Surfactants, Diffusion, and Reactivity of GaN Surfaces

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http://www.fhi-berlin.mpg.de/th/th.html

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Stoichiometry, geometry, stability, electronic structure of zincblende and wurtzite GaN

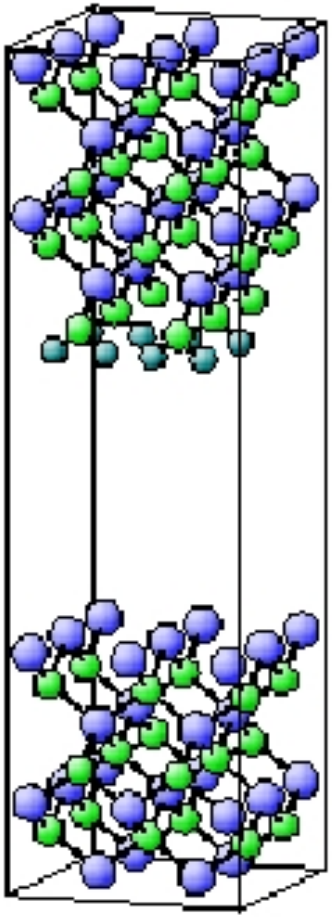
- clean surfaces
- arsenic covered surfaces
- indium covered surfaces

- surface diffusion and growth
- adsorption of oxygen

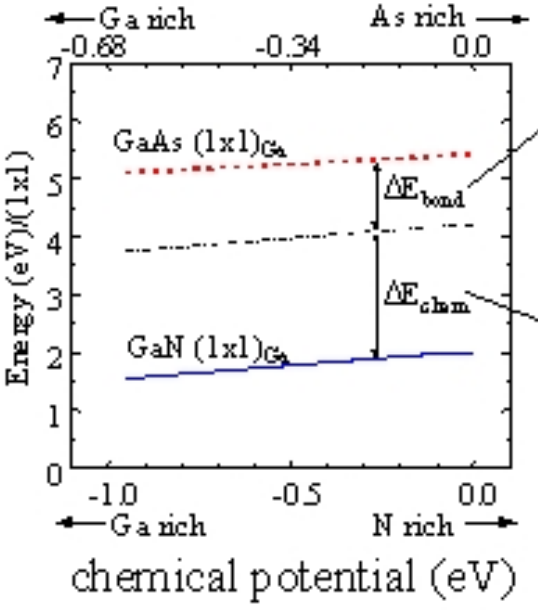
Computational Method

- Density-functional theory with local-density approximation for xc
- Pseudopotentials, plane-wave basis set (energy cutoff of 60 Ry)
- Ga *3d* electrons treated as *valence*
- Supercell geometry
  - -- containing up to 180 atoms
  - -- passivation of one side by fractional hydrogen
  - -- compensation of electric field
  - -- atomic relaxation

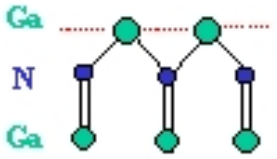
code: fhi96md → fhi99md
http://www.fhi-berlin.mpg.de/th/th.html



Why are Ga-terminated surfaces so stable?



Stronger Ga-Ga bonding (GaN lattice constant 20% smaller than GaAs)

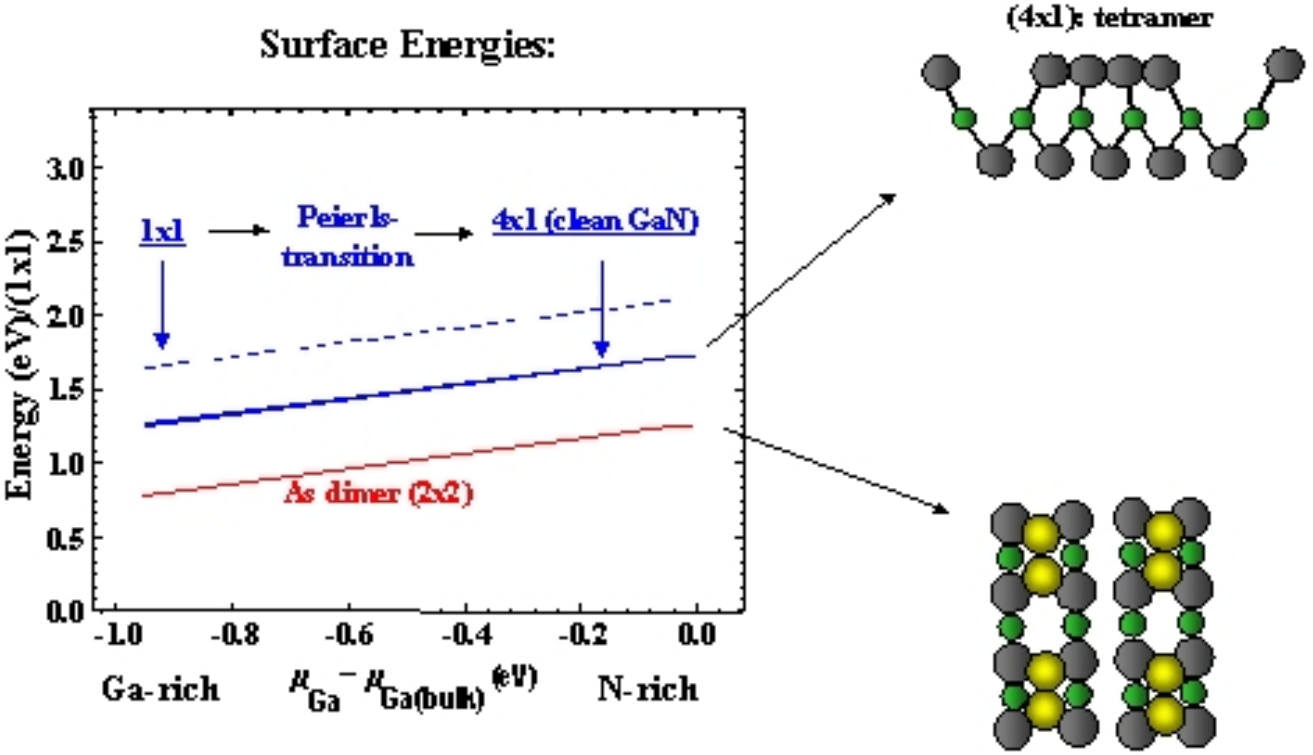


Difference in chemical potentials

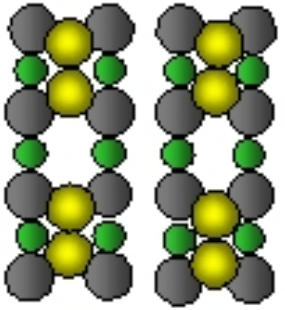
Cohesive Energies:

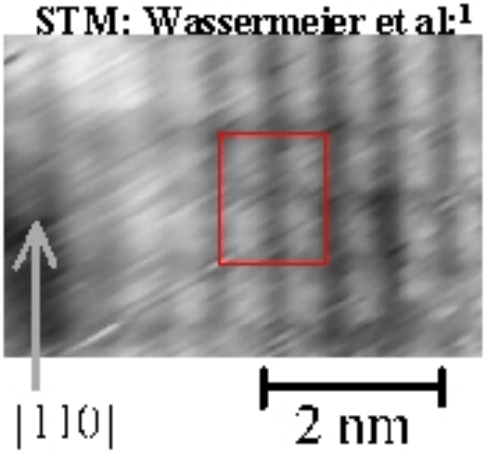
- Ga-bulk: 2.81eV
- As-bulk: 2.96 eV
- N_2-molecule: 5.0 eV

Reconstructions and Surfactants at Cubic Surfaces



Comparison with Experiment





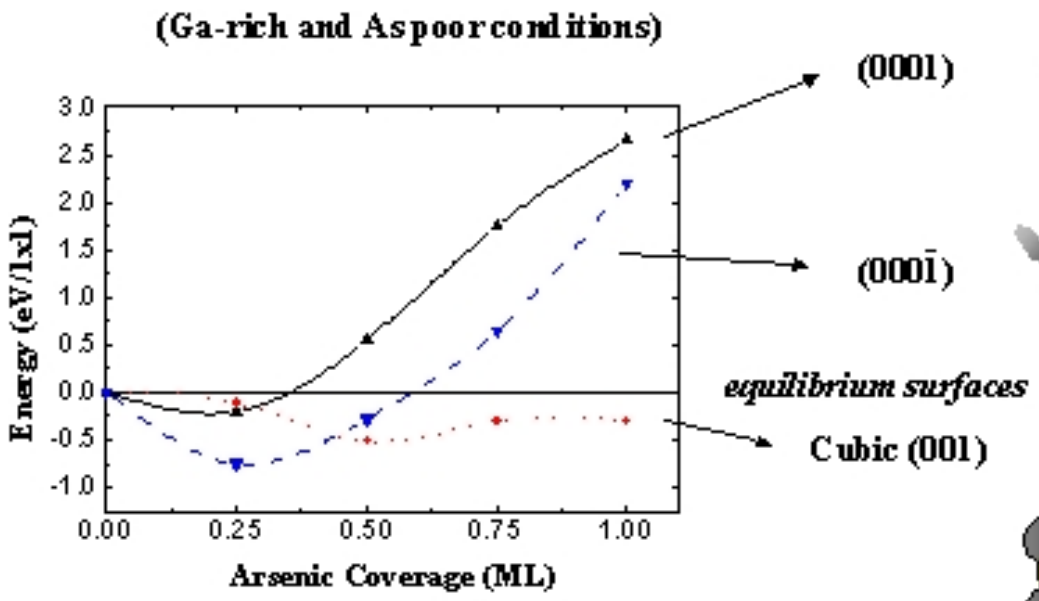
- Structure consistent with experiment
- Arsenic is more stable on the GaN surface than in GaAs (bulk)
- Significant reduction of the surface energy

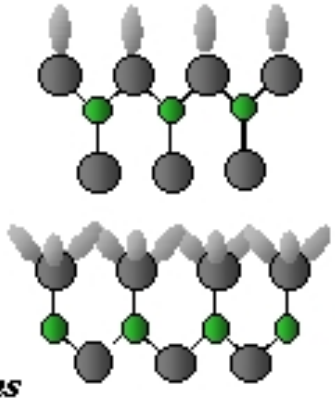
  ➡ Arsenic (or alike) might be a good surfactant

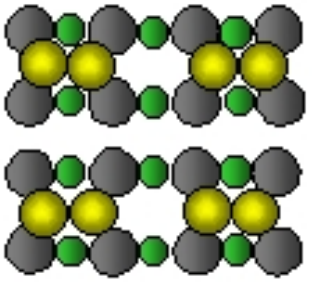
1. M. Wassermeier, A. Yamada, H. Yang, O. Brandt, J. Behrend, K. H. Ploog private communication.

Surfactants at Wurtzite Surfaces?

Surface Energy (relative to clean GaN equilibrium surfaces):



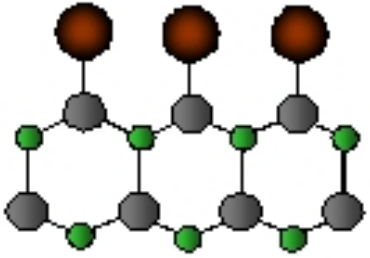




Arsenic may be incorporated;
Alternative surfactants (In, Sb)?

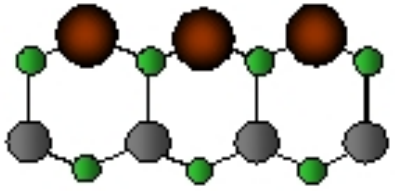
In at GaN (0001)

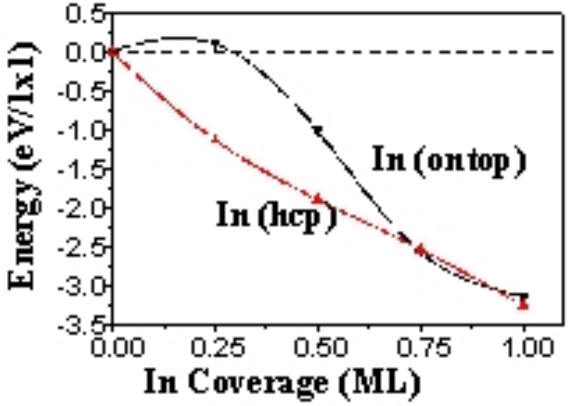
Ga terminated

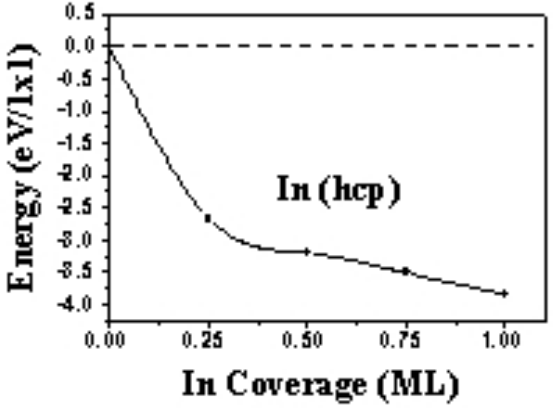


(Ga-rich conditions)

N terminated





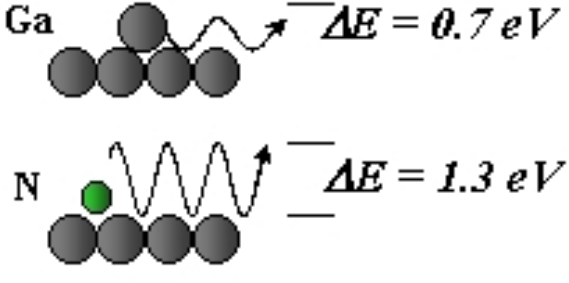


➡ **In reduces significantly the surface energy**

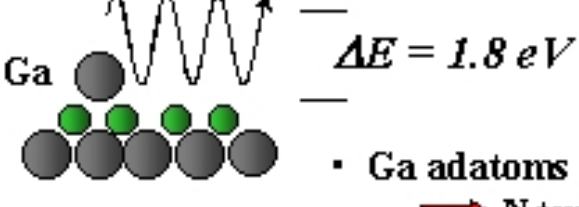
Adatom kinetics at the clean GaN surface

Diffusion barriers:

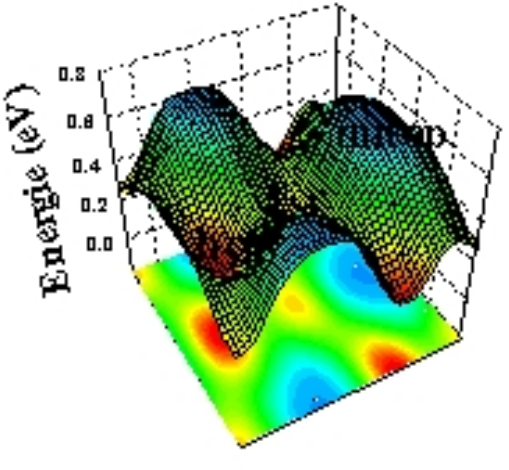
equilibrium surfaces:



kinetically stabilized surfaces:



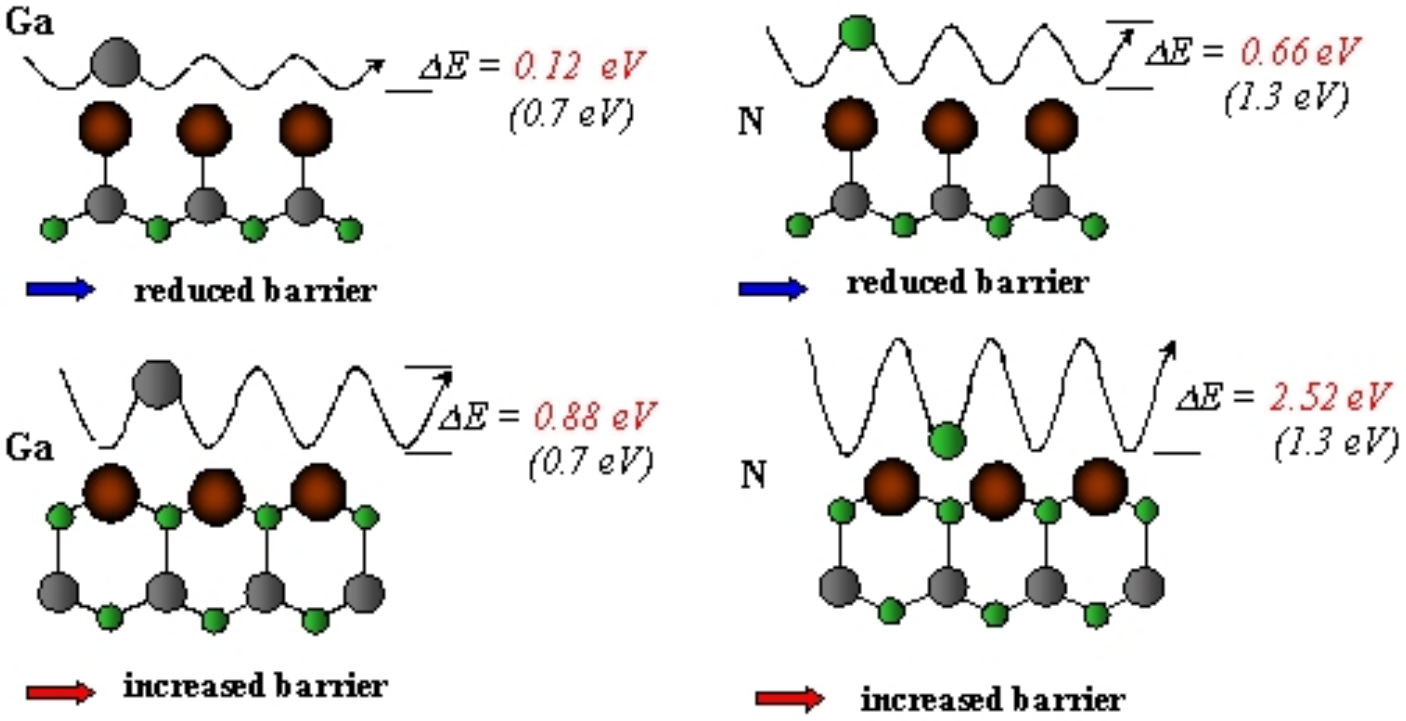
Example: Ga at (0001)



- Ga adatoms are very mobile compared to N adatoms.
  - ➡ N terminated surfaces can be kinetically stabilized
- Excess N decreases significantly the Ga mobility!

Theory: T. K. Zywietz, J. Neugebauer, M. Scheffler, *Appl. Phys. Lett.* 73, 487 (1998).
Experiment: E. J. Tarsa, B. Heying X. H. Wu, P. Fini, S. P. DenBaars, J. S. Speck, *J. Appl. Phys.* 82, 5472 (1997).

Adatom kinetics at In-terminated GaN (0001)



In does *not* uniformly improve adatom kinetics. More info needed: atomic exchange, what happens at steps?

Conclusions

Surfactants :

As- (mainly for zincblende) and In-adatoms lower the surface energy significantly.

Surface diffusion:

- at clean GaN: Ga is fast and N is slow
- at In-covered GaN:
  - significant reduction of energy barriers for adatom diffusion when In sits above a Ga-layer.
  - However, increased barriers when indium sits above a nitrogen layer.

Questions and plan:

What happens at steps, how can Ga replace In? Then a *predictive* kinetic Monte Carlo simulation of growth is becoming meaningful.