Supplementary Information

Ga Adlayer Model: Capturing Features of GaN(0001) Growth from Submonolayer to Multilayer Regime

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S1. N atom deposition

Deposition is allowed on the lattice site appropriate for the atomic species to be deposited as illustrated in the main article. In case the incoming N adatom encounters AdGa atom at the deposition site, then it occupies the AdGa site and subsequently pushes the AdGa atom to the site directly above and thereby transforms the AdGa atom to Ga atom. Thus, Ga atom becomes the top most atom at deposition site as shown in figure S1.

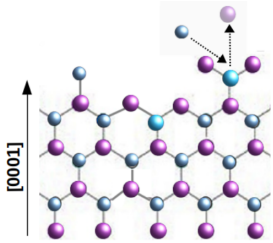

Figure S1: Side view of SOS model showing the transformation of an AdGa on the surface to a Ga atom in the presence of N adatom.

S2. Surface Diffusion

Surface diffusion is modelled by random hopping of surface atoms on to neighboring lattice sites. Our SOS model allows hopping to 18 sites which comprises of 3 nearest neighbor(NN) sites, 6 next-to-nearest neighbor(NNN), and 9 next-to-next-to-nearest neighbor(NNNN) sites as described in figure. S2 .

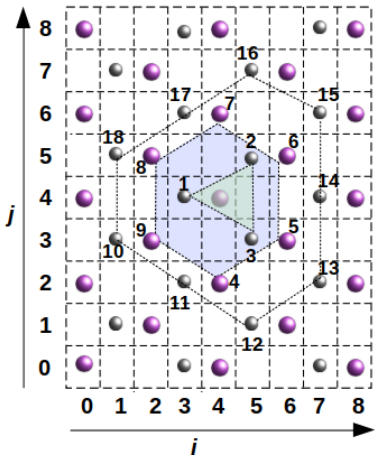

Figure S2: Illustrative top view of GaN(0001) surface showing 18 available site for diffusion of Ga: NN(1-3), NNN(4-9), NNNN(10-18) corresponding to the central site at (4,4).

Different atomic species present in the system hop from one site to the neighboring sites. Our system consists of Gallium (Ga), Nitrogen (N), Ad-layer Gallium (AdGa). Some of their hopping processes are shown in figure S3 and are described below.

Ga atom can hop to it's preferred lattice site i.e. a site having N as topmost atom in the column. Under special circumstances, Ga atom can hop on a site having Ga as a topmost atom thus forming an AdGa atom as discussed in the main article. AdGa atom in turn can hop on to a new site having Ga as the topmost atom forming AdGa. It can also hop to a site with a N as topmost atom. However, it cannot hop on a site where the topmost atom is an AdGa atom.

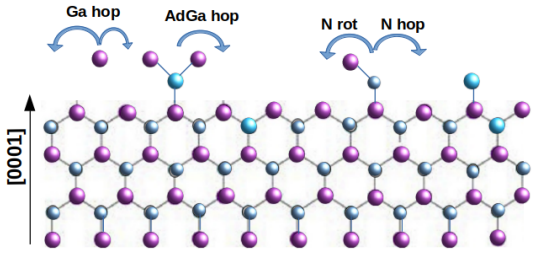

Figure S3: Side view of SOS model showing allowed processes: hopping for Ga, N, AdGa atom along with rotation for N atom[1]. Pink and cyan show Ga and AdGa atom, respectively while grey represent N atom.

N atoms on the other hand can hop onto lattice sites having Ga or AdGa as the topmost atom. N atoms can undergo rotation move is a hop where a N adatom connected to one Ga adatom retains the connection after the hop [1]. N atom can exchange positions with AdGa, converting AdGa atom to Ga as shown in figure S1. As AdGa atoms only form when there are no available neighboring sites with N as the topmost atom. It is possible that due to diffusion, a N atom could be the topmost site next to an AdGa atom. In this case, the N atom will occupy the AdGa site and push the AdGa atom atop, thus converting AdGa atom to Ga atom as shown in figureS4.

S3. Subsurface diffusion

Our model also takes into account subsurface diffusion of nitrogen as described below. In this process, the N atom below the surface Ga atom is able to diffuse under the surface with a relatively lower barrier [2] as shown in figure S4. As the N atom moves to an AdGa site, it pushes the AdGa atom to the surface (shown in light pink). Simultaneously, the Ga atom above the N atom moves down to the site vacated by the N atom and becomes an AdGa atom. Subsurface diffusion of N is attempted whenever the diffusion of the surface Ga atom directly above it is rejected in the kMC attempt. The subsurface N atom will hop to the site which is surrounded by Ga or AdGa in the nearest neighbour vicinity.

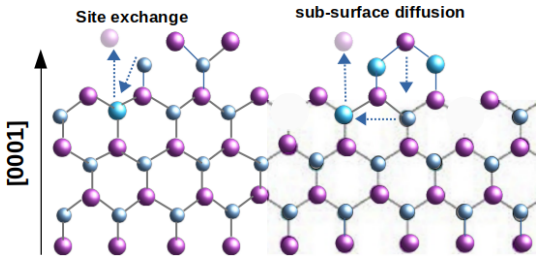

Figure S4: Schematic representation of site exchange of AdGa atom in presence of N atom along with the subsurface diffusion of N atom, allowed in our kMC SOS model. For details refer to the text. Pink color show Ga atom while cyan and grey color represent AdGa and N atom, respectively.

S4. Post Processing Tools for Analysis of Surface Morphology

In order to characterize the island growth at submonolayer level as well transition from rough-pitted to smooth surface, we use two different post

processing methods as discussed below.

S4.1. Cluster counting to analyze submonolayer growth

In order to characterize the island size and its distribution, it is necessary to calculate the size of islands. For this purpose, we use a cluster counting technique. There are various cluster counting algorithms available[3, 4, 5]. Our post processing code to count islands is based on depth first search(DFS), a recursive algorithm based on backtracking nodes of a tree[6]. This algorithm begins to explore from the root i.e.top node of a tree and proceeds down a given branch (path) searching an unexplored node, subsequently backtracks searching for an unexplored path, to explore. Here, backtracking in algorithm means that while moving in the forward direction, there are no more un-visited nodes along that current path, you start to move backwards on the same path to find nodes to traverse. Schematic figure representing DFS algorithm is shown in figure S5.

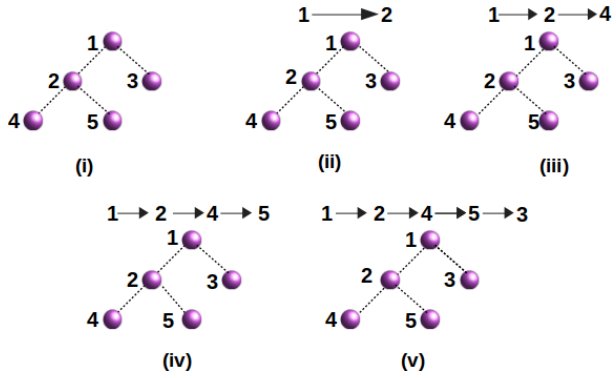

Figure S5: Schematic representation of DFS algorithm with spheres in pink representing nodes of tree. For details, see text.

In our implementation of DFS algorithm, we consider only Ga atoms that are present on top most layer in submonolayer regime. Figure S6(a) represent a Ga island on the top surface. To start, all the sites on top surface were labelled as 0 as shown figure S6(b). We start a search for Ga atom from top left and then moving on to the right. In case of encountering Ga atom during search, we start searching the Ga atom in next nearest neighbor sites of the encountered Ga atom. In case we find a Ga atom in NNN to Ga atom selected we re-label site as 1 and continue moving in forward direction till

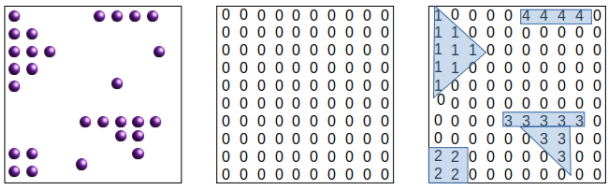

Figure S6: Working DFS algorithm (a) pink atom representing islands on surface (b) all sites are initialised by zero (c) Island labelled with set of number.

there is no further Ga atom attached to any of the member of current Ga atom island as shown in figure S6(c).

If no Ga atom neighbor is encountered, we leave the site labelled as 0 and move forward, thus ensuring this particular Ga atom is not counted as an island. As we are considering the minimum size of island is 2, so only that Ga atoms will be accounted for island size which is connected to at least one Ga atoms. Once there is no further Ga atom we exit from DFS algorithm loop and we move to the next site and repeat the same procedure and in this way we can get estimate of total number of islands.

S4.2. Roughness

The morphology of the film grown during multilayer growth is typically characterizes as either *rough* or *smooth* and is quantified using a parameter called *roughness*. In general, surface roughness is defined as the mean squared deviation of a real surface from the ideally flat surface and can be written as: $\sqrt{(< h(i,j)^2 > - < h >^2)}$, where $< h >$ is average height. For a perfectly flat film, the roughness is equal to zero. In the case of the GaN(0001) surface, we need to modify this calculation as described below.

Consider a perfectly flat Ga terminated GaN(0001) surface as shown in figure S7. It is clear that the height of a column over the top layer Ga atoms ($h = 16$ in figure) is different from the height of the column over the top layer N atoms ($h = 15$), implying that the roughness of a flat film will be equal to 0.5 and not 0. Another complication in the calculation of roughness is during conditions of excess Ga or N. For Ga(N) rich condition there is an excess of Ga(N) adatoms which are uncoordinated. In *ex situ* microscopy measurements of roughness, the film is subjected to degassing and sometimes taken out before the measurement.Thus, we believe that the uncoordinated adatoms should not contribute to the surface roughness. To

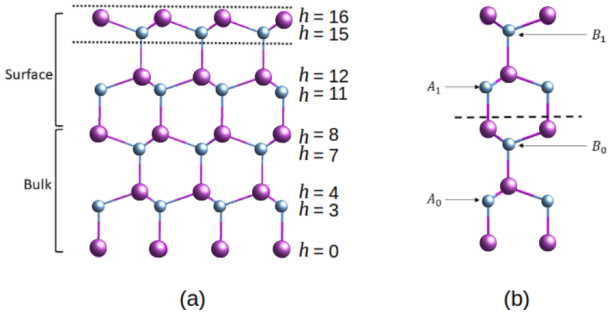

Figure S7: Schematic representation of GaN(0001)(a) flat surface showing N and Ga atoms at two different height. (b) top most N atom of type A and B.

resolve these problems, we propose a method for calculation of roughness by using only one of atoms to calculate the roughness. We use N atoms in growth conditions of excess Ga and Ga atoms in conditions of excess N.

Considering case of Ga excess condition where only surface N atoms will be used to calculate the surface roughness. In an ideally flat surface, the topmost N atom in different columns will be at two different heights, $h = 15$ and $h = 11$ as shown in figure S7(a). The roughness of the system is calculated bearing in mind that the average height is different for different columns. For a 4 bilayer (BL) film shown in figure S7(b), the Nitrogen sites are shown as $A_0 - A_1$ and $B_0 - B_1$, and the topmost site of a flat film is either A_1 or B_1. We note that the sites $A_0 - A_1$ have heights 3, 11, whereas the sites $B_0 - B_1$ have heights 7, 15. In other words the heights of sites $A_0 - A_1$ are 3 modulo 8 and the heights of sites $B_0 - B_1$ are 7 modulo 8. Thus a flat 4BL film will have average heights of 15 and 11 for different columns. Similarly a flat film of height 3 BL will have average heights of 7 and 11 for different columns. We interpolate the average height for films of intermediate thickness. Using these average heights, the roughness can be calculated using only the N atoms. We note that the roughness has same units as height and, in this work, we express it in units of $c/8$.

The method proposed above generally works well but can occasionally lead to unexpected results. One prominent feature in the curves is the increased roughness at integer values in the case of excess N conditions and stoichiometric conditions. This is usually not expected since the roughness should have a minimum value at integer roughness as is seen in the case of excess Ga conditions. Let us consider the case of excess N conditions. Under these conditions, the Ga atoms are used to calculate the roughness. Even for

a flat surface at integer coverage, the topmost Ga atom is at two different heights, as shown in figure S7(a). At 1.0 ML Ga coverage, the film exhibits average heights of 8 and 12 for different columns. However, due to the excess N conditions, there are significant number of N atoms at H = 11. This causes a significant number of Ga atoms were deposited at H = 16, even though the Ga coverage is 1.0 ML, leading to higher roughness observed at integer bilayer coverages. This is the cause of the unexpected behavior in roughness as shown in figure 9 of the main article.

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