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An atomistic mechanism study of GaN step-flow growth on vicinal m-plane orientations

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Free energy of a vicinal surface $\gamma(\theta)$, misoriented with respected to *m*-plane by an angle θ is given by: $\gamma(\theta) = f(0) + \frac{\beta}{d} + \frac{q}{d^3}$.[1]

$f(0)$ is the free energy of the low-index plane (*m*-plane), β denotes the step pair formation energies per unit length, d is the distance between successive steps. q represents the step-step interaction energy per unit area. $\gamma(\theta) = (E_{tot} - n_i \mu_{Ga,N(\mathrm{GaN}_{bulk})}) / A$, where A is the exposed area of the slab, n_i is the number of atoms for Ga, or N species.

Table S1 Vicinal surface formation energies. Distances between the terrace edges (d) and calculated vicinal surface energies (γ_θ) for the fitting procedure.

a direction vicinal surface	$(4\bar{3}\bar{1}0) + (\bar{4}310)$	$(6\bar{5}\bar{1}0) + (\bar{6}510)$	$(7\bar{6}\bar{1}0) + (\bar{7}610)$
d (Å)	11.594	17.904	21.087
γ_θ (x10^{-1}eVÅ^{-2})	2.055	2.034	2.024
$f(0) = 0.195(\mathrm{eV\,Å^{-2}}), \beta = 0.173(\mathrm{eV\,Å^{-1}}), q = -6.730(\mathrm{eV\,Å})$			
c direction vicinal surface	$(6\bar{6}01) + (\bar{6}60\bar{1})$	$(8\bar{8}01) + (\bar{8}80\bar{1})$	$(10\bar{1}\bar{0}01) + (\bar{1}0\bar{1}00\bar{1})$
d (Å)	15.962	21.141	26.334
γ_θ (x10^{-1}eVÅ^{-2})	2.402	2.303	2.239
$f(0) = 0.196(\mathrm{eV\,Å^{-2}}), \beta = 0.745(\mathrm{eV\,Å^{-1}}), q = -10.955(\mathrm{eV\,Å})$			
a+*c* direction vicinal surface	$(\bar{6}8\bar{2}1) + (6\bar{8}2\bar{1})$	$(\bar{1}0\bar{1}2\bar{2}1) + (10\bar{1}\bar{2}2\bar{1})$	$(\bar{1}2\bar{1}4\bar{2}1) + (12\bar{1}\bar{4}2\bar{1})$
d (Å)	9.979	15.322	18.025
γ_θ (x10^{-1}eVÅ^{-2})	2.743	2.488	2.411
$f(0) = 0.195(\mathrm{eV\,Å^{-2}}), \beta = 0.850(\mathrm{eV\,Å^{-1}}), q = -5.770(\mathrm{eV\,Å})$			

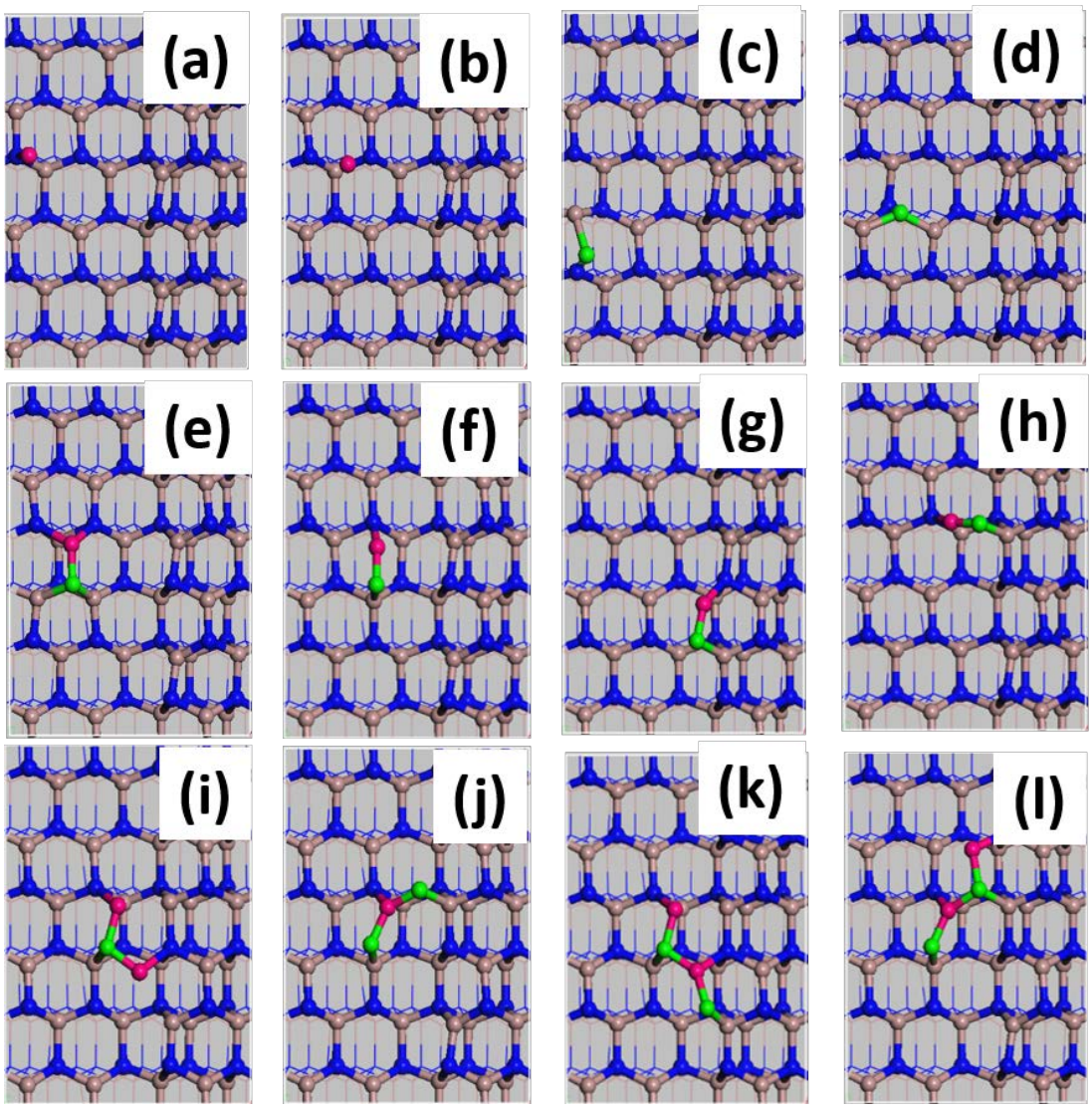

Fig. S1. Top view of calculated geometries for the adatom adsorption configurations in m-plane: the Ga (N) adatom highlighted by red (green) color, surface Ga atoms in blue and surface N atoms in brown, ball-and-stick view is used only for the top two monolayers of the surface. (a) Single Ga adatom adsorbed nearly above the surface N atom, (b) and on ridge site between the two N atoms. (c) Single N adatom adsorbed between the surface Ga and N atoms, and (d) on ridge site between the two Ga atoms. (e) Ga-N dimer on ridge site, (f) top site, (g) edge site, and (h) across the step edge. (i) Ga-N-Ga trimer kink nucleus, (j) N-Ga-N trimer kink nucleus, (k) Ga-N-Ga-N tetramer kink nucleus and (l) N-Ga-N-Ga tetramer kink nucleus.

Table. S2
The binding energies and chemical potential changes resulting from the growth species adsorption on the vicinal surface. The species used to define the reference chemical potential are marked by *.

Figure S1	Adsorption species	Binding energy E (eV)	$\mu_i - \mu_{Ga,N}^{ref}$ (eV)
(a)	Ga on top of surface N atom	-2.12	2.557
(b)*	Ga between the N atoms	-2.036	2.641
(c)	N between the Ga and N atom	-5.531	1.95
(d)*	N between the Ga atoms	-4.726	2.755
(e)	Ga-N dimer on ridge site	-9.327	2.831
(f)	Ga-N dimer on lower terrace edge	-9.107	3.051
(g)	Ga-N dimer on upper edge	-8.706	3.452
(h)	Ga-N dimer across the step edge	-9.163	2.995
(i)	Ga-N-Ga trimer	-13.834	3.001
(j)	N-Ga-N trimer	-14.587	5.052
(k)	Ga-N-Ga-N tetramer	-20.109	4.207
(l)	N-Ga-N-Ga tetramer	-20.171	4.145

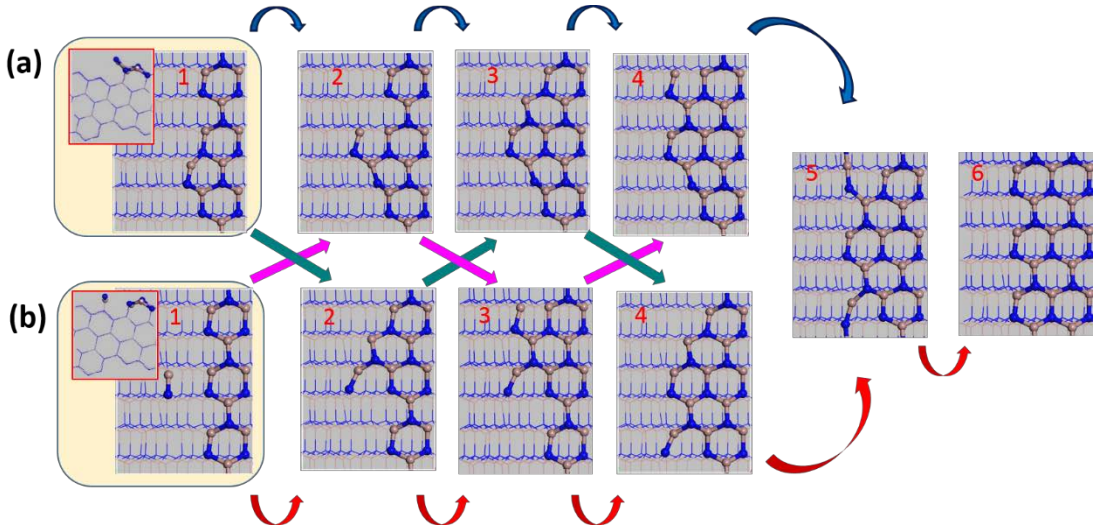

Fig. S2. Optimal atomic configurations during the kink growth by sequaential docking of (a) Ga-N dimers starting from the edge sites, and (b) from the lower terrace sites next to the edge. The two possible bypass approaches with exchanged adding sequence for the kink growth are indicated by the colored arrows. Atom colors are the same as Fig. S1, with ad-dimers shown in the same color as the surface layer.

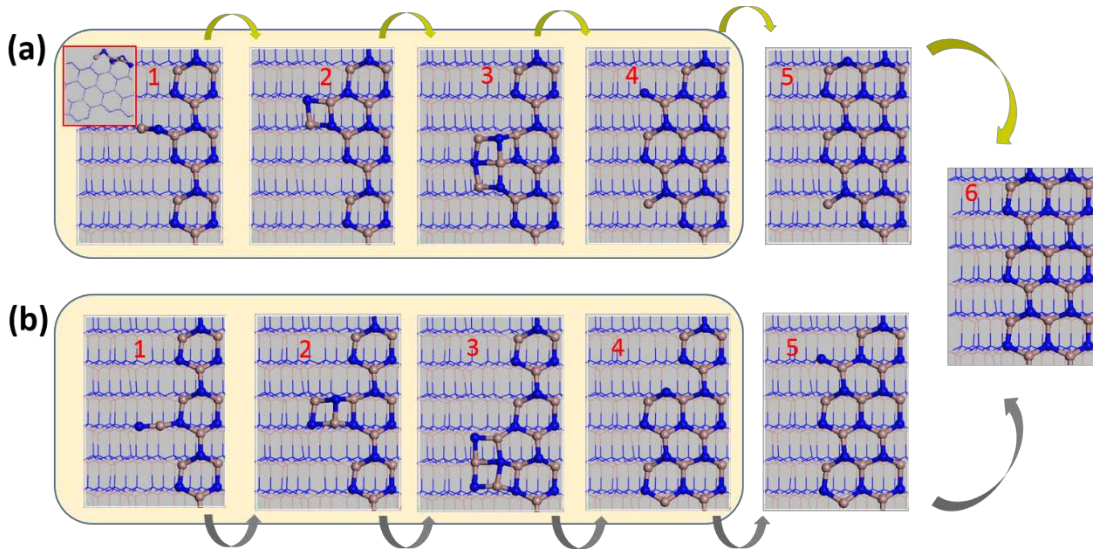

Fig. S3. Top view of optimal atomic configurations during the kinks growth by docking of Ga-N dimer started (a) bridging the upper Ga atom and lower N atom at the edge, (b) bridging the upper N atom and lower Ga atom at the edge. Atom colors are the same as Fig. S1, with ad-dimers shown in the same color as the surface layer.

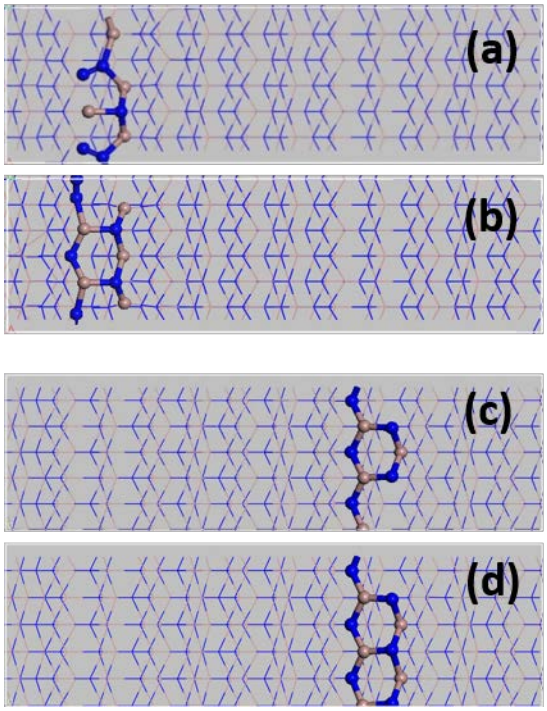

Fig. S4. Optimal atomic configurations for kink nuclei on the –*c*-step edges by nucletion of (a) N-Ga-N trimer, and (b) N-Ga-N-Ga-N pentamer. The bridging N atoms on the top bilayer are very unstable with respect to an N-N dimerization with the edge N atom. For the +*c*-step edges, intermidiate stage of kink pairs by nucleation of (c) N-Ga-N trimer, and (d) N-Ga-N-Ga-N pentamer are favorable configurations under N rich conditions. Atom colors are the same as Fig. S1, with ad-dimers shown in the same color as the surface layer.

[1] X. Q. Gong, A. Selloni, M. Batzill, and U. Diebold, Nat. Mater. **5**, 665 (2006).