessels	Ritala	Kratzer
9:15–10:00		Elliott	Shirazi	Miller
10:00–10:30		Coffee break	Coffee break	Coffee break
10:30–11:15		Carbogno	Steinbach	Timoshkin
11:15–11:35		Salles	Montalenti	van de Walle
11:35–11:55		Stegmüller		
11:55–12:15		Oelerich		Concluding remarks
12:15–14:00	Arrival	Lunch	Lunch	Departure
14:00–14:45	Registration	Pedersen	Social activity	
14:45–15:05		Todorova		
15:05–15:25		Panosetti		
15:25–15:45		Fortunelli		
15:45–16:15		Coffee break		
16:15–17:00		Fichthorn		
17:00–17:45	Welcome reception	Rahman		
18:00–18:45	Volz	Dinner	Conference dinner	
18:45–19:30	Dinner			
19:30–21:00		Poster session		