Multiscale Modeling of Au-catalysed GaAs nanowire growth

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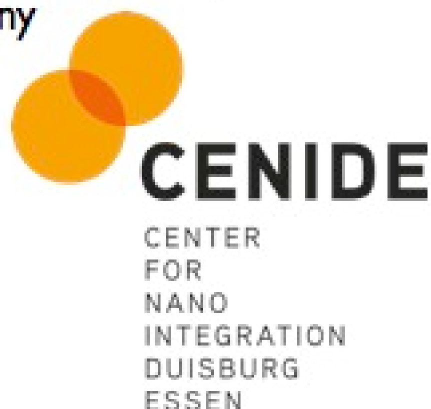

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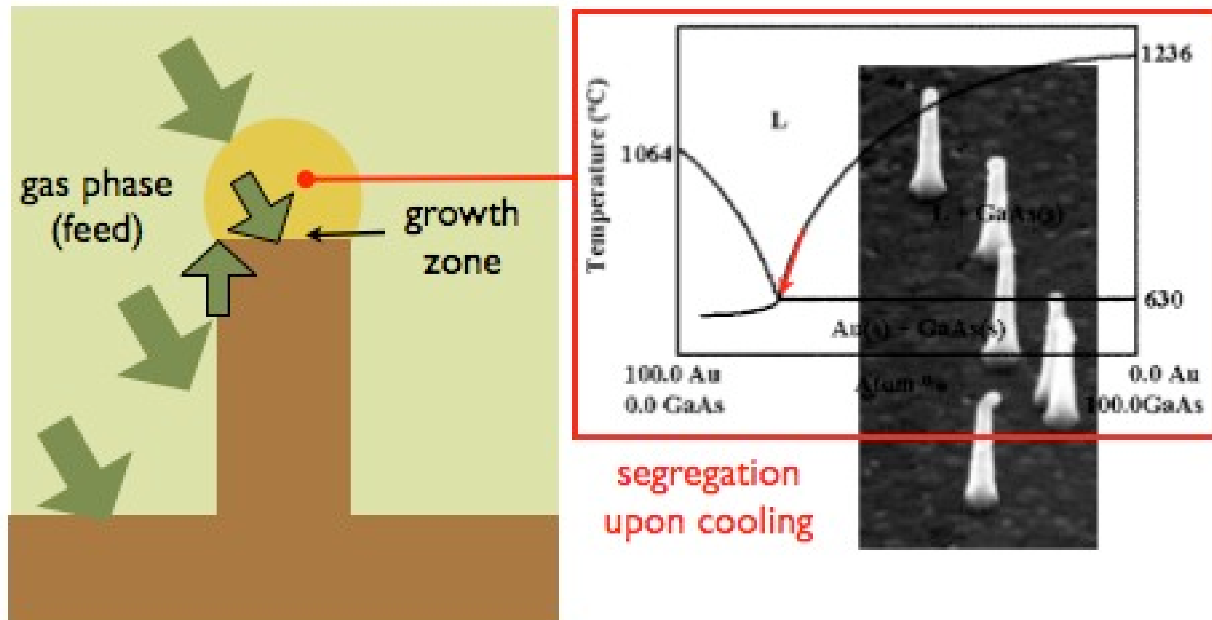
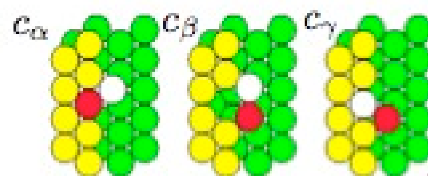
Metal-catalysed nanowire growth

- a challenge for multi-scale modeling in growth kinetics
- conventional interpretation: vapor-liquid-solid (VLS) growth



Kinetics: levels of description

- **level A:** microscopic
  Master eq.



example: diffusion on a stepped surface

$$\frac{dP(c_\alpha)}{dt} = \sum_\beta W(\alpha,\beta)P(c_\beta) - W(\beta,\alpha)P(c_\alpha)$$

(kinetic Monte Carlo provides a stochastic solution)

- **level B:** Smoluchowski eq. / Fokker-Planck eq.
  particle density

$$\frac{\partial n_1(x)}{\partial t} = D\nabla\left(\frac{n_1(x)}{k_B T}\nabla U(x) + \nabla n_1(x)\right)$$

- **level C:** local equilibria for each species $I \Rightarrow \mu_I(x)$

$$j_I(x) = -n_I(x)B\,\nabla\mu_I(x) \qquad D = Bk_BT$$

Rates from DFT total energies

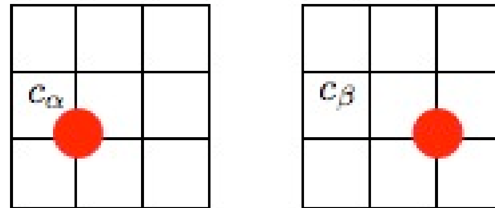
- Transition State Theory

$$W(\alpha,\beta) = \Gamma_{\alpha\beta}(T)\exp\left(-\frac{E_{\rm tot}({\rm TS}_{\alpha\beta}) - E_{\rm tot}(c_\beta)}{k_B T}\right)$$

- $E_{\rm tot}$ from electronic structure calculations (density functional theory)

- dilute limit / tracer diffusion
  e.g. on a square lattice

$$D_{\rm tracer} = \frac{a^2}{4} W(\alpha,\beta)$$



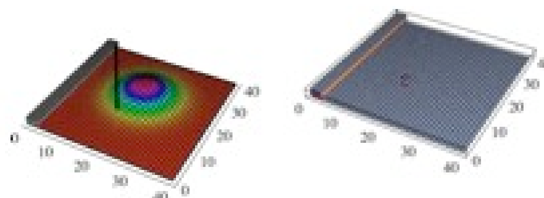
- chemical diffusion (requires thermodynamic approach)

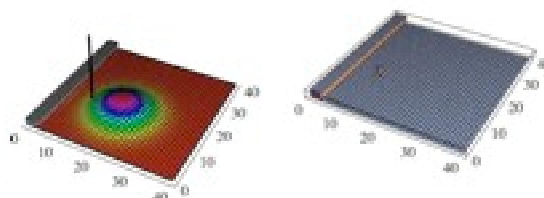
$$D = n_I B_I \frac{\partial \mu_I}{\partial n_I} = D_{\rm tracer} \frac{n_I}{k_B T} \frac{\partial \mu_I}{\partial n_I}$$

Coupling of levels

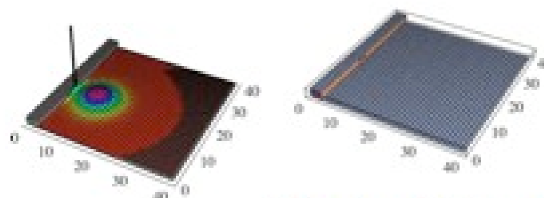
- **level A and B:**
  multiscale kinetic Monte Carlo

  iterative procedure:
  particle distribution 'collapses' (stochastical process) after given time interval, Smoluchowski eq. with initial δ-function





- **level B and C:**
  adatom kMC with sources and sinks (described by μ_I)



  at low concentrations:

$$\mu_I(x) = \mu_0(p,T) + U_I(x) + k_B T \log(a^2 n_I(x))$$

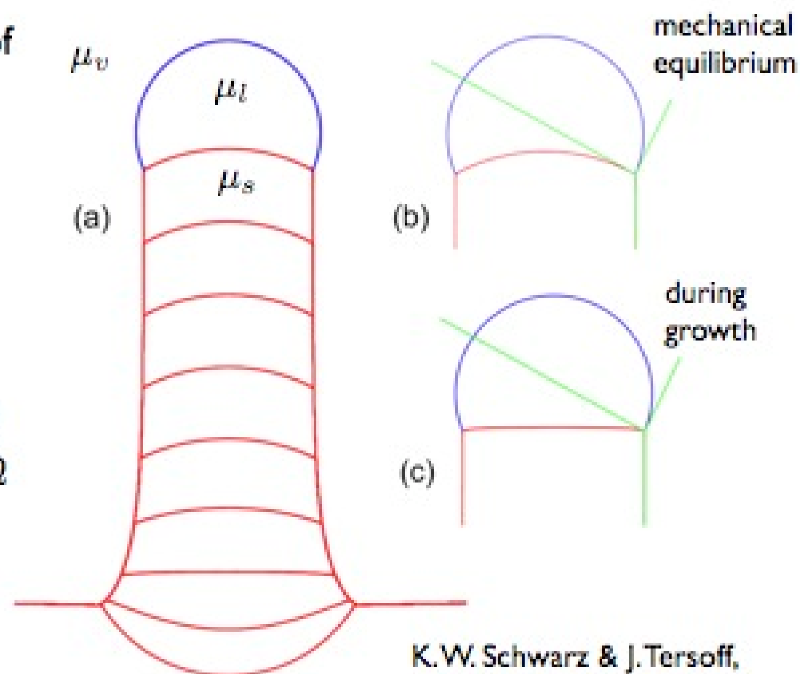
L. Mandreoli, J. Neugebauer, R. Kunert, E. Schöll, PRB **68**, 155429 (2003)

"level C" description of NW growth

- equilibrium properties of the three phases specified by chemical potentials
  $\mu_l = \mu_l(n_I, R, \theta)$
  $\mu_s = \mu_s(r, \theta, \phi)$
- kinetics:
  flux from the gas phase
  $F_g = r_{vl}(p_v, T) A_{vl}/\Omega$

  crystallization via interface reaction, axial **growth speed**
  $v_s \approx \alpha_{ls} \cdot (\mu_l - \mu_s)$

  $r_{vl}, \; \alpha_{ls}$ kinetic coefficients

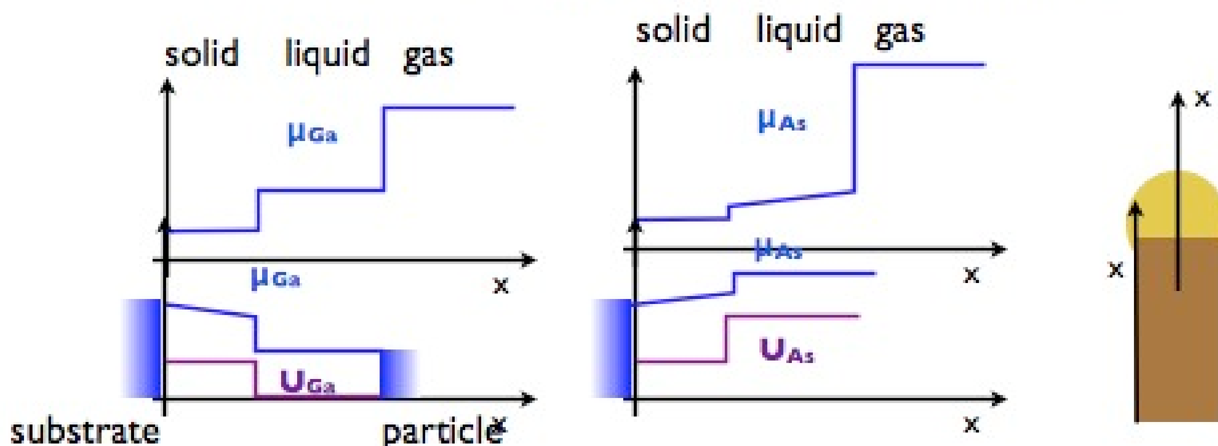


K. W. Schwarz & J. Tersoff, PRL **102**, 206101 (2009)

generalization to 2-component system GaAs

Multiscale modeling strategy

- restrict explicit modeling to nanowire tip / growth interface
- arsenic supplied as As_2 or As_4 molecules; surface-dependent reactive sticking coefficient ?
- **coupled level B/C:**
  sources and sinks defined by the gas phase and the planar substrate



Microscopic Aspects (ongoing work)

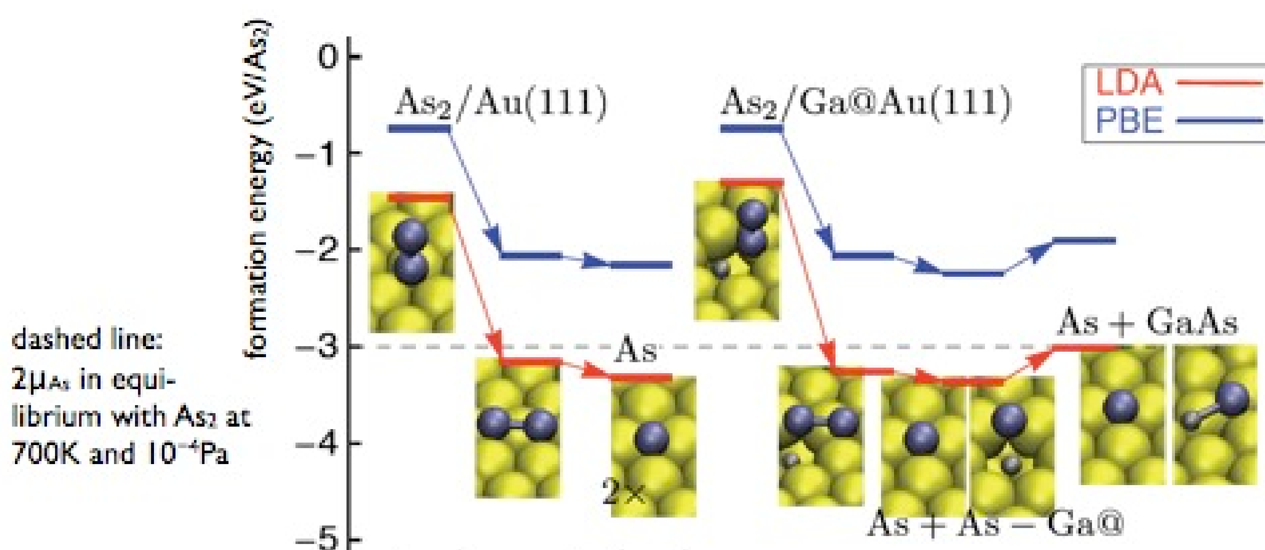
1. surface chemistry on Au particle

2. sidewall diffusion

3. arsenic supply to the interface:
   As vacancy diffusion in the solid *versus*
   As atom diffusion in the Au-Ga liquid

4. solid-liquid interface: mechanical equilibrium and defects

Arsenic uptake at Au(111)

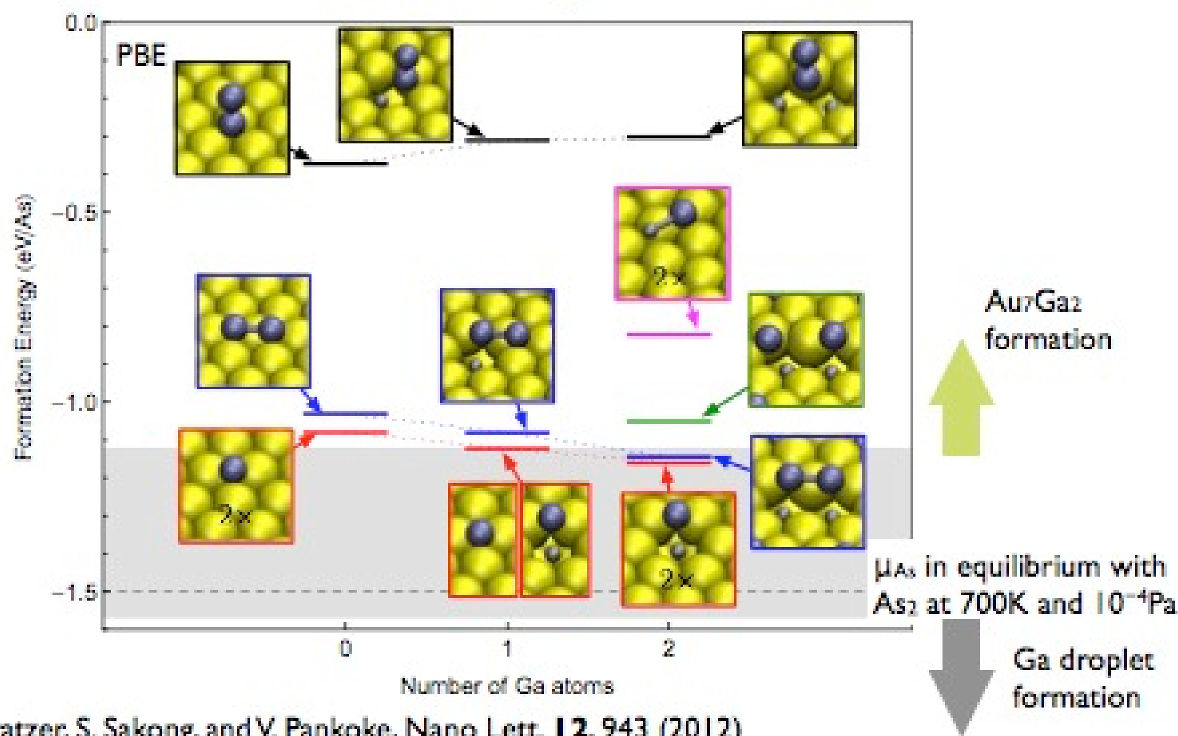


- As_2 binds to the Au surface
- dissociative adsorption is exothermic
- ad-species GaAs can be formed with little extra energy by extraction of Ga from the surface alloy

Equilibrium with gas-phase As_2

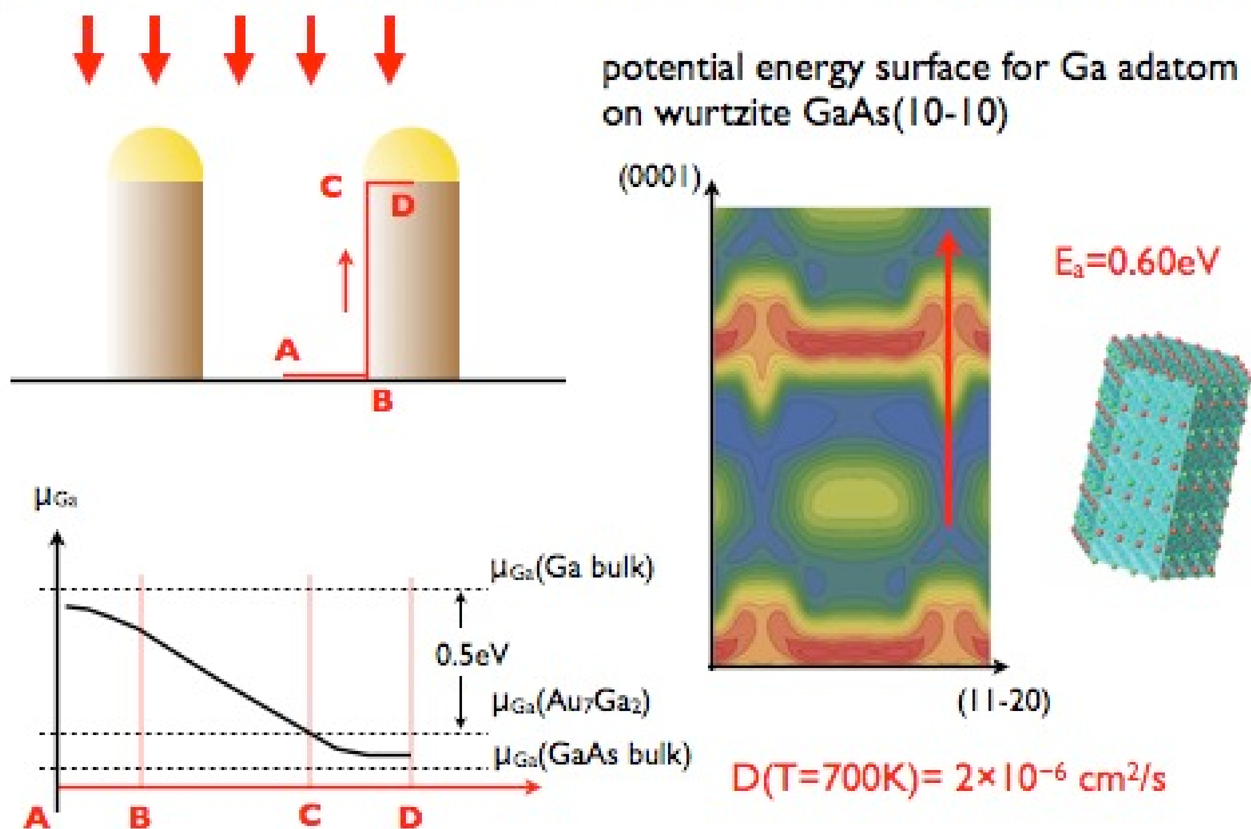
$$\mathrm{GaAs(bulk)} + \tfrac{7}{2}\mathrm{Au(bulk)} \rightarrow \tfrac{1}{2}\mathrm{As_2} + \tfrac{1}{2}\mathrm{Au_7Ga_2(bulk)} - 1.12\mathrm{eV}$$

$$\mathrm{GaAs(bulk)} \rightarrow \tfrac{1}{2}\mathrm{As_2} + \mathrm{Ga(bulk)} - 1.57\mathrm{eV}$$



P. Kratzer, S. Sakong, and V. Pankoke, Nano Lett. **12**, 943 (2012)

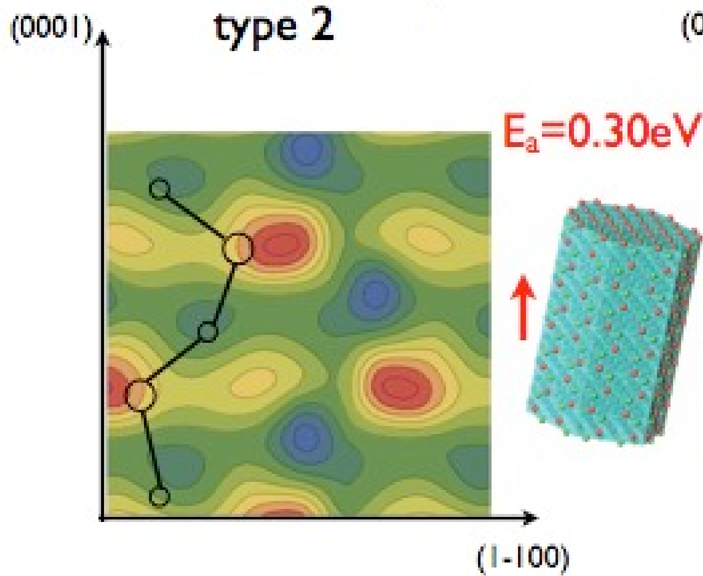
Materials exchange between substrate and growth zone

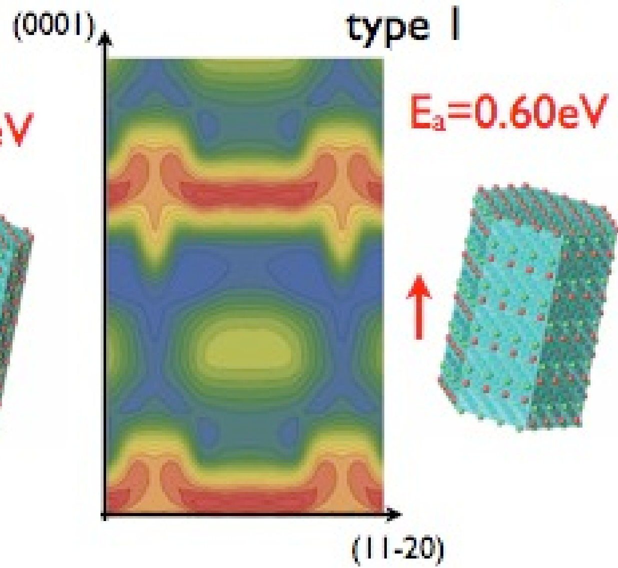


Facet-dependence of Ga diffusion

potential energy surface for Ga adatom

on GaAs (11-20) on GaAs(10-10)



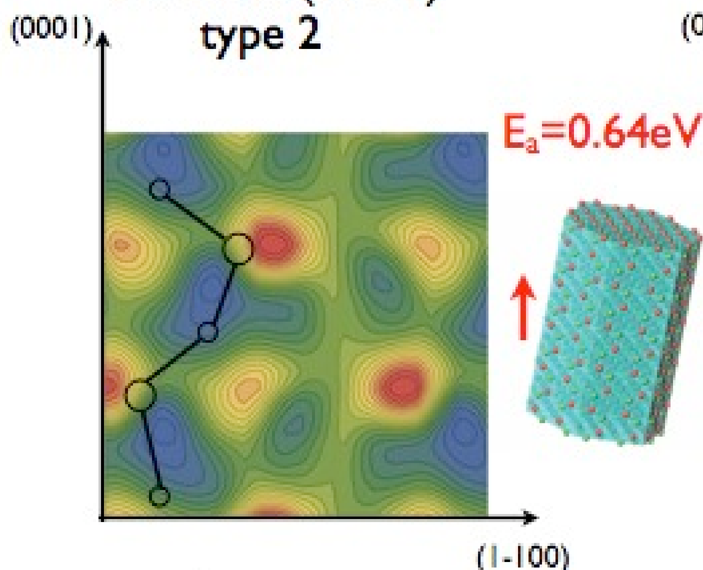


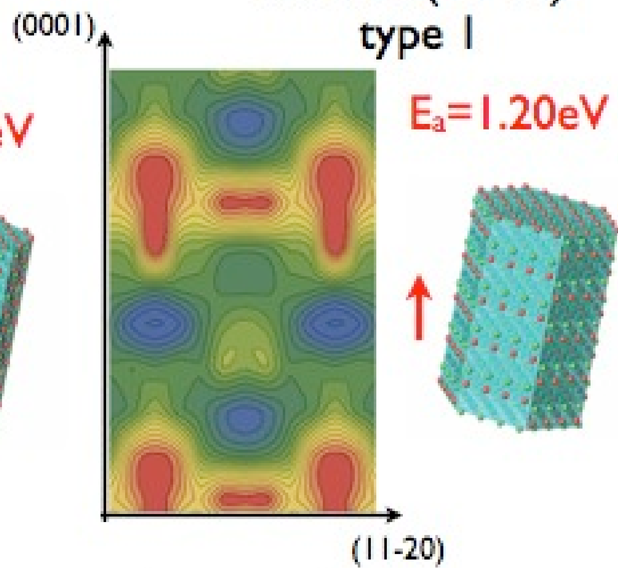
Type 2 wurtzite wire supports faster diffusion !

As diffusion is much slower !

potential energy surface for As adatom

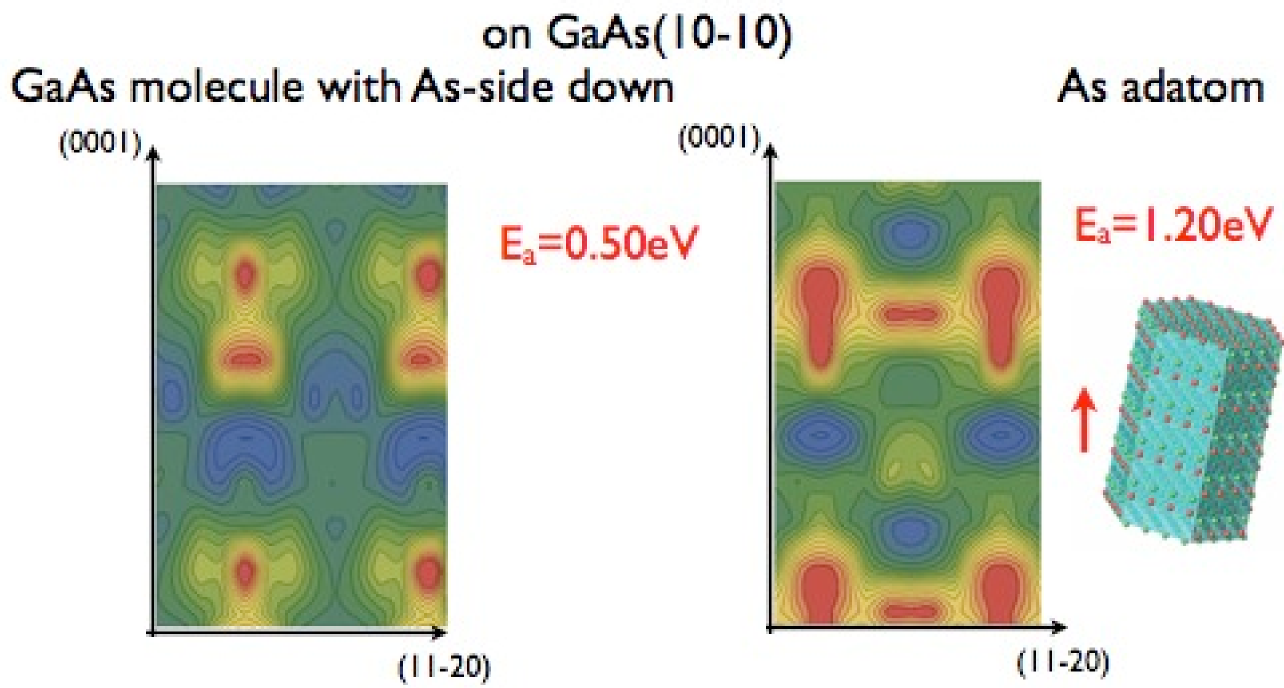
on GaAs (11-20) on GaAs(10-10)





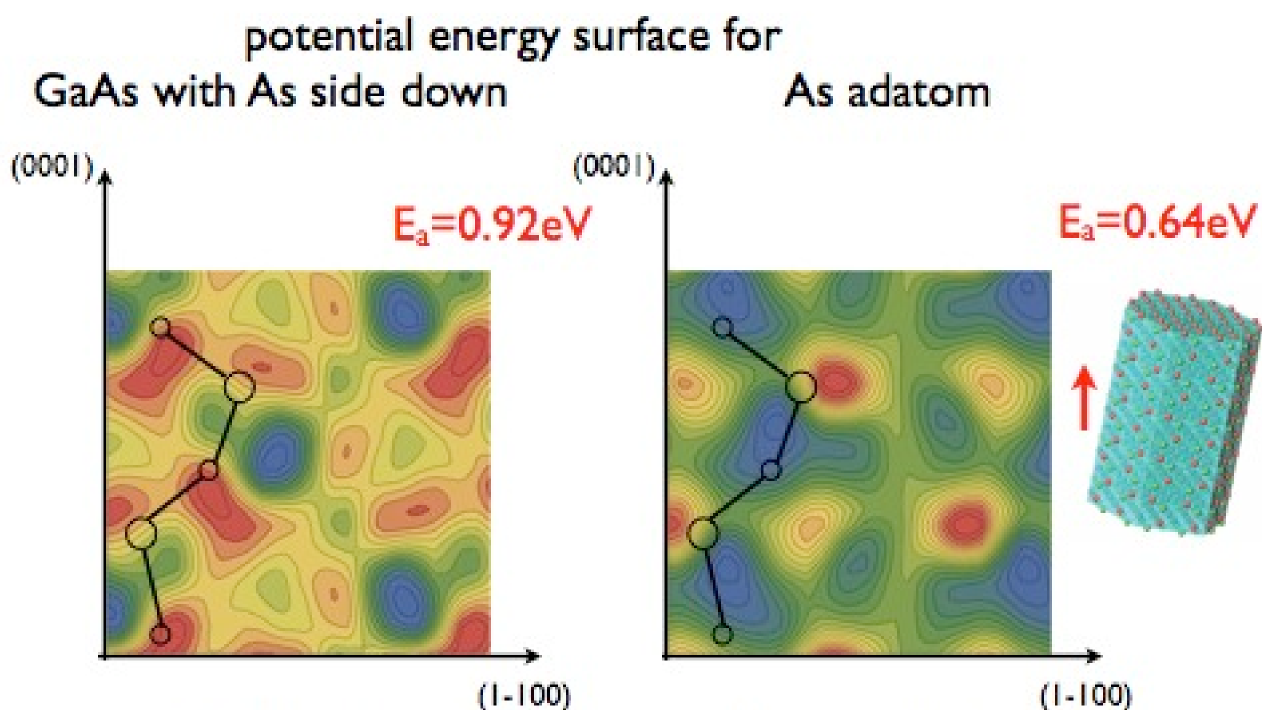
→ It is easier to supply arsenic to the growth zone via **direct impingement** on the Au particle, rather than via diffusion on the side facets.

Mass transport of As is carried by GaAs



→ On GaAs(10-10), GaAs has the highest mobility (compared to single Ga and As adatoms).

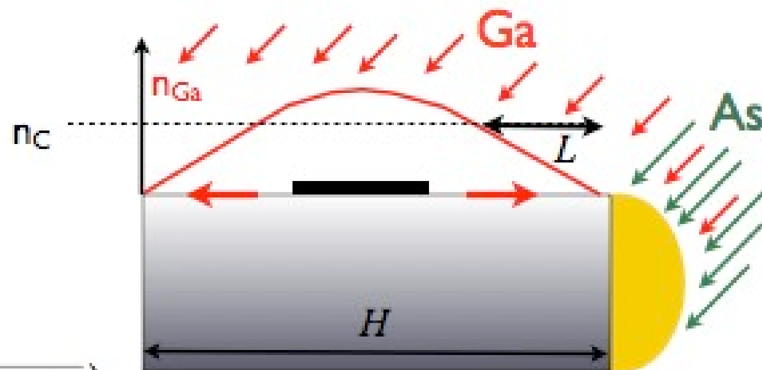
GaAs species on GaAs (11-20)



→ GaAs molecule gets trapped because it inserts itself into the GaAs chain on top of the substrate.

Side wall nucleation and radial growth

- type-II wires: immobile surface GaAs species leads to nucleation
- type-I wires: critical nucleus of more than one Ga atom (+ some As), critical adatom density n_C



$$L = \frac{H}{2}\left(1 - \sqrt{1 - \frac{16 n_c^{1/2} D(T)}{H^2 a_0^2 F_{\mathrm{Ga}} \sin\theta}}\right)$$

$D = 2\times10^{-6}$ cm²/s; $H = 80$ µm
$\Rightarrow L = 22$ µm

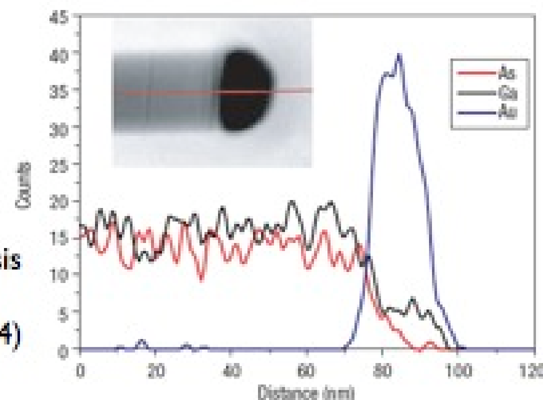
- Tapering of the wires after sidewall nucleation if L exceeds the collection length

V. Pankoke, S. Sakong and P. Kratzer, PRB **86**, 085425 (2012)

Arsenic supply to the interface

- arsenic vacancy emission into the solid

$$D_{\mathrm{V_{As}}}(T) = \Gamma_0 \exp\left(-\frac{\Delta E}{k_B T}\right)$$

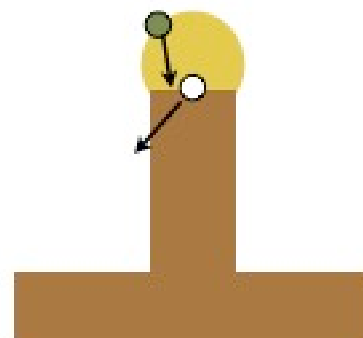


element-specific XEDS analysis
A.I. Persson et al.,
Nature Materials **3**, 667 (2004)

or

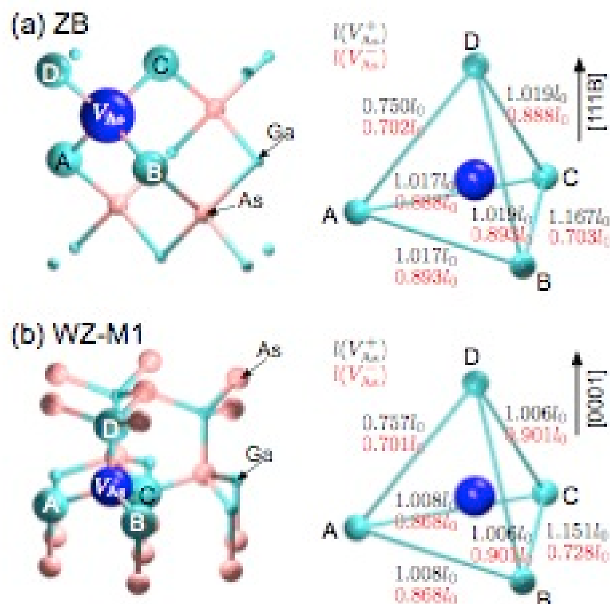
- diffusion of As dissolved in the liquid
  Stokes-Einstein relation

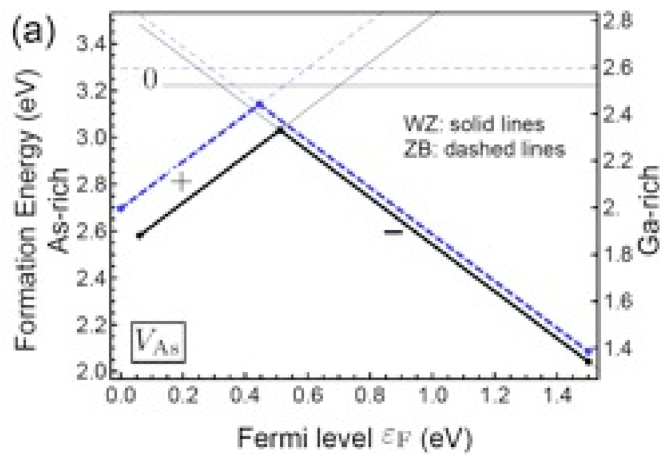
$$D_{\mathrm{As@Au}}(T) = \frac{k_B T}{6\pi r_{\mathrm{As}} \eta_{\mathrm{Au}}(T)}$$



Arsenic vacancies

- unstable as neutral vacancy (a so-called "negative-U" system)
- strong contraction of the vacancy tetrahedron for negatively charged vacancy, as bonding linear combination of Ga dangling bonds becomes occupied

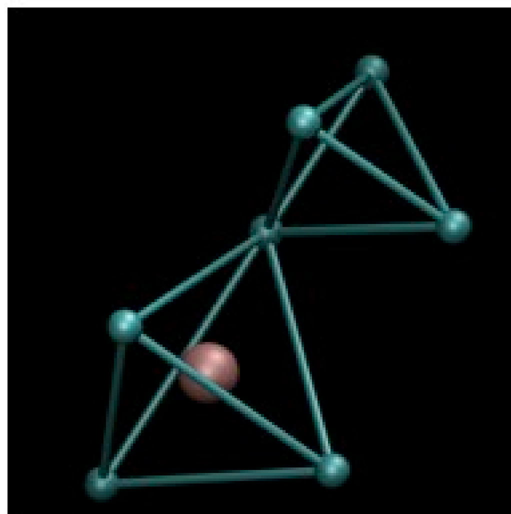


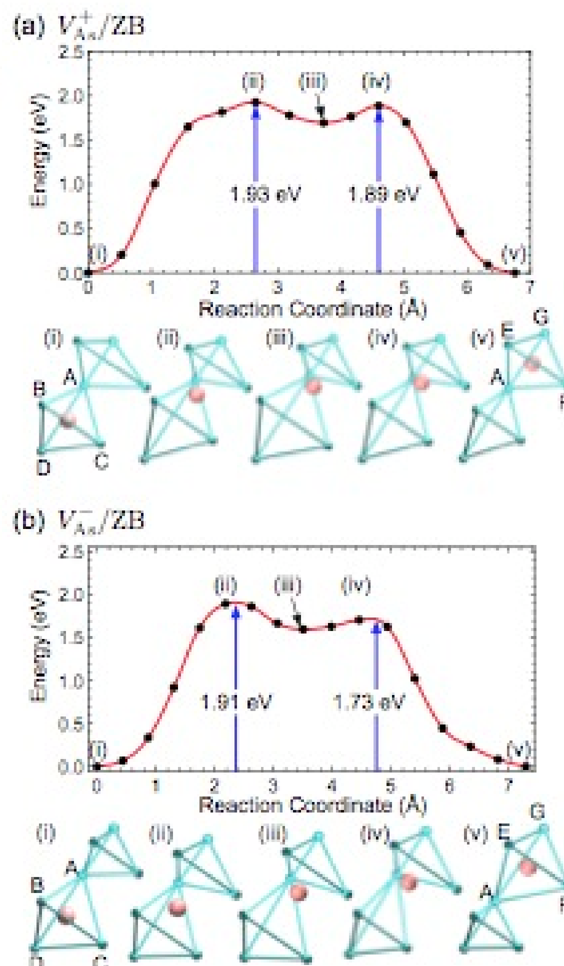


Y.A. Du, S. Sakong and P. Kratzer, PRB **87**, 075308 (2013)

V_{As} diffusion in zincblende

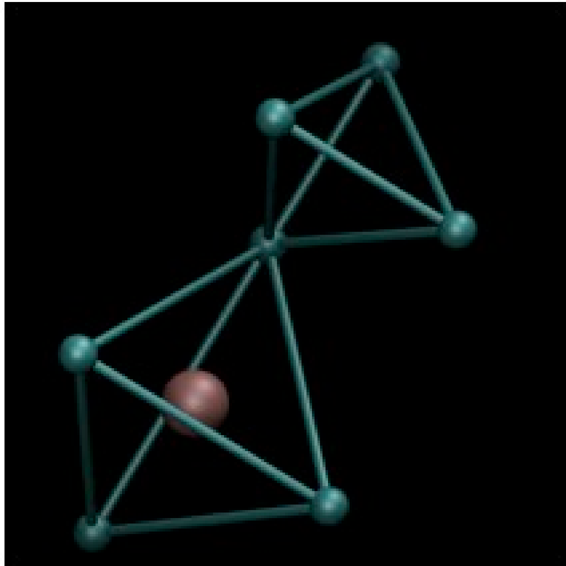
- octahedral interstitial as intermediate minimum
- asynchronous diffusion of electronic charge and of As atom

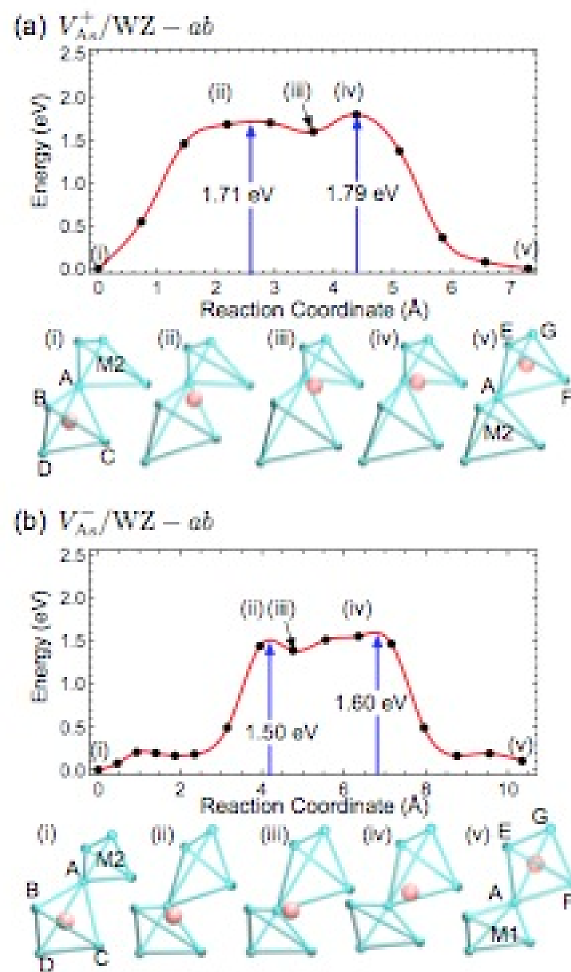




V_{As} diffusion in wurtzite

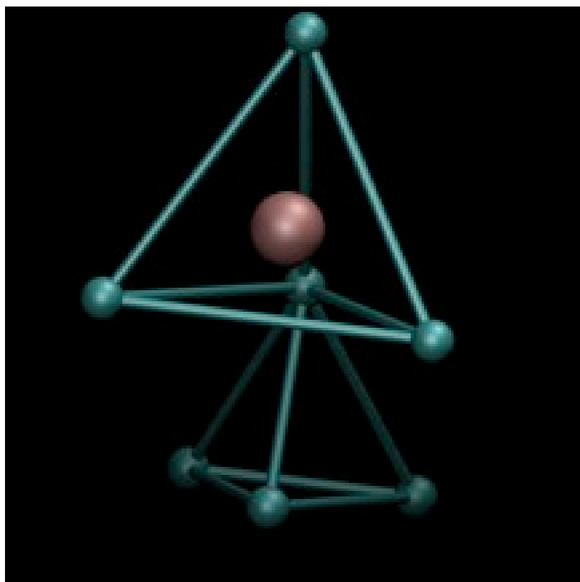
- in wurtzite *ab*-plane, barriers are lower as compared to zincblende case

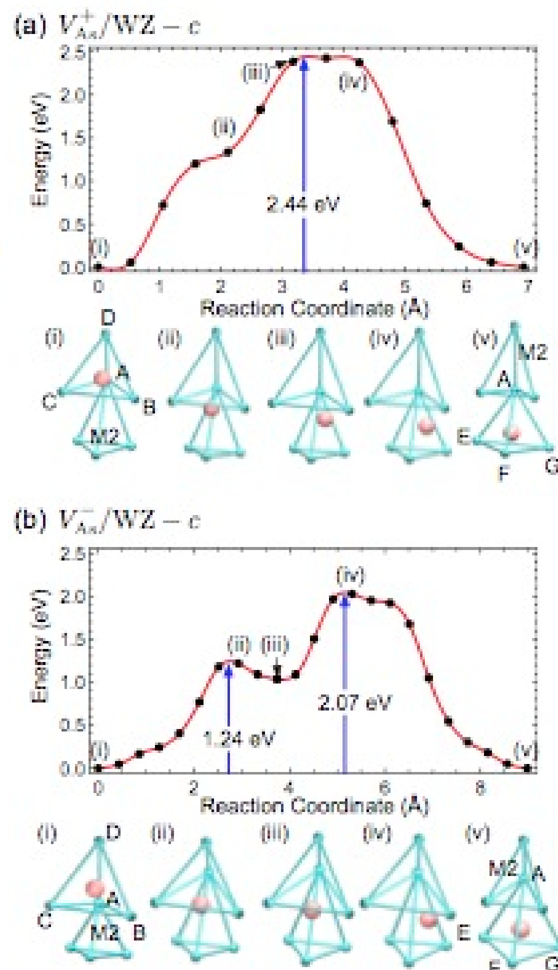




V_{As} diffusion in wurtzite

- along the c-axis, V_{As} needs to go a detour to avoid crossing the Ga-Ga coordination line → higher barrier than in zincblende





Arsenic supply to the interface

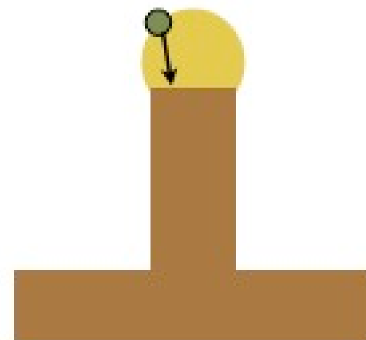
- arsenic vacancy emission into the solid

$$D_{V_{As}}(T) = \Gamma_0 \exp\left(-\frac{\Delta E}{k_B T}\right)$$

Vacancy formation energy and barriers are too high (~2 eV)

- diffusion of As dissolved in the liquid
  Stokes-Einstein relation

$$D_{\mathrm{As@Au}}(T) = \frac{k_B T}{6\pi r_{\mathrm{As}} \eta_{\mathrm{Au}}(T)}$$

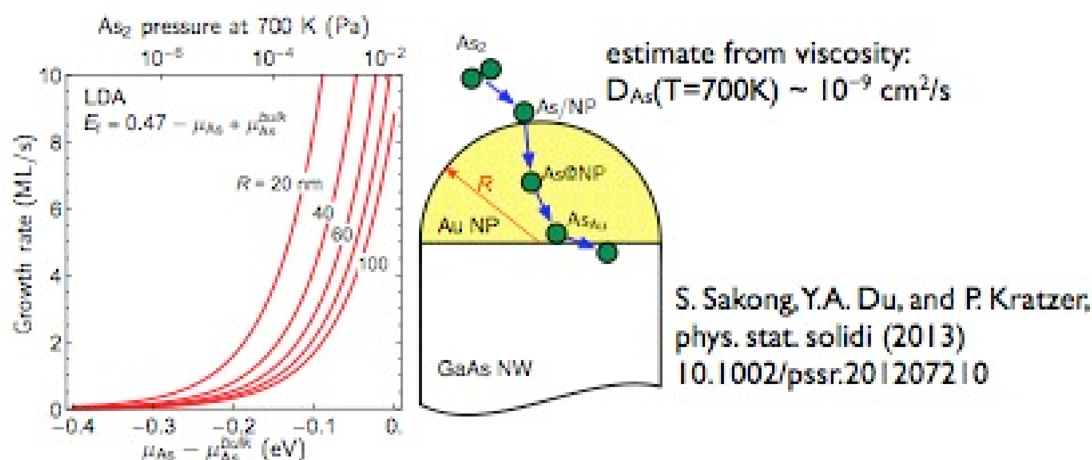


Role of As diffusion inside Au-Ga particle

- low solubility, low concentration of As inside the particle

$$c_{\mathrm{As}} = N_{\mathrm{Au}} \exp\left(-\frac{E_{\mathrm{As@Au}}(\mu_{\mathrm{As}})}{k_B T}\right)$$

- estimated growth rate is compatible with experiment

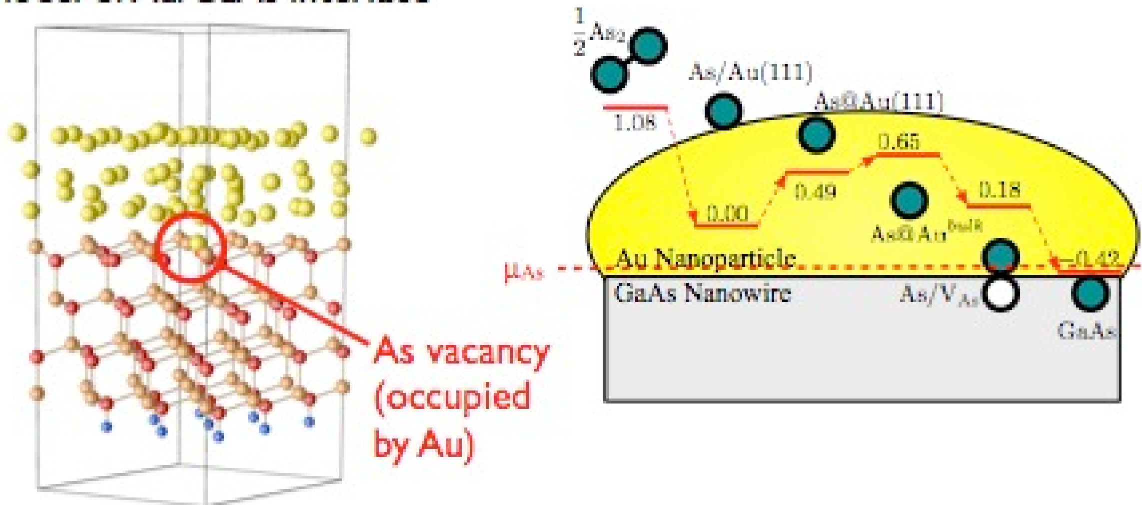


- if As diffusion is rate limiting, the growth rate scales like $1/R$

Model for As supply to growth zone

- Diffusion of As atoms through the liquid AuGa particle dominates
- Very low substitutional As@Au concentration of 10^{-4}% in Au; but may still be sufficient to supply As to the interface
- kinetic coefficient for reaction/ incorporation of As at the interface ?
- atomistic understanding of the interface structure and defects required

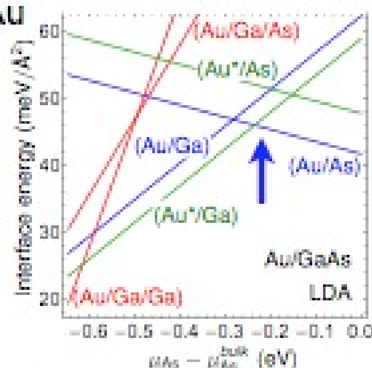
model of Au/GaAs interface



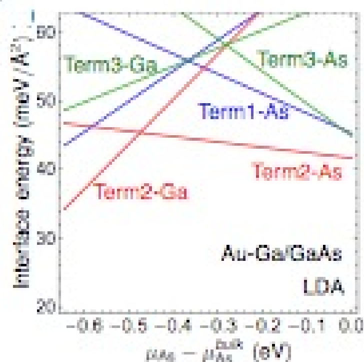
Au-GaAs interface in equilibrium

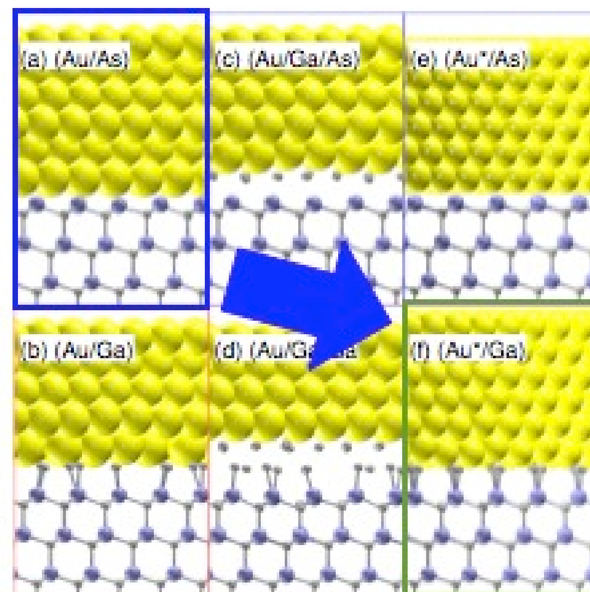
- interface energies from DFT-LDA calculations

pure Au



alloy



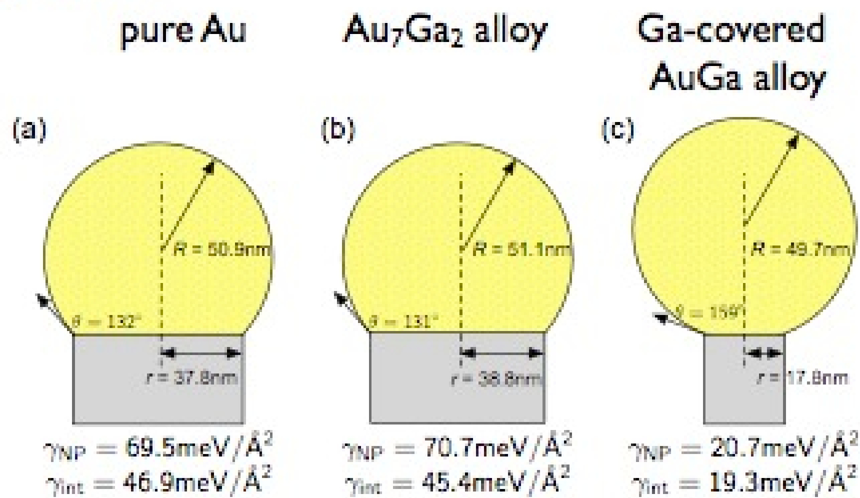


S. Sakong, Y.A. Du, and P. Kratzer, PRB submitted

Mechanical equilibrium determines shape

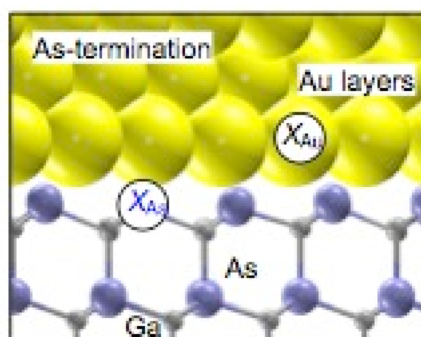
- minimization of Gibbs potential $\Omega(\mu_{As}, r, \theta)$ under geometrical constraints and given chemical potential, using DFT-LDA surface and interface energies
- optimized shape for an (initially) spherical Au particle with $R_0 = 50$ nm

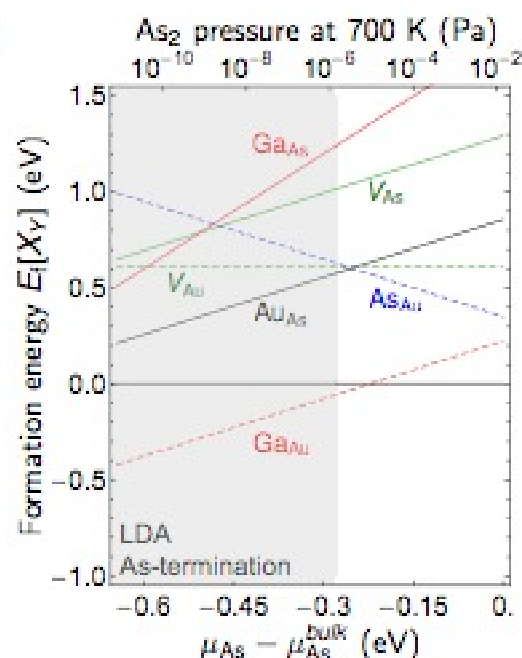
pure Au | Au_7Ga_2 alloy | Ga-covered AuGa alloy



As-terminated GaAs(111)B/Au(111) interface

- prevalent interface under As-rich growth conditions
- Ga segregation from Au particle initiates layer growth
- Au_{As} formation activated by 0.6 to 0.8 eV

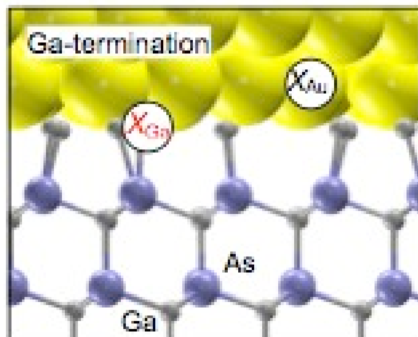


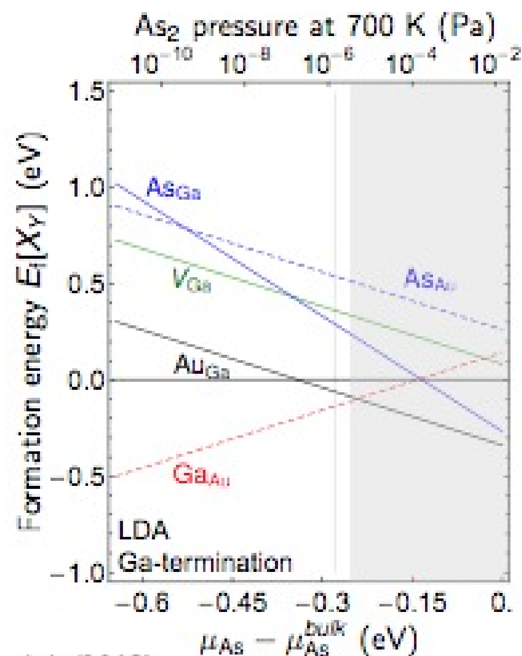


S. Sakong, Y.A. Du, and P. Kratzer, phys. stat. solidi (2013)
10.1002/pssr.201207210

Ga-terminated GaAs(111)B/Au(111) interface

- prevalent interface at Ga-rich growth condition
- unstable against further Ga segregation
- possible source of Au_{Ga} defects when growth conditions become less Ga-rich





S. Sakong, Y.A. Du, and P. Kratzer, phys. stat. solidi (2013)
10.1002/pssr.201207210

Conclusions

- shape of the nanowire tip region is determined by surface tensions at or close to **mechanical equilibrium**
- **Au-GaAs interface oscillates** between As-rich and Ga-rich triggered by interface defects
- Ga forms **surface alloy** with Au
- Au particle is able to bind gas-phase As_2
- As-Ga complexes formed at the Au surface act as **growth intermediates**
- **facile Ga diffusion** on wurtzite side facets; fastest on GaAs(11-20)
- arsenic sidewall diffusion hampered by larger barriers
  ⇒ As supply mostly due to **impact of As_2 on Au particle**
- **side wall nucleation** and radial growth is easier on GaAs(11-20) compared to GaAs(10-10)