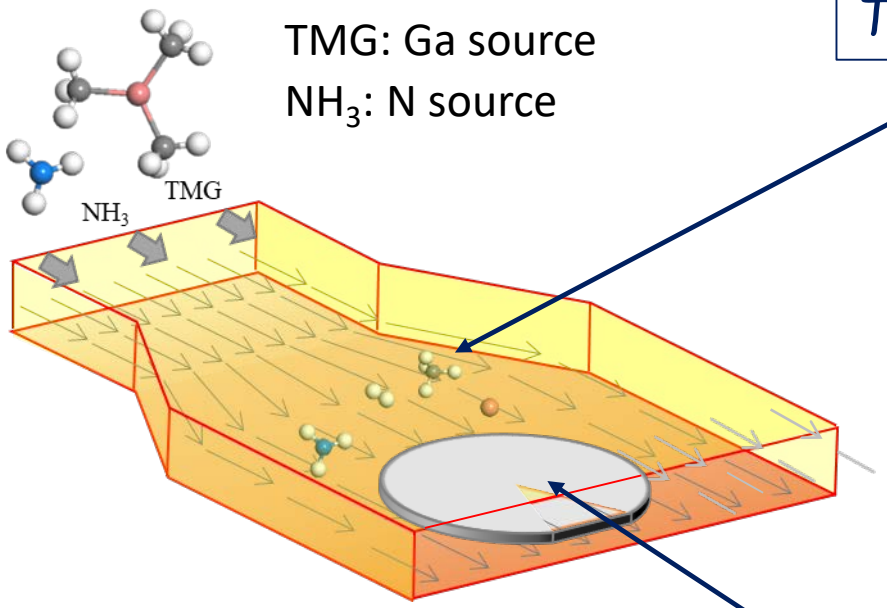
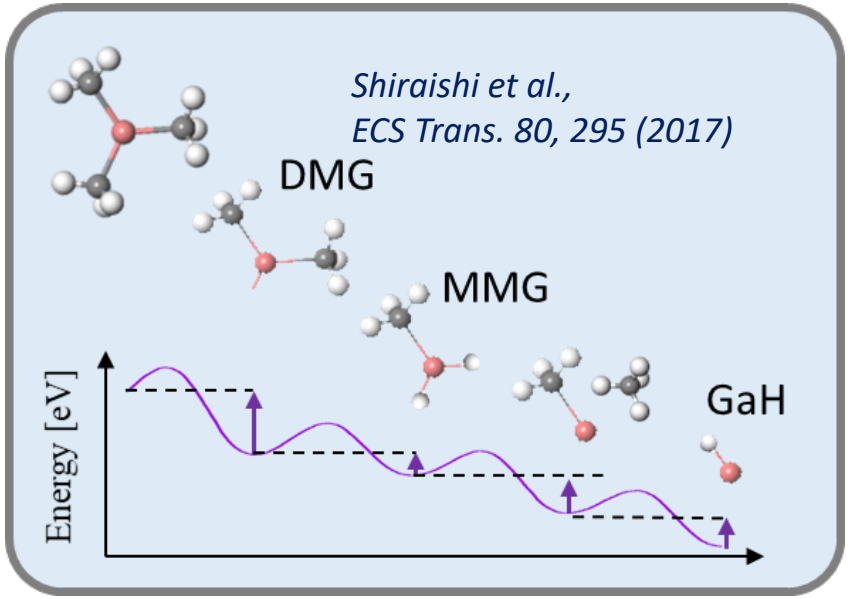
MetalOrganic Vapor Phase Epitaxy (MOVPE) of GaN



TMG: Ga source

NH_3: N source

TMG is decomposed in the gas phase



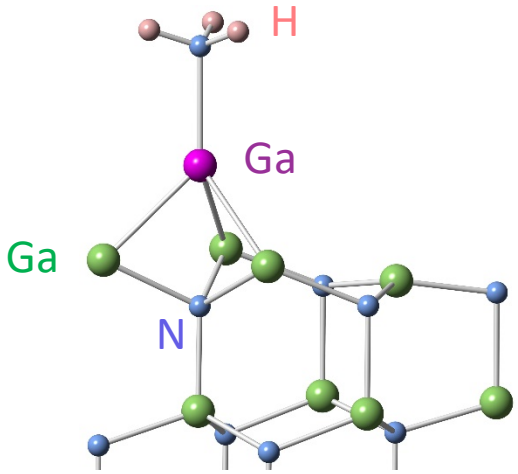
Decomposition of NH_3 is UNKOWN. But,,,High-ResolutionTOF measurements in Amano group show the existence of only NH_3 in the gas phase plus very small amount (0.1 %) of NH_2.

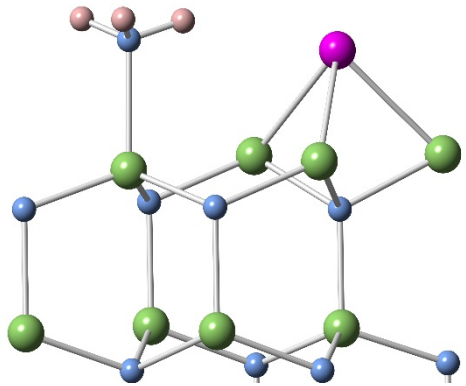
Nagamatsu et al., Phys. Sttus Solidi B 254, 1600737 (2017)

Need to know:

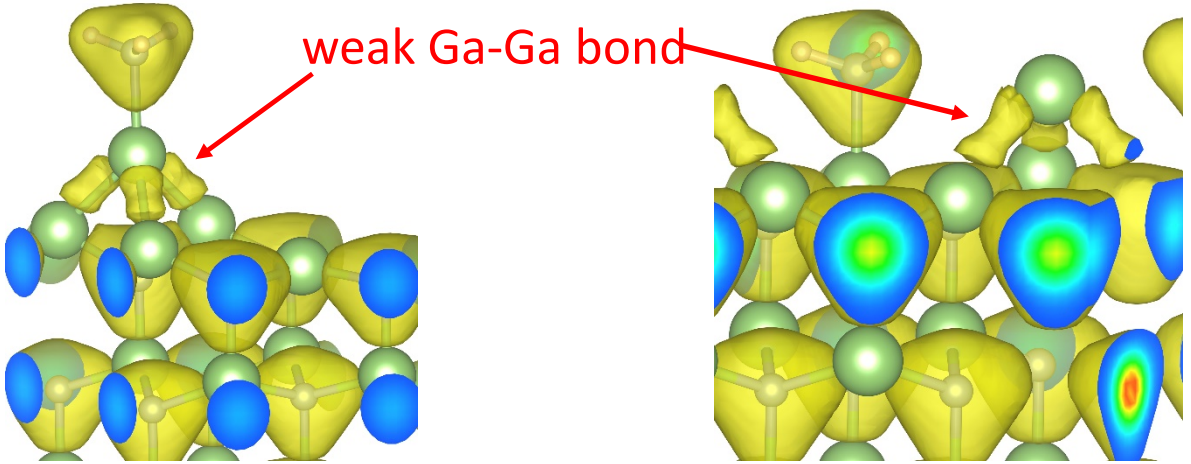
Behaviors of NH_3 and possible NH_x on the growing surface, which is Ga rich

NH_3 Adsorption on Ga-rich Surface





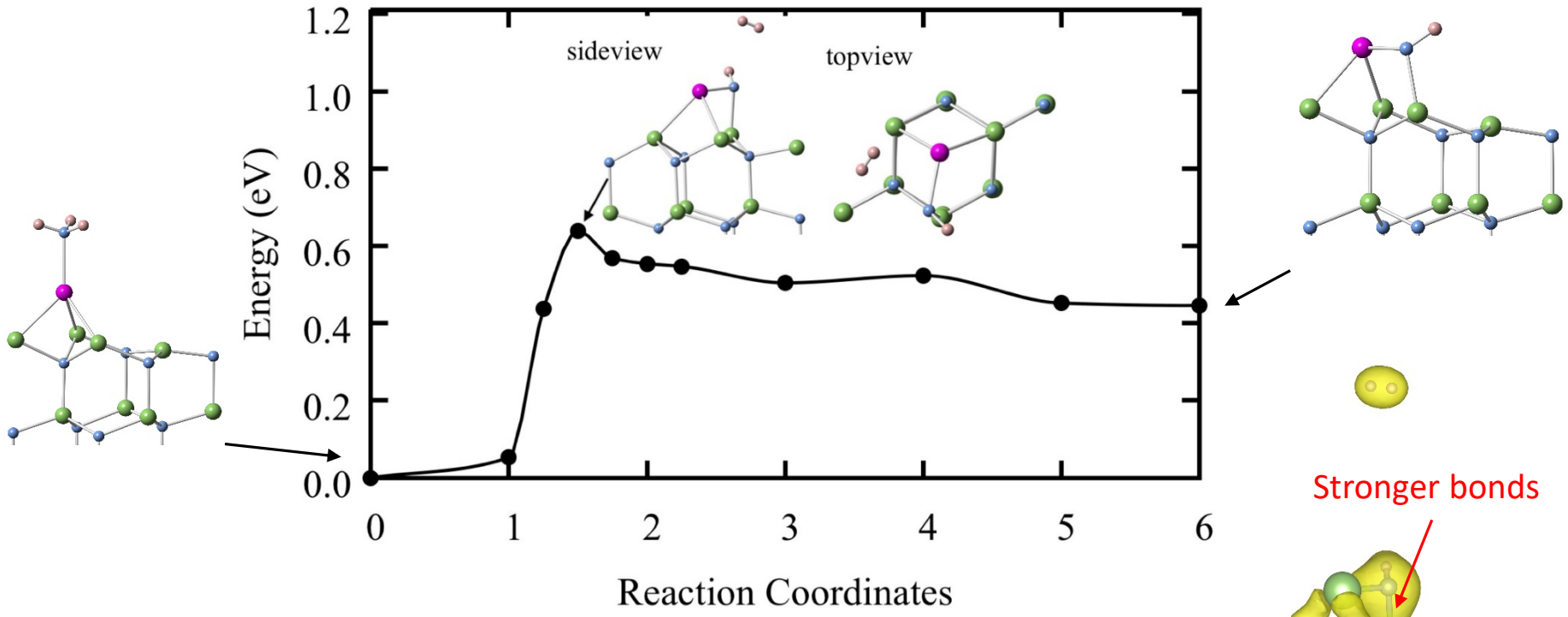
Stable Geometries



Electron Density

Ga dangling bond UNOCCUPIED: Electron Counting Rule

Decomposition of NH_3 ($NH_3 \rightarrow NH/GaN + H_2$)



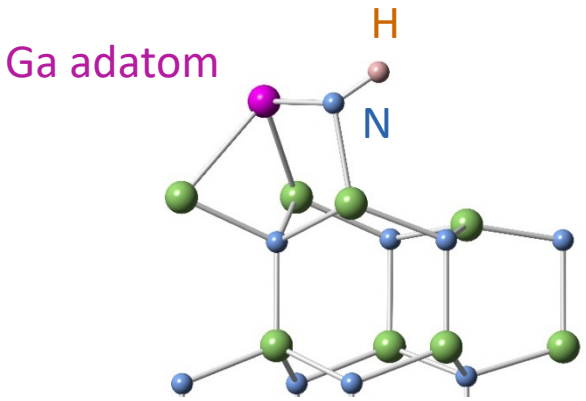
- ✓ Small Barrier 0.63 eV for the bond breaking reaction
- ✓ Weak Ga-Ga bond is converted to two strong Ga-N bonds
- ✓ When we consider free-energy gain of H_2 in the gas phase,

  $\mu_{H2} = -k_B T \ln[gk_B T / p\varsigma_{trans}\varsigma_{rot}\varsigma_{vibr}]$ = -2.1 eV under growth condition

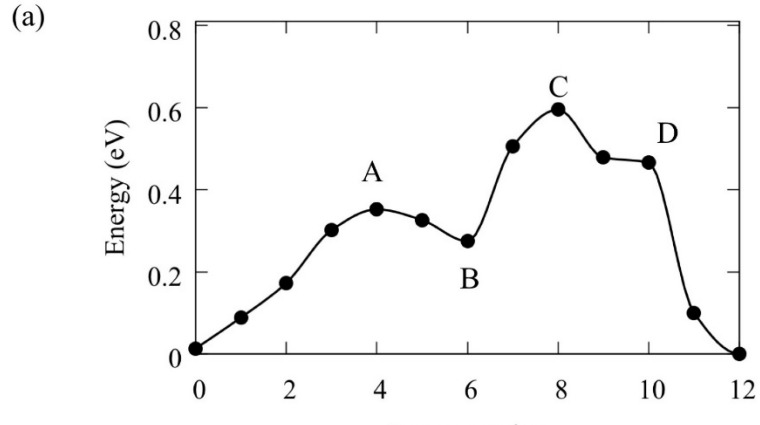
  the reaction becomes exothermic

Diffusion of the NH unit on GaN(0001) Adatom Surface

Stable NH Unit

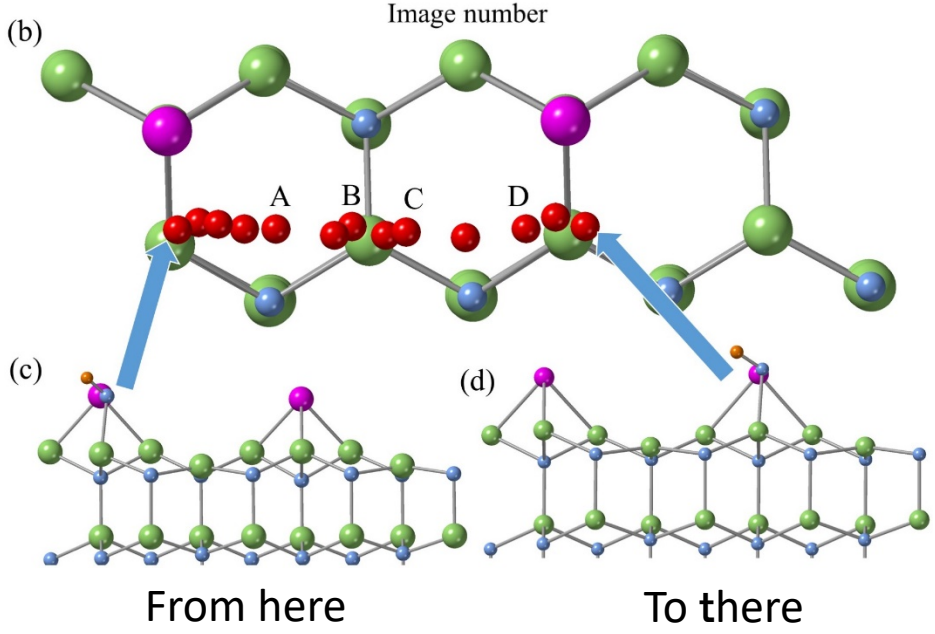


Diffusion to the Adjacent Ga-adatom site



Search for the diffusion pathway by Hyperplane Constraint Method

Diffusion barrier = 0.59 eV



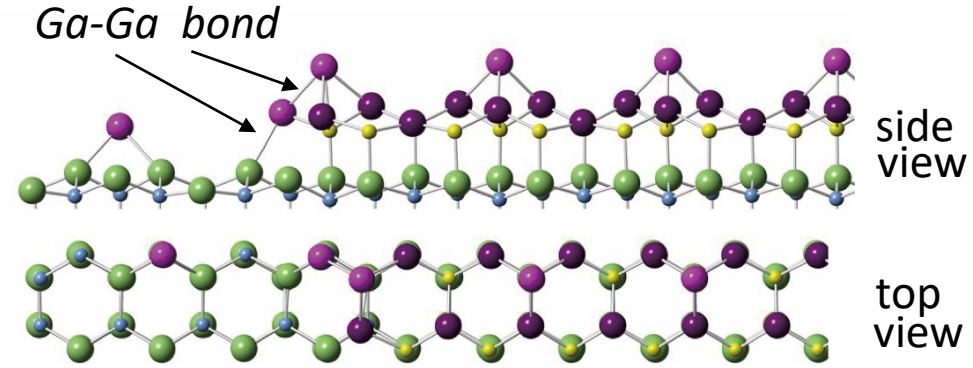
⇒

NH unit wanders on the terrace and is expected to approach surface steps

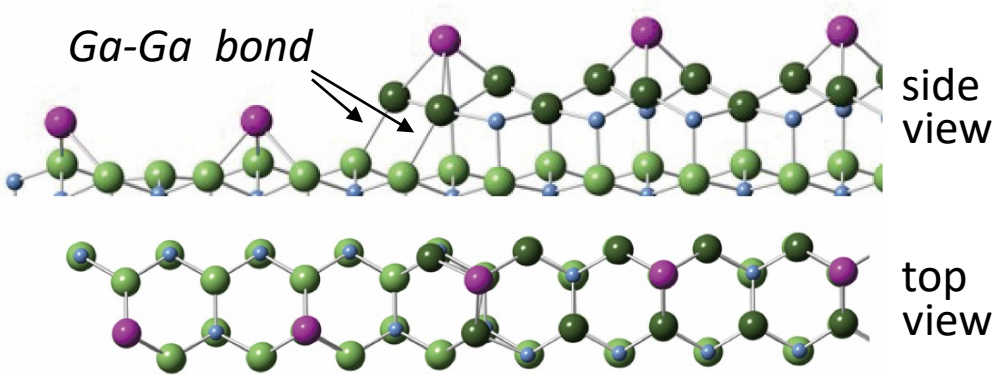
Electron Density at Step Edges: Ga-Ga Weak Bonds

● ● ● [Ga Atoms near Step Edges]

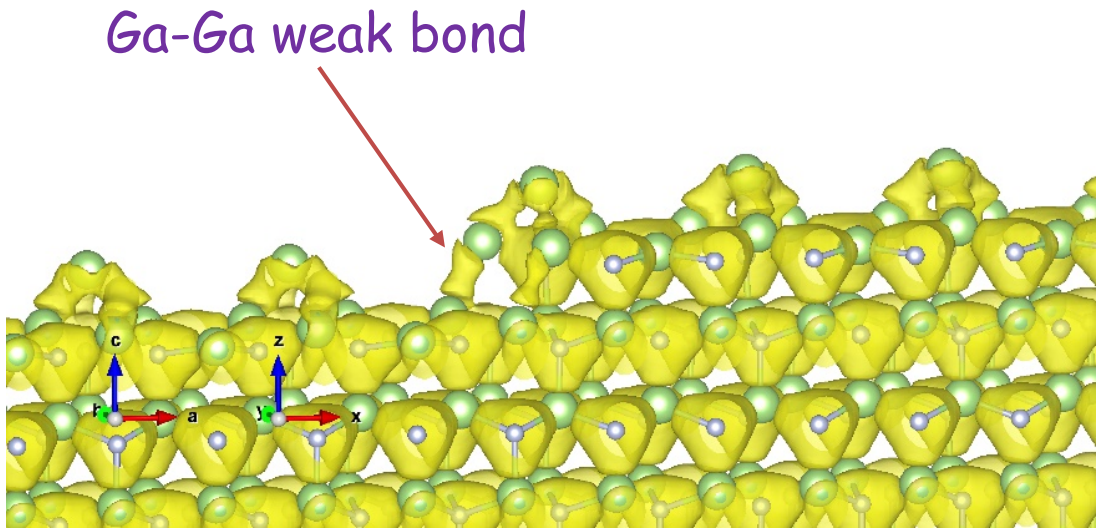
GN Step



Ga2 Step



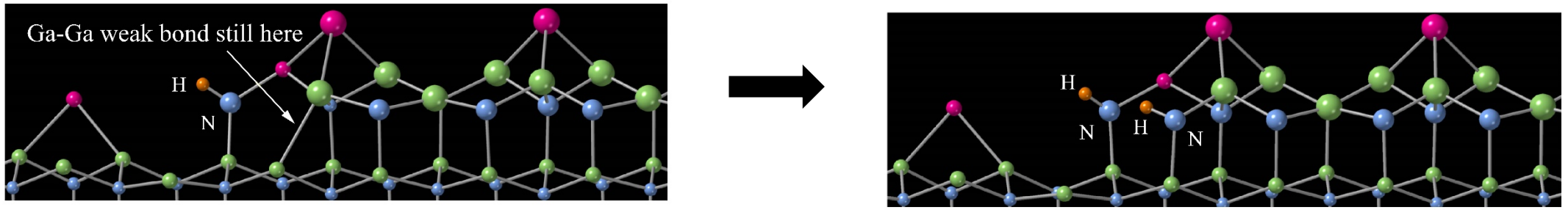
Electron Density near GN Step Edge



Ga-Ga weak bond:
Hot spot for the growth

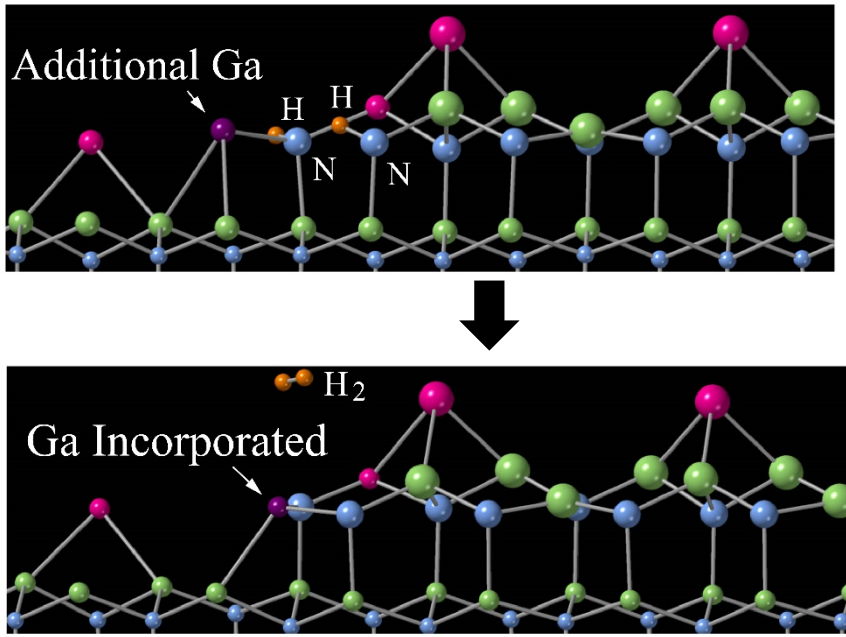
NH Incorporation at GN Step Edges,,, and then Step-Flow Growth

NH Intervening in Ga-Ga Weak Bonds at GN Step Edges

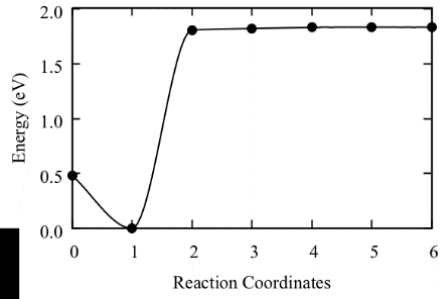


✓ 2 isolated NH in Ga-Ga bond on terrace -> 2 NH at step edge + 0.45 eV *Exothermic Attraction at Step Edges*

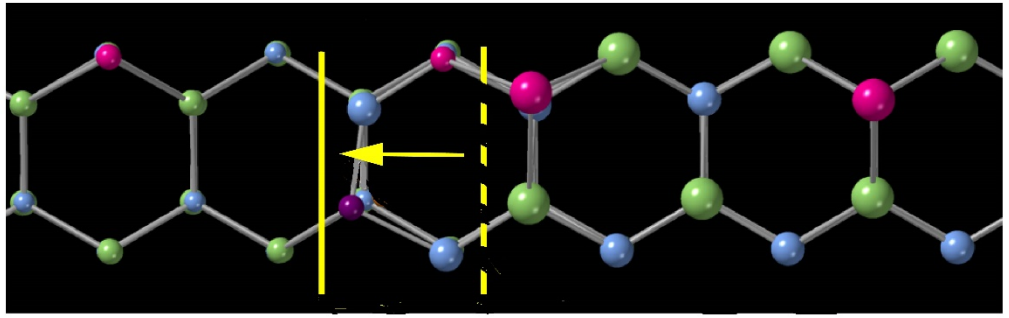
New Ga on Ga-rich Surface -> Incorporation of the new Ga with H2 Desorbed



ΔF of H2 =-2.1 eV



top view



Step Edge Proceeds

Possible Microscopic Process of Step-Flow Growth