Clean and As- covered GaN surfaces: cation-stabilized structures and surfactant behavior

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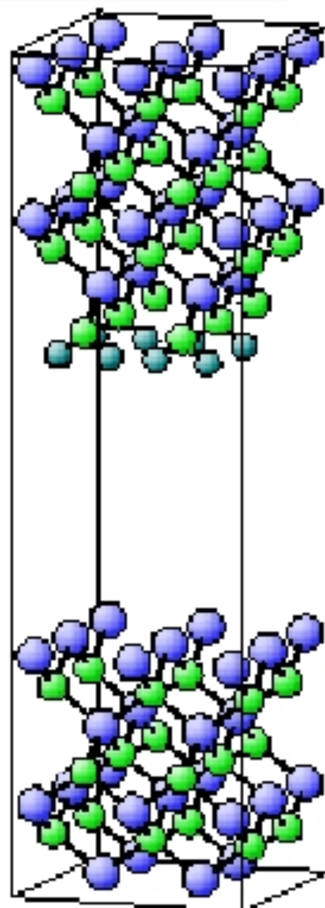
to be published in PRL (March 1998)

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

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: fhi97md

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Experiments (cubic GaN)

observed reconstructions (MBE + RHEED):

Conditions: **Ga-rich** **N-rich**

Substrate:

(001) GaAs c(2x2) 2x2 1x1 } [2]Brandt et al. [3]Schikora et al.

(001) SiC 1x1 4x1

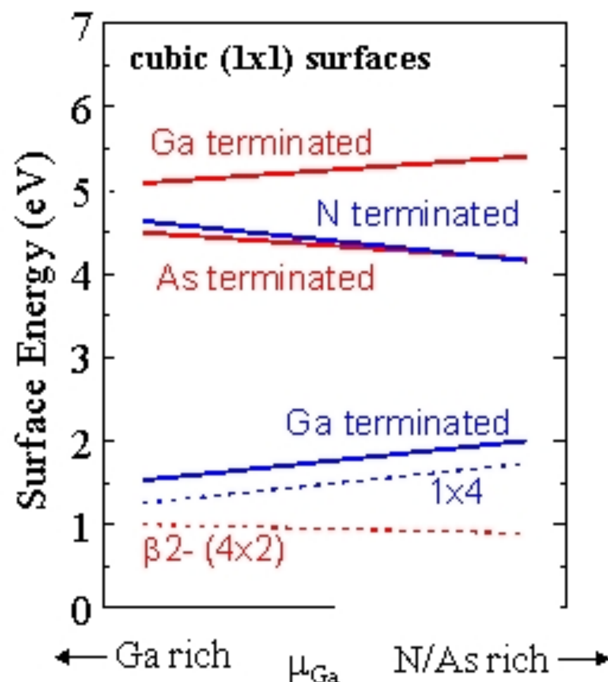
c(2x2) 2x2 **Arsenic on** } [1]Feuillet et al.

What is the role of Arsenic?

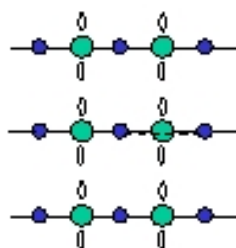
1. G. Feuillet, H. Hamaguchi, K. Ohta, P. Hacke, H. Okumura, S. Yoshida, *Appl. Phys. Lett*, 70, 1025 (1997).
2. O. Brandt, H. Yang, B. Jenichen, Y. Suzuki, L. Daweritz, K. H. Ploog, *Phys. Rev.* B 52, R2253 (1995).
3. D. Schikora, M. Hankeln, D. J. As, K. Lischka, Phys. Rev. B 54, R8381 (1996).
4. H. Yang, O. Brandt, M. Wassermeier, J. Behrend, H. P. Schönherr, K. H. Ploog, *Appl. Phys. Lett.* 68, 244 (1996).

Comparison between GaN and GaAs

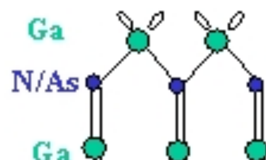
Surface Energies:



top view



side view



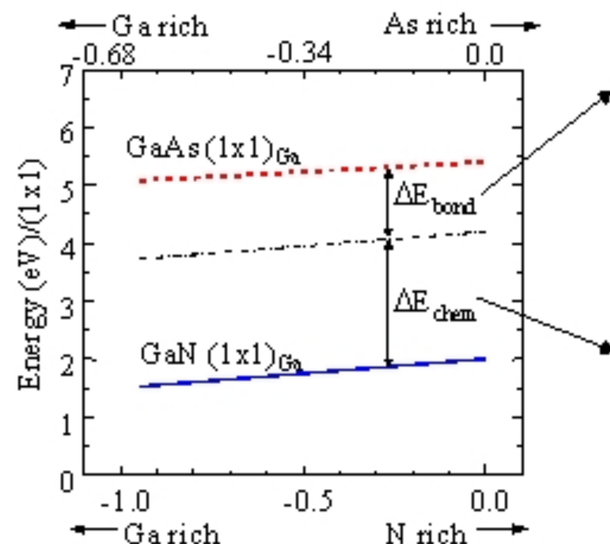
GaAs:
(Traditional III-V Semiconductor)

- (1x1) surfaces highly unstable

GaN:

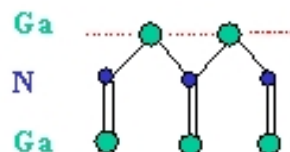
- Ga-terminated surface has exceptionally low energy

Why are Ga-terminated surfaces so stable?



Due to stronger Ga-Ga bonding

(GaN has a by 20% smaller lattice constant than GaAs)



Due to difference in chemical potentials

Cohesive Energies:

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

Surface Bandstructure

Energy (eV)

5
3
1
-1

S_1
S_1

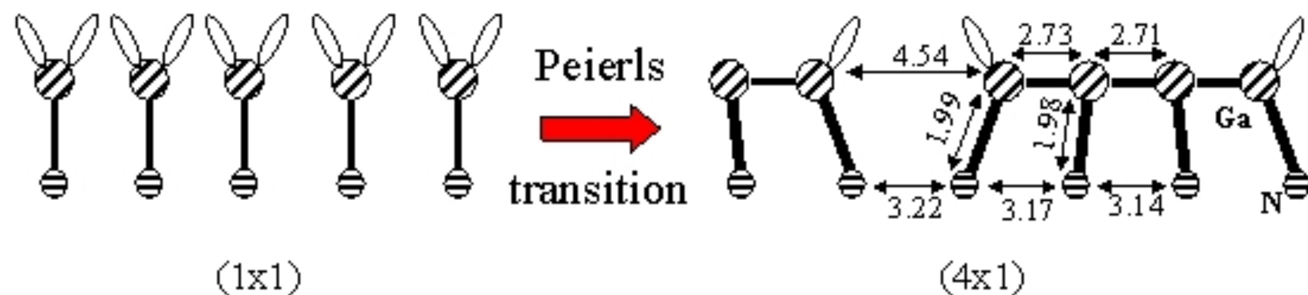
J K
Γ J'

(a) J Γ J'

Energy (eV)

5
3
1
−1

(b) J Γ J''



Reconstructions and Surfactants at Cubic Surfaces

Surface Energies:

Energy (eV)/(1x1)

3.0
2.5
2.0
1.5
1.0
0.5
0.0

-1.0 -0.8 -0.6 -0.4 -0.2 0.0

Ga-rich N-rich

1x1 → Peierls-transition → 4x1 (clean GaN)

As dimer (2x2)

non-polar $1\bar{1}00$[1]

(4x1)

tetramer

Facetting:

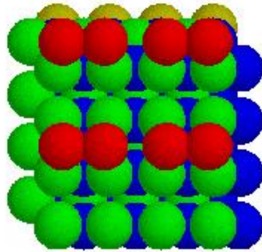
[001]

[110]

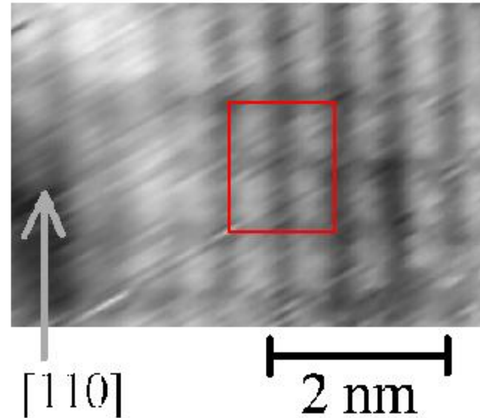
A ⇨ 2 A

1. J. E. Northrup, J. Neugebauer, *Phys. Rev.* B53, R10477 (1996).

Comparison with Experiment



STM: Wassermeier et al:[1]



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

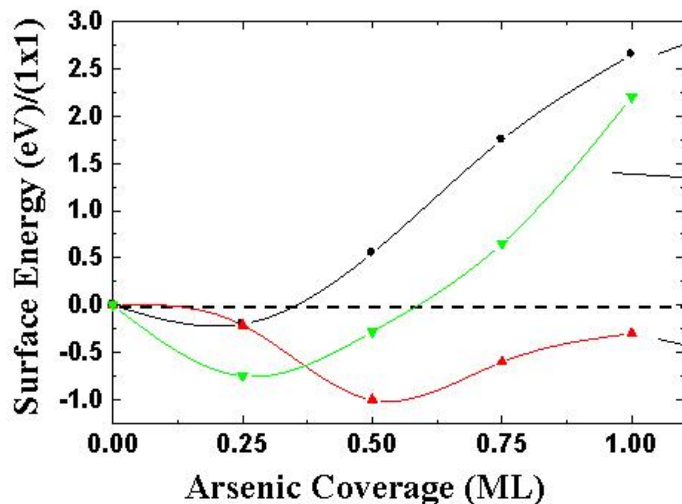
➡ Arsenic might be a good surfactant

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

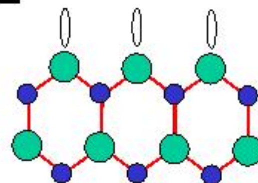
Surfactants at Wurtzite Surfaces?

Surface Energy (relative to clean GaN equilibrium surfaces):

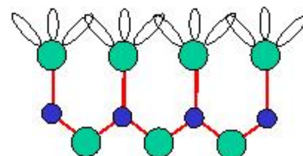
(Ga-rich and As poor conditions)



(0001)



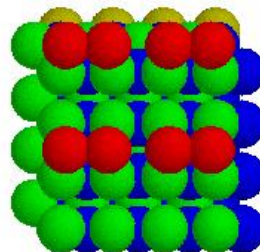
$(000\bar{1})$



equilibrium surfaces

Cubic (001)

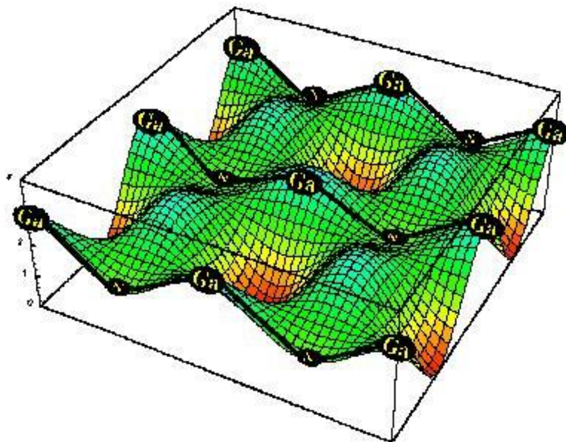
As dimer (2x2)



Ga and N Adatom-Diffusion

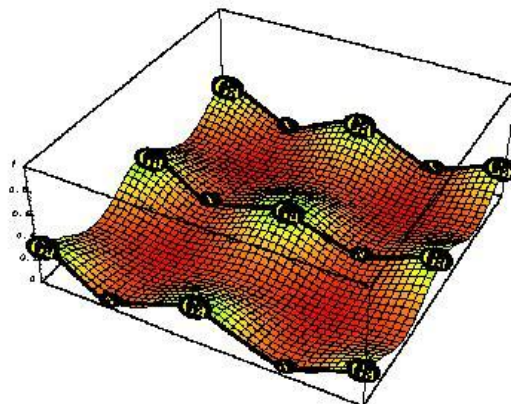
Total Energy Surfaces in eV (1x1 GaN (001)):

N-Diffusion



Barrier ~ 1.3 eV

Ga-Diffusion



Barrier ~ 0.2 eV

Ga adatom is by orders of magnitude more mobile than N!

Conclusion

Stabilization of Ga-terminated GaN surfaces:

- Stability of the N_2 molecule ("chemical reservoir")
- Stabilization by metallic bonding

➡ unusual behavior of polar GaN surfaces compared to traditional III-V semiconductors

Surfactants on Ga-terminated GaN surfaces:

- **Cubic (001):**

  surface energy is significantly reduced (at 0.5 ML)
  arsenic stays always in the first layer

➡ *Arsenic might be a good surfactant!*

- **Wurtzite (0001) and $(000\bar{1})$:**

  surface energy significantly reduced for $(000\bar{1})$ surface, smaller effect at (0001)

Alternative elements (e.g. Sb, Bi)?

Diffusion and Consequences for Growth:

- Ga diffusion orders of magnitudes faster than N diffusion

  ➡ Since N needs to be captured by Ga to avoid desorption, N incorporation can be enhanced by Ga access!

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