Analysis of High Mg-Incorporation into GaN via PAMBE Modulation Doping and Molecular Dynamics Simulations

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Abstract

This work concerns the investigation of high Mg incorporation in GaN. Mg is a widely used p-dopant for GaN, which could benefit from high dopant concentration, as well as high activation, through novel growth methods. This has the potential to create high performance GaN devices, owing to the use of quality p-doped GaN. We carry out this investigation on two fronts. First, we explore the feasibility of PAMBE based modulation doping as the growth method of choice for high incorporation. We conduct growth experiments based on variations of Ga, N, and Mg fluxes, and assess the quality of the films and resulting p-doped samples using SIMS, XRD, CV, and Hall measurements. Second, we carry out atomistic simulations, using MD and KMC, to develop insights into the growth of GaN crystals, guiding the growth process as a result. We incorporate 3-body Tersoff potentials, developed specifically for GaN, to simulate GaN growth through MD. We extract migration, absorption, and desorption statistics, and utilize these transition rates in a computationally efficient method, KMC. Use of high quality p-doped GaN in power devices will help further advance this technology in terms of efficiency, compactness, and power handling.

INTRODUCTION

P-type doping in GaN is traditionally done via incorporation of Mg acceptors into the lattice. However, Mg dopants are deep acceptors and suffer from a low activation percentage (typically around 1%) due to their high activation energy. In addition, p-type GaN often suffers from low mobility due to reduced crystallinity. The growth conditions therefore have a profound effect on the resulting p-GaN films. The purpose of the present investigation is to examine the effect of dynamic modulation of growth conditions including Ga, Mg and N flux. Under static conditions, crystal growth occurs under a single equilibrium. For example, under Nitrogen rich conditions, Magnesium dopants preferentially sit on Gallium sites, acting as a substitutional defect, and the formation energy of compensating Nitrogen defects increases, thus reducing the concentration of compensated dopants [1] [2]. However, rapid incorporation often leads to heavy faceting and increased grain boundaries and long range ordered defects. Under Gallium rich conditions, long range defects are not an issue, however, a lack of Gallium leads to reduced Mg incorporation and the formation energy of Nitrogen vacancies decreases, leading to reduced activation of Mg [1] [2]. The goal of exploring several methods of modulation is to take the advantages of each surface state and meld them into one coherent growth.

The first technique to be explored is Metal Modulated Epitaxy (MME) and is defined by the syncopated flux of both matrix and dopant; the second is Phase Shift Epitaxy (PSE) which offsets the flux of matrix and dopant. These techniques allow for the exploration of changing surface conditions, alternating between matrix rich and dopant rich and encompasses a broad scope of physically realized timing schemes. In the past, similar techniques have been demonstrated to produce the record for dopant incorporation [2] [3]. The result is the separation of the dopant atoms from the conductive channels of the device. The ultimate goal is to improve carrier mobility by reducing defect scattering and through intermixing surface conditions of dopant accumulation and depletion and obtain pristine layers with proper dopant incorporation into active lattice sites. Film quality via reflected high energy electron diffraction (RHEED) and x-ray diffraction (XRD) is scheduled and CV and Hall-effect data will reveal carrier concentration and thus activation of Mg dopants. This will give data on elemental composition and crystallinity.

To gain comprehensive understanding of growth dynamics, part of this work consists of analysis and confirmation of our experimental findings through computational modeling of PAMBE growth dynamics. Multiphysics simulation of GaN crystal growth through high-performance computing is a promising direction, with potential for meaningful validation, prediction, and guidance of the growth process. The computational tools involved in this work consist mainly of Molecular Dynamics (MD), and Kinetic Monte Carlo (KMC), with use of density functional theory (DFT) as needed. The efficacy of these methods can be put in perspective using the computational micro/nanotech hierarchy as shown in Fig. 1. DFT is the most computationally

expensive technique, hence, we are only interested in using it to extract useful physical quantities, e.g., interaction potentials between atomic species, and consequently using them in more efficient methods like MD, as shown in Fig. 2.

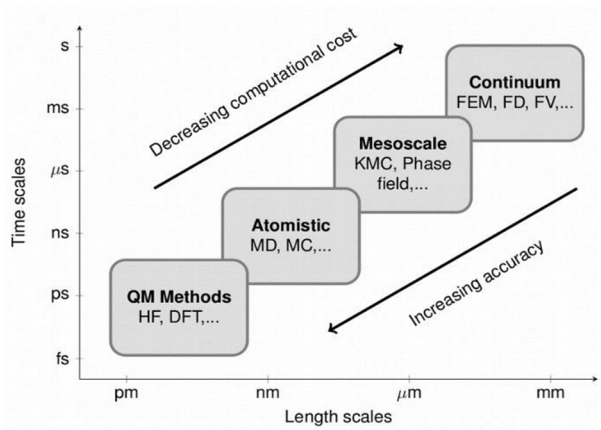

Fig. 1. Computational micro/nanotech hierarchy

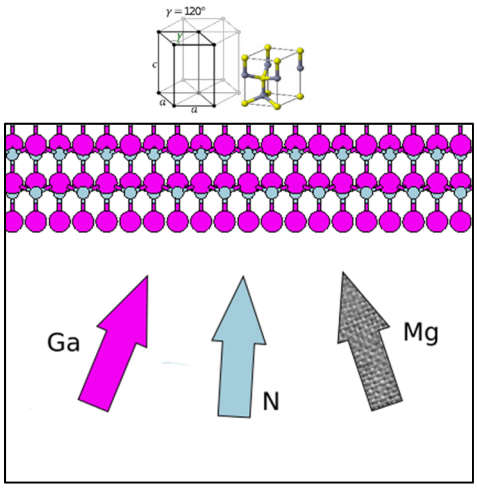

Fig. 2. (Top): Wurtzite conventional and primitive unit cells. (Bottom): Structural layout for simulation of Mg-doped GaN epitaxy on a pure GaN substrate (arrows represent atomic Ga, N, and Mg fluxes inside the PAMBE chamber; white represents empty space.).

However, even MD is not efficient enough to comprehensively model thin film crystal growth dynamics. To put things in perspective, typical GaN growth rate using PAMBE is 250 nm/hour, translating to about one monolayer of growth every few seconds. Since the time-steps involved in MD are of the order of 1 fs, it would require 10^{15} time-steps in an MD run to simulate one second of growth. A typical MD run of 2-5 ns worth of growth takes about an hour of computation time. There are two main approaches to overcome this difficulty. Zhou et. al. [4] have utilized accelerated MD to speed up their growth simulation. However, this results in insufficient diffusion of add-atoms on the deposition surface. Another approach is to extract rates of statistically significant events from an MD run and carry out longer timescale simulations using a more efficient method like KMC. This is the approach adopted by Piana et. al. [5] and is the focus of this work. In this work, we utilize the pair potential of the Tersoff type for Ga and N interaction [6].

We utilize MD and KMC modeling to calculate sticking coefficients as well as adsorption and desorption ratios that best approximate the growth behavior and experimental measurements. This will be followed by an exploration of the optimal growth conditions with regards to improved crystallinity, as well as high Mg-incorporation, resulting in improvement in p-type GaN material properties. Due to the generality of this approach, our computational models have the potential to be applicable beyond GaN, to process simulation of III-nitrides and other compound semiconductors.

INITIAL FINDINGS

In order to isolate the effects of modulation, growth conditions from previously successful unmodulated runs were left untampered. The timing schemes regarding the synchronous modulation of metals (MME) are centered around on/off or open/closed ratios. Modulation recipes of ratios 1:2, 1:1, and 3:1 with a constant off timing of 10 seconds were tested. For PSE, the phase shift is the critical component. With dopants either leading or trailing, the growth surface has potential to achieve saturation at either elemental extreme, allowing for the exploration of saturated incorporation behavior. Timing schemes were locked to a 1:1 on/off ratio and the phase shifts are notated Leading-Element: Phase-Shift; as such the trials are described Mg:2, Ga:2, Ga:5. For consistency, a 10 second total off time per cycle was carried over from the MME samples. Preliminary Secondary Ion Mass Spectroscopy (SIMS) data reveals the average unmodulated Mg incorporation with the set growth parameters achieves 1.66E16 dopant density per cubic centimeter as the point of comparison. The average incorporation densities are summarized in Table I, below. Early results of the MME samples suggest beneficial kinetics for short 'on' windows. Regarding PSE, further analysis is required.

TABLE I
REPORTED MG INCORPORATION FROM SIMS

No Modulation	MME 1:2	MME 1:1	MME 3:1	PSE Ga:5
Control (1x)	44x	9x	2x	7x

Moving forward, tuning of the growth conditions will advance such that non-modulated doping density is increased. Secondly, our goal is to advance MME tactics regarding short

'on' cycle windows, and collect further PSE data with the goal of observing the transition between detrimental Ga-rich and alloying Ga-rich accumulation, which has been reported to prevent desorbing of Mg and enhance incorporation, and likewise observe the effects of Mg accumulation. After MME and PSE regimes are improved, Nitrogen modulation tactics can be explored.

Regarding simulation efforts, we have conducted a preliminary computational study in atomistic GaN growth, consisting of two methods (MD and KMC) mentioned above. Firstly, we conduct an MD simulation for a pure GaN system comprising 1280 atoms (640 Ga, and 640 N atoms) as shown in Fig. 4 [8]. The wurtzite structure was set up using the lattice parameters, a and c, of 3.18 and 5.16 angstrom respectively. The choice of interatomic potential is based on [6], which describes the three-body Tersoff potential [7] for Ga, N, and GaN. The effect of the third body on a pair potential can be seen in Fig. 3. The simulation consisted of two steps, energy minimization, and temperature equilibration. The total energy of the system needs to minimize in order to have a low energy stable structure. This was followed by raising of the temperature from 2K to 120K, as shown in Fig. 5. The equilibration run was carried out for a total time of 50ps, and we can see that the temperature of 120K was reached well before that, indicating a stable numerical configuration. Further work in this direction would consist of selecting one sides of the crystal as the top (growth) layer, to be populated with an incompletely filled monolayer, which will allow us to simulate the migration of atoms on the growth surface. In Fig. 6, we can see the performance scaling of our simulation on HPC cluster. More compute cores result in faster simulation, allowing more MD time to be simulated in the same amount of computer time (24 hours).

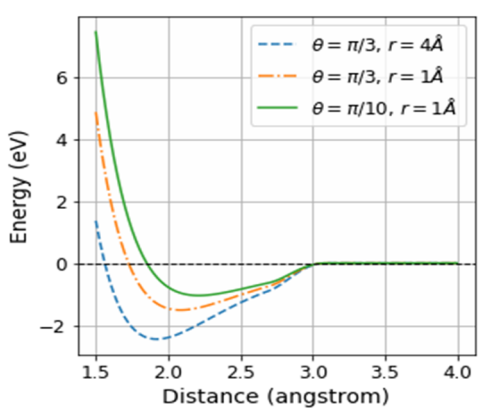

Fig. 3. Tersoff 3-body-potential [7] for N-Ga-Ga based on [6], showing variation of pair-potential in presence of a third atom. Theta, θ, represents angle between atom pairs 1-2 and 1-3; r represents distance of atom 3 from atom 1.

In addition, we have carried out initial KMC simulation in 2-D over a partially filled honeycomb lattice, representing the growth surface. This simulation consisted of fictitious transition rates, since realistic rates still need to be extracted using computationally expensive MD runs (a work in progress).

Snapshots of KMC run can be visualized in Fig. 7. The two snapshots represent the state of the top film of hexagonal monolayer in the process of formation, at two points in time. Going forward, we plan to carry out realistic KMC runs simulating the growth conditions of GaN based on transition rate calculations resulting from MD, so that we can compare our computational results with the experimental data from the modulation doped GaN growth.

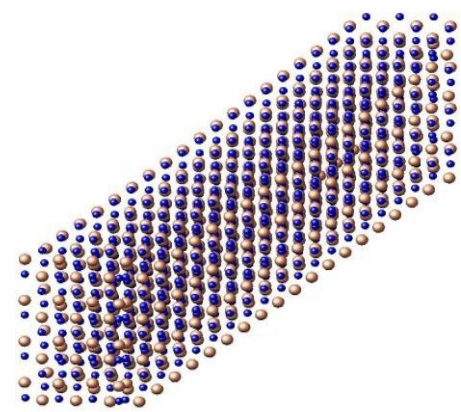

Fig. 4. Simulated wurtzite crystal structure consisting of 1280 atoms (640 Ga in orange/light, 640 N in blue/dark)

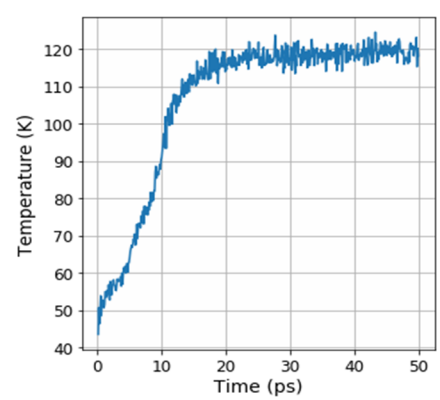

Fig. 5. Temperature equilibration in an NVT (canonical) ensemble simulation.

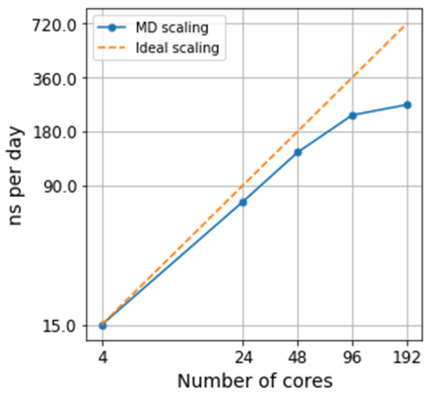

Fig. 6. Simulation performance of a test MD system on XSEDE Comet HPC cluster [9]

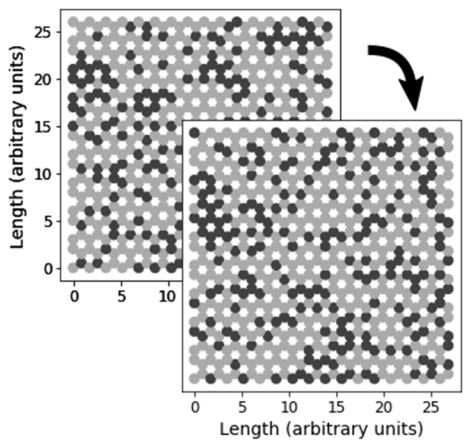

Fig. 7. Top down view of a preliminary Kinetic Monte Carlo run at two points in time. Dark circles are occupied sites on a pure monolayer (either Ga or N), light circles are unoccupied. (This is a work in progress).

Conclusions

To summarize, GaN technology has the potential for massive further advancements resulting from quality p-doped GaN. One of the promising means of realizing this is to increase incorporation of Mg in GaN. In this work, we approach this problem through the exploration of PAMBE based modulation doping growth, analysis of the quality of resulting samples, as well as atomistic simulations of the crystal growth process. Preliminary growth runs consist of MME and PSE of various modulation ratios and off timings. Initial computational results consist of equilibrated 1280-atom pure GaN MD simulation at 120K, as well as 2D setup for KMC.

We continue this study with further tuning of growth conditions, with a follow up sample quality assessment. In addition, we extend the simulation time of MD growth simulation to enable calculation of transition rates, and incorporate them into KMC simulation to help develop insight into the physics of GaN crystal growth and dopant incorporation.

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Acronyms

MME – Metal Modulated Epitaxy
PSE – Phase Shift Epitaxy
MD – Molecular Dynamics
KMC – Kinetic Monte Carlo
SIMS – Secondary Ion Mass Spectroscopy
RHEED – Reflected High Energy Electron Diffraction
PAMBE – Plasma Assisted Molecular Beam Epitaxy
XRD – X-Ray Diffraction
CV – Capacitance-Voltage
HCP – Hexagonal Close Packed