

Epi-Grow Simulator User Manual

MBE/CVD/MOCVD Reactors based Epitaxial Growth Process Simulation Software

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All the third party data taken from reputed published journal papers, Books and elsewhere mentioned anywhere in this manual is properly cited.

List of Abbreviations & Keywords

1.	Activation
2.	Atom
3.	Atomistic
4.	Adsorption
5.	Adatoms
6.	Arrhenius
7.	Barrier
8.	CVD – Chemical Vapor Deposition
9.	Chemical
10.	Crucible
11.	Defects
12.	Dislocation
13.	Doping
14.	Desorption
15.	Diffusion
16.	DMG – Dimethyl Gallium
17.	Epi – Ordered Layers
18.	EpiGrow
19.	Epitaxy
20.	Effusion
21.	Edge dislocation
22.	Flow
23.	Flux
24.	GeH4 – Germene
25.	Gas
26.	Hopping
27.	Interstitial
28.	Incorporation
29.	kMC – Kinetic Monte Carlo
30.	Kinetics
31.	Lattice Parameter
32.	MC – Monte Carlo
33.	MD – Molecular Dynamics
34.	MMG - Monomethyl Gallium
35.	MBE – Molecular Beam Epitaxy
36.	MOCVD - Metallorganic Chemical Vapor Deposition
37.	Monoclinic
38.	n - n – Nearest Neighbor
39.	Precursors
40.	Pressure
41.	Phase
42.	Roughness
43.	Reactions
44.	Strain

- 45. Surface
- 46. Sch-Schwoebel
- 47. SiH4-Silane
- 48. SiCl4 Silicon Cloride
- 49. SiO2 Silicon Oxide
- 50. Stacking fault
- 51. Substrate
- TMG Trimethyl Gallium 52.
- 53. TBAs Tributhyl Arsenide
- 54. TNL Tech Next Lab Inc.
- Temperature
 TCAD Technology Computer Aided Design
- 57. VPE Vapor Phase Epitaxial
- 58. Vacancy
- 59. Wurtzite
- 60. Zincblende



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CHAPTER 1 INTRODUCTION



Abstract

The feasibility for the optimization and in-line control of thin film growth under real time atomistic epitaxial deposition techniques based on CVD, MOCVD and MBE reactors conditions can be accurately predicted with the help of **TNL-EpiGrow simulator**. The off-lattice homoand hetero-epitaxy simulation experiments for growth of elemental and compound semiconductor materials thin films in steps. TNL-EpiGrow simulator provides help in optimization of epitaxial growth technologies based on Chemical Vapor Deposition (CVD), Metal Organic Chemical Vapor Deposition (MOCVD) and Molecular Beam Epitaxy (MBE) reactors processes. The chemical reactions kinetics in gas phase and surface phase play dominating role in deciding the growth mechanisms. The innovative in-house developed numerical technique in form of **TNL-EpiGrow simulator**, exploiting atomic scale kinetic Monte Carlo algorithms for simulation of thin films deposition with interfacing to choose chemical reactions provides flexibilities to replicate the MOCVD, MBE and CVD reactors based epitaxial growth processes with appropriate reactor's input conditions. The simulator retains atomic scale information while enabling simulation of process relevant features such as roughness, growth rate, strain, creation of various types of defects, surface morphology evolution etc.

The substrate temperature, chamber pressure and temperature, precursors, gas phase and surface phase chemical kinetics and flow rate are employed as control variables. The various energies e.g. Schwoebel barrier, incorporation barrier, nearest neighbor barrier and desorption barrier, are also play significant role in deciding the adsorption, hopping and desorption events rates probabilities. The control robust algorithms of **TNL-EpiGrow** simulator is investigated using a reliability analysis & calibration against various experimental studies for various elemental and compound semiconductors epitaxial growths under a wide range of conditions and applications.



1.1 Thin Film Deposition through Epitaxy

The term epitaxy was used first time in 1928 by Royer [1]. The word epitaxy has Greek root; " $\varepsilon \pi \iota$ " or epi that means "ordered on" and " $\tau \alpha \delta \iota \sigma$ " or taxis which means "in ordered manner". It is defined by growth of the monocrystalline layer on a monocrystalline substrate in a particular crystallographic orientation. There are two different epitaxy; homoepitaxy and heteroepitaxy. The homoepitaxy is the depositing a film on a substrate with the same material for example Si on Si (100). Its application is depositing very pure material on substrate or depositing with different doping levels. The heteroepitaxy is defined by depositing a film on a substrate with different material for example SiGe on Si (100). Both homoepitaxy and heteroepitaxy have a lot of tremendous applications in CMOS, HEMT and HBT industries [1-7].

Thin film deposition through epitaxy based on various reactor's geometry is widely used to deposit a monocrystalline layer of material onto the surface of a substrate. The Molecular Beam Epitaxy (MBE), Chemical Vapor Deposition (CVD), Metalorganic Chemical Vapor Deposition (MOCVD) and Metalorganic Vapor-Phase Epitaxy (MOVPE) are common variants of epitaxial deposition processes used extensively in the semiconductor and coatings industries [3-7].

CVD and its variant processes refer to a process in which gaseous reactive precursors are used to deposit a monocrystalline layer on a monocrystalline substrate. A gaseous mixture containing atoms flows continuously through a controlled reactor environment, lot of chemical reactions and intermediate reactants form under gas phase mechanisms through chemical kinetics. When these gaseous reactants strike on the substrate surface, the surface chemical kinetics takes place in form of surface phase chemical reactions. The adsorption process initiated. The temperatures, at which these processes occur, as well as the concentration of the inlet vapor, are extremely important factors in determining the way in which atoms are adsorbed onto the substrate surface [8 - 11].

MBE process refers to a process chamber in which a thin single crystal layer is deposited on a single crystal substrate using atomic or molecular beams generated in Knudsen cells contained in an ultra-high vacuum chamber without any collision [12 -13].



Metalorganic chemical vapor deposition (MOCVD) is also known as metalorganic vaporphase epitaxy (MOVPE) and organometallic vapor-phase epitaxy (OMVPE). It is a chemical vapor deposition (CVD) method used to produce single- or polycrystalline thin films. It is used for growing crystalline layers to grow complex semiconductor multilayer structures. The growth of crystals is govern by chemical reaction and not physical deposition as compare to in molecular-beam epitaxy (MBE) process. The chemical reactions, thermodynamics and chemical kinetics are similar as in the CVD based deposition processes [14 - 18].

Many different reactor geometries exist for these types of epitaxial growth processes. The monocrystalline epitaxial growth through **TNL-EpiGrow simulator** consists of three deposition reactors inbuilt. It has capabilities to focus on any specific reactor or deposition process by choosing appropriate reactor at the time of initialization of simulation by providing reactor's specific parameters to fit the user's needs.



1.2 Products of Epitaxial Deposition Processes

Epitaxial deposition processes are commonly employed for micro- and nanoelectronic manufacturing. It is used to produce advanced semiconductor epiwafers for possible applications in Micro-Electro-Mechanical Systems (MEMS), solar cells, CMOS, HEMT, power devices, HBTs, integrated circuits (ICs) Industry etc. The electrical and mechanical properties of these products are highly dependent on crystalline quality of epiwafers in terms of surface uniformity, composition, types of defects and microstructure. Due to the need for defect less, smooth and uniform surfaces, measuring and controlling surface roughness is necessary for quality production of these items.

The modeling of the vapor phase and its variants deposition of thin films involves a large number of competing chemical reactions occurring on vastly different time scales, whereas, the modeling of molecular beam epitaxy deposition process is based on effusion mechanism in which individual molecules flow without any collisions and also includes adsorption, hopping and desorption events probabilities. The kinetic Monte Carlo kMC with chemical kinetics and surface phenomena is an ideal solution methodology for describing the atomic / molecular-scale surface evolution during vapor phase and effusion mechanism based epitaxy.

Four of the most challenging problems in modeling deposition of thin films at atomistic scale through CVD, MOCVD, MBE reactors are the accurate prediction of strain, roughness, defects etc. and optimum conditions for epitaxial growth successfully. The predictive rate of growth of the film, distinction between the type of defects with location on the lattice, mapping strain in each monocrystalline layer and capturing the morphology of the surface as a function of reactor conditions i.e. pressure, temperature, flow rates etc are the challenging issues with growth industry and can be modeled through TNL-EpiGrow simulator.



1.2.1 Growth Rate

Growth rate is dependent on temperature. At high temperature, it is limited by mass transport. In this case, most of the surface sites are free and the deposition is limited by adsorption. However, at low temperature regime the growth is limited by desorption events which is strongly dependent on temperature. In general, different parameters affect the growth rate: temperature, flow rate, geometry, deposition pressure, gas source, and contents. The Fig. 1.1 depicts the simplified vapor phase epitaxy [18].



Fig. 1.1 reference [18]



1.2.2 Defects

Any irregularity in the pattern of crystal arrangement in monocrystalline layer form during epitaxial growth is called imperfection in thin film. The occurrence of defects takes place when the process of formation of crystals happens. It may occur at a very fast or at an intermediate rate. It happens because atoms/molecules do not get enough time to make bonding with the beneath atoms/molecule of the monocrystalline layer in a regular pattern. Defects can be of several types as described by Fig. 1.2 taken from reference [19].

- a) Vacancies in the lattice
- b) Dislocation of a atoms in the lattice
- c) Nonstoichiometric proportions of the ions
- d) Interstitials i.e. atoms sitting at undesired location in the lattice
- e) Impurities in the lattice



Fig. 1.2 reference [19]



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1.2.3 Strain

Strain in heteroepitaxy can be obtained through structuration at a nanometer scale. Heteroepitaxy involve multi-component systems where lattice mismatch leads to elastic strain. The elastic strain stored in the lattice during epitaxial growth can induce various phenomena which have to be evaluated, understood and predicted. The many questions regarding strain creation are still unanswered and not well understood by experimentalists.



Fig. 1.3 showing compressible and tensile strain due to lattice mismatch



1.2.4 Surface Roughness Measurement Techniques

A number of experimental methods currently exist to measure the surface roughness of a thin film, including Atomic Force Microscopy (AFM) and Ellipsometry. AFM is implemented by bringing a microscope cantilever with a sharp tip into close proximity of the surface in order to detect forces such as Van der Waals forces. The topology of the surface, and therefore the surface roughness, can be measured by this method due to the principle that the measured forces change as the distance between the tip and the surface change. The tip scans the surface while maintaining a constant force measurement by preserving a constant distance from the surface, and the amount the tip must move to maintain constant force and distance is used to determine surface morphology and roughness. Ellipsometry is used to measure surface morphology by detecting the change in polarization of light as it is reflected off of a surface and relating it to height of the substrate. While these methods of real-time roughness measurement exist, it is difficult to implement these techniques into a feedback control system.

The time necessary for these measurement techniques is too great to compete with the rates of molecular movement and growth on the surface. This conflict has led to interest in a control system based on accurate modeling of the dynamics of thin film growth.



1.3 Chemical Kinetics

In the vapor phase and its variants deposition processes, the probabilities of a possible thermodynamic chemical reaction either in gas phase or surface phase depends on a criterion which is necessary but not sufficient to obtain the adsorption, it must also be established whether the process is kinetically favorable or not. Indeed, there are many thermodynamically favorable reactions that are, however, kinetically unfavorable because of their very low adsorption rates. Therefore, the study of the chemical kinetics is particularly important for both understanding of a vapor phase deposition process and optimization of its controlling parameters in order to obtain layers having properties required in various practical applications. Various general aspects of the chemical kinetics in gas phase and surface phase mechanisms of vapor phase systems have previously been surveyed in details [8 -11], [14 - 18].



1.4 The kinetic Monte Carlo Method

In a generic epitaxial deposition process, thin film properties such as defects and strain creation, evolution of surface roughness and growth rate are highly dependent on macroscopic system inputs such as substrate temperature and inlet gas concentration and flux rate. The macroscopic scale determines how these input process parameters will affect the overall growth dynamics of a system. This is often modeled using Partial Differential Equations (PDEs) to describe the relevant momentum, energy and mass balances. However, in order to obtain precise control of film properties, the microstructure of the surface must also be considered; these properties are functions of much smaller length scales, typically on the order of several atoms. This dramatic decrease in length scale renders the use of continuum type PDEs invalid, and a microscopic technique must be used to model the growth and development of the surface nano- and microstructures.

The kinetic Monte Carlo (kMC) method is ideal technique for the modeling of epitaxial deposition processes at the atomic scale, and in general it can be coupled to the macroscopic reactor-scale continuum description. The kMC method is an efficient stochastic technique for numerically solving the underlying "master equation" system, which describes the rates of all atomic scale events in the system as a function of time. The kMC simulations are used to predict average properties of the thin film, and at increasing lattice sizes, give a numerical solution to the master equation [20-23].

Two balance criteria must be satisfied by the kMC method:

(1) The ability to calculate the lifetime of each event, and

(2) The guarantee of the stochastic nature of the system by using a random number generator to make certain each event is independent.

The stochastic nature of the kMC method is incredibly important in modeling a real system, as the exact movement on the atomic scale is probabilistic. However, despite the random stochastic nature, the model must still be able to accurately predict the thin film growth on a small scale, which is proven by the convergence of the kMC method to the master equation at increasing lattice sizes.



1.5 Validation for Use of Kinetic Monte Carlo Method

The capability of TNL-EpiGrow simulator is to successfully simulate complicated chemical processes on multiple length and time scales is limited strongly by the available computing hardware power. There are many simulation methods currently in use, each having applicability to different areas of interest. The most rigorous method of simulation is ab-initio method, which makes minimal assumptions and calculates movement based on first principles (i.e. including quantum mechanical forces between individual atoms). Due to the computational demands of this method, only atomic scale simulations in the femto second (fs) time range can be carried out in most cases. Molecular dynamics (MD) simulations, based on classical force fields, are computationally cheaper but are still limited to the nano second (ns) time scale, and are far too slow for use in real-time applications such as model predictive process control. The application of various methods proposed for epitaxy based deposition process can be understood form below figure.



Fig 1.4: Modeling with various techniques.

The kMC method, on the other hand, retains the overall atomic picture, but removes the need to consider atomic vibrations, greatly increasing the simulation scope. Furthermore, it requires the specification of every possible atomistic event allowable in the simulation. These events must be specified in advance as any omission of important events can lead to severe model error. The precision of the rates imputed to the kMC model determine the validity of the simulation.



1.6 Need of TNL-EpiGrow simulator

The fabrication of modern semiconductor's devices technology could became possible due to availability of deposition techniques for monocrystalline layer on mono-crystalline substrates which relies over a large extent on the controlled growth. In recent years, the importance of semiconductor and optoelectronic devices fabricated in strained-layer epitaxy has increased continuously [24]-[25]. As a consequence, homo- and hetero-epitaxial growth has been a matter of significant interest in both experimental and theoretical studies [24]-[26]. This is mainly due to the improved performance of semiconductor and optoelectronic devices which can be achieved using strained layer epitaxy. Strained hetero-epitaxial crystal growth attracts significant interest as a promising technique for the production of, for instance, high crystalline quality semiconductor films. A particularly attractive aspect is the possibility to exploit self-organizing phenomena for the fabrication of nano-structured surfaces by means of molecular-beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD) or similar techniques [26]-[28]. By means of epitaxial methods it is, for example, possible to achieve very sharp interfaces between layers of different material species in compound semiconductors. In this context epitaxial growth techniques such as MBE and its variants play an important role as they allow for a very precise control over growth conditions. In many cases, adsorbate and substrate materials crystallize in the same lattice but with different bulk lattice constants and thermal conductivities. Frequently, the adsorbate grows layer by layer, initially, with the lateral spacing of atoms adapted to the substrate. The misfit induces compressive or tensile strain in these films and, eventually, misfit dislocations will appear [27], [29] - [32]. These relax the strain and the adsorbate grows with its natural lattice constant far from the substrate, eventually. Dislocations will clearly dominate strain relaxation in sufficiently thick films and for large misfits. In particular, the strain-induced formation of self-assembled three-dimensional (3d) islands offers a promising route to the fabrication of quantum dots [33]. Despite the successful application of epitaxy in the fabrication of numerous material systems, there are still many open issues and challenges concerning, for instance, the influence of atomistic processes at the crystal surface on the macroscopic growth behavior. In recent years, a set of complimentary methods have matured that are very useful for understanding processes on the atomic scale. The size of semiconductor devices shrinking toward the size of individual atoms, and increasingly complex material



systems are being exploited for the development of new growth processes, which are much sophisticated and having technological challenges.

The numerical computational techniques provide a particularly important solution for the theoretical understanding of the involved microscopic mechanisms. For the simulations point of view, for length scales around micron and time scales are on the order of seconds, even with great advances in accelerated molecular dynamics (MD) methods it is evident that MD simulations on these scales are impossible for the foreseeable future [34]-[36]. Closely related to MD and, in principle, nearly as faithful to the underlying physics, are off-lattice kMC methods.

In a sense, these are the ultimate accelerated MD methods, but they are still too slow for simulations on the desired length and time scales as depicted in Figure 1.4. In case of MD simulations, the forces acting on each atom are computed, using a molecular mechanics force field. Integration of the equation yields a trajectory that describes the positions, velocities and acceleration of each atom as they are varied with time. Once the positions and velocities of each atom are known, the state of the system can be predicted at any time. But as mentioned earlier that it is very difficult to run the MD simulations for large dimension crystal structures.

In contrast, simulation of the growth and evolution of pure crystals (e.g., homo- & heteroepitaxy) at the nanoscale is dominated by lattice based kMC. Many of the important technological applications involve multi-component systems where lattice mismatch leads to elastic strain. Incorporating elastic effects into kMC simulations in a way that retains the simplicity and speed of the basic method has emerged as a central challenge. The algorithm inbuilt in **TNL-EpiGrow simulator** is capable to addressing these above challenges successfully.

On the other hand in *On-lattice* kinetic Monte Carlo approach, the states are assumed in the form of a perfect lattice most often simple cubic, face centered cubic (fcc) and other lattices. In On-lattice model, the allowed transitions are restricted to a limited catalog of characteristic events, and the transition rates are parameterized which are based on the local lattice configuration. The model is capable to capture the physical effects of homo- or hetero-epitaxial growth, such as surface diffusion and nucleation. This method is faster than off-lattice kMC method, but the on-lattice method is based on assumption and could not replicate the real growth environment as



they cannot capture some important physical effects such as surface reconstructions and dislocations [24-48].

The *off-lattice* kMC model inbuilt in **TNL-EpiGrow simulator** for crystal growth is based on observations of MD simulations. Previously reported simulations are based on transition state theory (TST). The main issues associated with the model are as follows:

- The system spends most of its time randomly oscillating within the N-particles and N-dimensional configuration space about a local minimizer x_mof the system potential energy U(x), with rare transitions between these basins of attraction.
- 2. The energy barrier in terms of $\Delta U = U(x_s) U(x_m)$, requires searching of both the initial local minima (x_m) and the saddle point (x_s) separating the basins of attraction. These local minima and saddle points are, in principle, determined by the motion of all of the particles simultaneously within the configuration space.

The off-lattice method implemented in **TNL-EpiGrow simulator** provides an opportunity to replicate and calibrate reactors based epitaxial growth of various semiconductor materials used for various applications.



1.7 Innovation

The inhouse developed inbuilt algorithms of **TNL-EpiGrow** simulator for monocrystalline layer growth based on specific deposition reactors are unmatched solution including chemical kinetics, thermodynamics and atomistic scale atomic/molecular adsorption, diffusion, desorption events. The innovation of **TNL-EpiGrow** simulator includes growth model in which the position of atoms are not fixed like in *on-lattice* model and it does not spend too much time for locating local minima and saddle points to make bond as in *off-lattice* model. The model used in **TNL-EpiGrow** simulator is simply based on hybridization approach which itself find the bonding position following the natural phenomenon of the growth process in the real reactor environment. The surface grows like an actual sample with atoms taking position according to their bond angles and distances. The model is capable to capture the important physical effects such as strain, dislocations, defects and roughness etc at atomistic scale. The flow chart of TNL-EpiGrow simulator flow chart can be found in reference [49]



1.8 Features

- User Friendly with Graphical User Interface (GUI) capabilities on Windows platform
- Modeling of Epi-growth process based on MOCVD/MBE/MOVPE Reactors
- Extremely accurate prediction of epitaxial growth
- No Statistical / thermodynamically assumptions
- Gas phase and Surface phase chemical kinetics
- Based on Adsorption, Diffusion, Desorption rates calculated on the basis of impinging atom and substrate energies
- Growth process, involves four stages: Impact, Physisorption, Chemisorptions, Incorporation
- Sticking coefficient dictate the flux of atoms on the substrate
- Several possible surface morphologies can occur during a given deposition, based upon the growth parameters
- Includes three distinct growth regimes for thin film growth
 - > Frank-van der Merwe (FM)
 - > Volmer-Weber (VW)
 - > Stranski-Krastanov (SK) growth processes.
- Surface diffusion depends on step-edge barriers from both descending steps (Schwoebel barrier) and ascending steps (incorporation barrier)



1.9 Benefits can be realized

- User's Reactor based growth conditions can be inputted
- MBE / CVD / MOCVD reactors inbuilt with various material database
- Predictive Growth rates with Molefractions
- Defects Extraction (point defects, vacancies, edge dislocations, stacking faults etc)
- Extraction of Strain within each monolayer
- Surface & interface profiling (Extracting Roughness)
- Fewer experiments for optimization
- Reduction in waste during experimentation
- Ability to deal with different reactive species and reactor geometries
- Explore information at Atomistic Scale
- On-line growth process control
- Cost effective solution for Thin / Thick film growth technology



Chapter 2 Start using TNL-EPIGROW Simulator

	- L X
File Commands Material database Plot Help	
Welcome to Innovative A	Atomistic based TNL Simulator!!!
TNL Framework accomodates innovative atomistic solution from epi-growth	(MOCVD, MBE, VPE etc)to particle device simulation based on Monte Carlo Technique.
Epi- Growth Simulator	
Full Energy Band Simulator	
Electron Mobility Simulator	
Spectroscopy	
Particle Device Simulator (2D Poisson Solver)	Fit



2.1 Summary

Growth of monocrystalline layer of semiconductors on various monocrystalline substrates is a sophisticated, expensive and time consuming process. Especially for the growth of costly and rare materials, too much hit and trials can't be tolerated. TNL-EpiGrow simulator provides an efficient and cost effective solution with capabilities to handle most of the issues and challenges associated with the various reactors geometries based epitaxial growth at atomistic scale through modeling. The TNL-EpiGrow simulator simulates the process of thin film growth in the best possible manner. The real reactor (MBE and CVD, MOCVD reactors) geometries and conditions can be easily inputted in the TNL-EpiGrow simulator through GUI enabled features. The other information such as partial pressure (CVD, MOVCD reactors) or vapor pressures (MBE reactor) of elements or semiconductor materials to be grown, flow rates, reactor chamber temperature, substrate temperature and other relevant informations require for thin film growth are used as input parameters in TNL-EpiGrow simulator. By default simulator has various semiconductor materials physical properties and other relevant properties stored in its database for various. Users have flexibilities to define own input values to overwrite the default values based on their reactor input conditions. The TNL-EpiGrow simulator adopts a well-developed and calibrated kinetic Monte Carlo (kMC) technique with appropriate chemical kinetics for the growth of thin films. The ultimate goal of simulation at atomistic scale is an accurate extraction of the values of physical parameters which cannot be extracted easily with sophisticated instruments in reality and to understand the atoms / molecules behavior inside reactor during growth mechanism under real reactor conditions, such as evolution of strain, deformation, various types of defects, surface morphology in terms of surface and interface roughness of the films etc.

New materials and reactor geometries can be added in TNL-EpiGrow simulator for each generation of devices to match new accuracy demands for future epitaxial monocrystalline growth based deposition technologies.

This chapter will describe how TNL-EpiGrow simulator can be used effectively. Being as a GUI enabled feature based simulator, it is easy to learn the working of TNL-EpiGrow simulator.



2.1.1 The Graphical User Interface

The graphical user interface (GUI) capabilities on windows operating system platform of TNL-EpiGrow simulator extend a convenient and comfortable approach for users to replicate the real time epitaxial growth experiments of thin films through using real time input conditions of depositions reactors (MBE and CVD & MOCVD) by running the simulations and extracting outputs at atomistic scale. The run output window allows users to check the initial data provided by them and analyzing the results as output data stored in the work folder. The atomistic nature of TNL-EpiGrow simulator makes it capable to extract various kinematics and dynamic properties associated with single atom/molecule inside reactor whose realization is not possible through any sophisticated instruments.



2.1.2 Start Using Epi-Growth Simulator

The GUI feature fully integrates TNL-EpiGrow simulator in TNL Framework and takes advantage of the framework environment to interface with other family of TNL simulators. To run the TNL-EpiGrow simulator, users will require genuine license from Tech Next Lab Inc. After getting the official license for the TNL-EpiGrow simulator, users may verify it by opening the TNL-Framework. At framework user will see a tick mark on the side of the name 'Epi-Growth Simulator' in green color which confirms the license for same as represented in Fig. 2.1. in case, if a cross mark in red color is shown under TNL Framework, it simply meaning that user are not using valid license (in this case user needs to contact Tech Next Lab Inc.). For more information user needs to go through the License Manual.



Figure 2.1



There are two ways to open the TNL-EpiGrow simulator from the *TNL Framework* as shown in Fig. 2.1. Those ways are shown in red rectangular boxes (box1 and box2).

- This box1 contains icon and name. By a single click on icon or name user gets access to use the simulator
- This box2 contains sub menu named as 'Epi-Growth Simulator'. By clicking on the menu command, user will get several sub-menus containing the names for other simulators of TNL family. By a single click on name user gets access to use the simulator.

🖳 Epi-Grow				- 0 X
File Edit Simulate Hel	lp			
Reactor	CVD V		CVD Precursor Source	***** Epigrowth Input Conditions *****
Steps Time (Step 1) Time for Roughness Upper layer atoms Substrate Dimension Orientation	1 1 1 1 5licon •	Barrier Energies (eV) Schwoebel 0.05 Incorporation 0.05 Desorption 3.0 No. of Interactive Elements 1 + Atomic Number 14 Neighbouring Energy (eV) 0.05	Chamber Condition Temperature (C) 622 Pressure 0.4 Cross Sectional Diameter (cm) 12.0 Length (cm) 100 Substrate to Edge distance (cm) 1 Precursor Condition 1	
Surface Energy (ev) Temperature (C)	 111 110 2.0 800 Add Step 	(Reset	Number of Precursor 2 Gas Source Solid Source G Source 1 SH4 Flow Rate 20 Sc Weight (mg) Load Source	
Output				
				Run Exit
A product by Tec	h Next	: Lab Pvt Ltd.🗷		© Copyright Tech Next Lab. All Rights Reserved



2.1.3 Display Window

TNL-EpiGrow simulator frame will be open as shown in Fig. 2.2. This frame contains four major sub windows for various information to be inputted in the simulator:

- 1. *Sub-window 1:* it contains all the information regarding various barrier energies, time, substrate dimensions & orientations require initiating with TNL-EpiGrow simulator.
- 2. *Sub-window 2:* it contains the information about the various reactor's geometries and chamber conditions with selection of effusion source in case of MBE reactor or precursor sources in case of CVD or MOCVD reactor chosen.
- 3. *Sub-window 3:* it provides the information chosen in step 1 & 2 for all input condition selected.
- 4. *Sub-window 4*: It provides run time information of a simulation.

File Edit Simulate He	lp				
Reactor	CVD 🔻		Effusor Source Gas Source Prec	cursor source	***** Epigrowah Input Conditions *****
Steps Time (Step 1) Time for Roughness Upper layer atoms	1 ×	Barrier Energies (eV) Schwoebel 0.05 Incorporation 0.05 Desorption 3.0	Number of Precursor Precursor 1 Flow Rate Temperature (C)	0 Select Precursor V 1 atm cc/s V 1000	Reactor Constition :=> CVD Substrate, Silicon Orientation : 100 Substrate Domain : 10.0 X 10.0
Substrate Dimension Orientation Surface Energy (ev)	Silicon 10 ✓ 100 111 110 2.0	No. of Interactive Elements	Chamber Pressure Cross Sectional Area (cm2) Length (cm) Chamber Volume (ltrs) Ceiling Height Area Substrate to Edue dictance (cm)	140 torr 12.0 100.0 1 1 2	Number of Steps : 1.0 Step 1 Time (sec) : 5.0 Tem erature (C) : 800.0 Surface Energy (eV) : 2.0 Desc ption Barrier (eV) : 3.0 Schwoebel Barrier (eV) : 0.05 Incorporation Barrier (eV) : 0.05 Number of Interactive Elements for
* EPIGROW * FULL BAND * HALL MOBILITY * TH2 SPECTROSCOPY	800 Add Step	Reset		1	Nearest Neighbour Energy : 1
* MC PARTICLE DEVICE * STRVIEWEB * TNLPLC Simulation Starts 12/1/2021 12:12:33 Working directory => C:V Time (sec) - 1 on 12/11 Deposited Number of At Time (sec) : 3 on 12/11 Deposited Number of At Time (sec) : 3 on 12/11	Users'fanis'Docur 1/2021 12:42:44 e toms : 885 1/2021 10:26:33 e toms : 889 1/2021 13:37:46 e	* 4 ments\SHA622_3 lapsedTime = 29 min & 44 sec lapsedTime = 53 min & 54 sec lapsedTime = 1hr & 25min			Length of Charloger : 100.0 cm Distance between Substrate and Edge 1.0 Number of Precursor Cell : 3.0 Precursor Cell port : 2 Gas Name : H2 Flow Rate : 158.0 sccm Chamber Temperature : 622.0 Chamber Temperature : 622.0 Chamber Pressure 1.5 torr Cross Sectional Area : 12.0 cm ²

Figure 2.2a



2.1.3.1 Sub-window 1

Sub-window 1 as shown in Fig.2.2, the sub-frame of TNL-EpiGrow simulator frame where real reactors (Molecular Beam Epitaxy (MBE), Metal Organic Chemical Vapor Deposition (MOCVD) and Chemical Vapor Deposition (CVD) are inbuilt need to be chosen first. The substrate's dimensions & orientation with growth temperature and various energies require for deposition need to be given to initiate the simulation. Users have flexibility to choose any of the inbuilt reactors at a time from the Reactor list i.e. MBE/CVD/MOCVD. Based on type of reactor chosen users need to select their respective Precursors or Effusion tab (as shown in *Sub-window 2* of figure 2.2). MBE rector contains the Effusion sources and associated condition. However, precursor and precursor condition are reuired for CVD and MOCVD reactors respectively. These reactor source information is discussed later in section 2.1.3.2.

Reactor	CVD 💌		
Steps Time (Step 1) Time for Roughness	1 ×	Barrier Energies (eV) Schwoebel Incorporation Desorption	0.05 0.05 3.0
Substrate Dimension Orientation	Silicon	No. of Interactive Eleme Atomic Number Neighbouring Energy (e	ents 1 + 2V) 14 0.05 Add
Surface Energy (ev) Temperature (C)	2.0 800	Reset	

Figure 2.3

- → In Fig.2.3, the *Steps* provide growth steps input information i.e. users may choose 1 means growth in single step, 2 means growth is done in two steps e.g. first step growth for AlN material and second step for GaN material and so on.
- → *Time (Step)* textfield gives information regarding the time duration (in seconds) for growth of every step. Users need to provide time for each chosen.
- → *Time for Roughness* textfield provides information regarding the time steps for the measurement of the roughness parameters of the growth. Surface roughness is the



measure of the finely spaced micro-irregularities on the surface texture which is composed of three components, namely roughness, waviness, and form.

→ Upper layer atoms gives information of the atom which is on the top of the substrate before start of the deposition for e.g. if GaAs substrate is selected if 1 is given here then Ga atom will be on top and exposed for the bonding else if 2 is given then it gives information about the As atom for same.

2.1.3.1.1 Substrate





- → Users may fill the *Substrate* information in window as shown in Fig.2.4. *Substrate* Select drop-box contains various substrate materials inbuilt in the TNL-EpiGrow simulator. The list of inbuilt substrate with their most stable symmetries as follows:
 - Silicon
 - Gallium Arsenide (GaAs)
 - Indium Phosphide (InP)
 - Gallium Nitride (GaN)
 - Silicon Carbide (SiC-β-3C)
 - $Cd_{0.95}Zn_{0.05}Te$
 - $Cd_{0.7}Zn_{0.3}Te$
 - $Cd_{0.5}Zn_{0.5}Te$

→ Dimension field gives the information of size of the substrate surface chosen in one dimension in A⁰ unit.



- → The three options for the substrate Orientation i.e. [100], [111] and [110] are inbuilt in the TNL-EpiGrow simulator. At a time user may choose any orientation by checking any one of three check-boxes to invoke substrate orientation. This information refers to the orientation of the crystal lattice with respect to a coordinate system fixed in the substrate sample. The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the Miller Indices (hkl), which are a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface. Thus, any crystallographic plane corresponding to a face of the unit cell is generically called a "[100]" plane. Likewise, any crystallographic plane that "cuts" a unit cell face diagonally and is also parallel to an edge of the unit cell is called a "[110]" plane. Similarly, any crystallographic plane that intersects three non-adjacent vertices of the unit cell is called a "[111]" plane. The details of generic planes are illustrated in figure 2.5.
- → In practice, physical crystals are generally designated by the orientation of their surfaces. In the case of semiconductor crystals, e.g. silicon substrates, this is the crystallographic plane parallel to the surface used for device fabrication. Thus, a silicon crystal, i.e., a substrate, which has a surface parallel to the unit cell face, is designated [100]. Similarly, if the surface can be thought of as intersecting three opposite corners of the unit cell, then the crystal is designated [111]. These two orientations are essentially the only ones ever used for device fabrication with [100] being much, much more common since it is used exclusively for fabrication of CMOS devices. The [111] orientation materials are extensively used for fabrication of bipolar devices for which very shallow doping is desirable. In principle, [110] orientation substrates is manufactured.
- → Surface energy is a term used to describe the substrate surface details; surface energies range from high to low. The molecular force of attraction between unlike materials determines their adhesion. The strength of attraction depends on the surface energy of the substrate. High surface energy means a strong molecular attraction, while low surface energy means weaker attractive forces.





Figure 2.5

 \rightarrow Substrate Temperature (°C) is the value which determines the degree or intensity of heat present at the surface of the substrate. The substrate temperature is the most important parameter during epitaxial growth because it influences all processes on the substrate surface, the surface morphology, the crystalline growth, the abruptness of doping transitions or the relaxation processes in hetero-structure systems etc.



2.1.3.1.2 Energies

Schwoebel	0.05
Incorporation	0.05
Desorption	3.0
No. of Interactive E	lements 1
No. of Interactive E 	iements 1
No. of Interactive E Atomic Number Neighbouring Energ	iements 1 gy (eV) 14 0.05



→ Schwoebel Barrier: The Schwoebel–Ehrlich barrier refers to energy barrier in the case when an adatom diffuses down an island of one monolayer. During thin film deposition in TNL-EpiGrow simulator, an adatom often needs to diffuse down an island of multiple layers. This energy diffusion barrier is known as Schwoebel–Ehrlich barrier. The effects of an atomic step on the diffusion of atoms on the surface can be understood by the diagram below. ΔE_{ES} is the Schwoebel–Ehrlich barrier that the atom on the surface (a dark brown circle) has to bridge in addition to the E_{diff} diffuse barrier on the terrace in order to cross the edge of stage and descend to the lower terrace.



Figure 2.7

→ Incorporation Barrier: The crystal growth in TNL-EpiGrow simulator, growth steps play a central role because they provide the kink sites at which new atomic units are incorporated into the crystal. The kink site is a 'repeatable step' in the formation of the crystal. Fig. 2.8 shows the sketch of a step on a crystal surface of four fold symmetry. The upper terrace is shaded. The step consists of straight (close packed) segments separated by kinks and



corners. Adatoms diffuse on the terraces and can be incorporated into the crystal by attaching at kinks sites. An atom moving along a straight segment of the step is called a step atom. The energy required to incorporate the adatom is referred as *Incorporation barrier*.





- → Desorption Barrier: The process in which adsorbate species gain enough energy from the thermal vibrations of surface atoms to escape from the adsorption well and leave the surface is called thermal desorption. In order to leave the surface, the adsorbate species has to surmount the activation barrier for desorption, called the desorption energy.
- → Nearest Neighboring Energy: Thin films are stable structures due to strong attractive interatomic force and interactions among atoms which hold them together. This also implies that the energy of the crystal is lower than the energy of the free atoms. The amount of energy required to pull the crystal apart into a set of free atoms is known as the cohesive energy of the crystal.

Cohesive energy = energy of free atoms – crystal energy

Magnitude of the cohesive energy of different solids varies from 1 to 10 eV/atom. However, in the case of inert gases the cohesive energy is of the order of 0.1eV/atom. A typical potential energy (binding energy) curve representing the interaction between the two atoms is shown in Fig. 2.9.

It has a minimum at some distance $R = R_0$. For $R > R_0$ the potential energy increases gradually, approaching 0 as $R \rightarrow \infty$, while for $R < R_0$ the potential energy increases very rapidly, tending to infinity at R = 0. Since the system tends to have the lowest possible energy, it is most stable at $R = R_0$, which is known as the equilibrium interatomic distance.


The corresponding energy U_0 at $R = R_0$ is known as the cohesive energy and is termed as *Nearest Neighboring Energy* in the TNL-EpiGrow simulator. Its unit is in eV/atom.



Figure 2.9



2.1.3.1.3 ADD/REESET Step

Temperature (C)	800	
	Add Step	Reset



- \rightarrow The two buttons as shown in Fig.2.10,
- → Add button function are used to add and write the reactor and process details filled by users as described in previous sections for initiating the epitaxial growth experiment through TNL-EpiGrow simulator. Add button needs to be clicked for each number of steps assigned to simulator selected at *Steps* selector option.
- \rightarrow *Reset* button is used to reset simulator to its initial or default stage.
- → In case if any data found to be filled by users are wrongly *Added* in the TNL-EpiGrow simulator, clicking *Reset* button can be used to do the job of removal of wrongly filled data by removing all the information of that step.



2.1.3.2 Reactor Conditions

2.1.3.2.1 MBE Reactor:

Molecular Beam Epitaxy (MBE) processes inbuilt in TNL-EpiGrow simulator include the essence of a vacuum evaporation technique with ultra high vacuum (UHV). In TNL-EpiGrow simulator, MBE processes used to generate molecular beams from the thermal Knudsen sources. These molecular beams interact on a heated monocrystalline substrate and chemical reactions take place at surface of substrate to deposit a monocrystalline layer. Each source contains one of the constituent elements or compounds required in the thin film growth and it may be part of the matrix or one of the dopants. The temperature of each source is chosen so that films of the desired composition may be obtained. The sources are arranged around the heated crystalline substrate in such a way as to ensure optimum film uniformity both in composition and thickness are obtained.

The MBE reactor option provides a virtual growth condition of the MBE process as discussed above.

Reactor	MBE	1			2		
Steps Time (Step 1) Time for Roughness Upper layer atoms	1 1 1 1	Barrier Energies (eV) Schwoebel Incorporation Desorption	0.05 0.05 3.0	Number of Effusior Cell Ports Effusior Cell Port Element	i of ii Sel iii Cati	ect Element	Elemental
Substrate Dimension Orientation	Silicon	No. of Interactive Element Atomic Number Neighbouring Energy (eV)	ts 1 + 14 0.05 Add	Cell's Orifice Area Distance from Substrate Crucible Temperature Sticking Coefficient of Element	iv 5 v 15 vi 300 vii 1.0		
Surface Energy (ev) Temperature (C)	2.0 800					3	oad Source

Figure 2.11

When the MBE reactor is selected under *Reactor* option tab (as mark in red box with 1 in Fig. 2.11) the simulator is ready with virtual MBE growth reactor. It requires effusion sources parameters to process and MBE reactor geometries for further proceedings. Information under



the *MBE Effusion Source* tab (as shown in red box 2 in figure 2.11) is the important one for MBE growth process. Here the information according to the monocrystalline layer to be grown requires the number of the effusions cells and elements in each cell's at their evaporization temperature details. After that, effusion elements need to be differentiated from the available inbuilt options in form of cation, anion or elemental (e.g. if Ga and As are chosen for the growth in MBE process of GaAs crystal then Ga act as a cation and As as anion, however, in the case of Si crystal MBE growth, Si need to chose as an element).

Contents and details of red marked box 2 of Fig 2.11, are as follows:

- i. Clicking on top or bottom arrow button in front of the *Number of Effusion Cells Port* option, users may define number of effusion cells as per their own requirements.
- ii. Under *Select Element* tab button, it will open a new pop-up window of periodic table (Fig. 2.8), all the physical information associated with the each element given in periodic table are inbuilt in TNL-EpiGrow simulator. Clicking on any symbol, it will select that particular element and its physical properties. Name of that element is appearing in the field besides that button.



Figure 2.12

iii. Three checkboxes named *Cation*, *Anion* and *Elemental* are showing the behavior of that element in the making of bond with each other. Selection of one of the check-box for each element is mandatory.



- iv. Value of *Cell's Orifice Area* of each effusion cell's is define the area of the opening from where the beam originate. Effusion process takes place from an orifice when the orifice area is smaller than the mean free path of the particles in motion, whereas diffusion occurs through an opening in which multiple particles can flow through simultaneously. Effectively, this means that only one particle passes through at a time. Therefore, *Orifice Area* should be specified initially in the simulator. Its unit is in square centimeter (cm²).
- v. Value of the *distance* between substrate and effusion cell is an important parameter to be given by users as per their real reactor property. Its unit is taken in centimeter (cm).
- vi. *Crucible Temperature* of the source in cell is an important parameter which determines the vapor pressure and thus the flux or concentration of molecular beam in the TNL-EpiGrow simulator. Extra care needs to be taken by users while filling this information as concentration or flux of molecular beam is dependence on temperature by the equation;

$$J = 1.12 * 10^{22} (ap/l^2 M T^{\frac{1}{2}})$$
(2.1)

where p is the pressure in the cell in Torr and M is the molecular weight of the source material, a is the cell orifice area and l is the distance between cell and substrate (l >> a). After a threshold temperature small change in temperature will produce large difference in vapour pressure and the flux. It's unit is centigrade.

vii. Users need to provide the value of the *Sticking Coefficient* for the every element in TNL-EpiGrow simulator. It simply shows the probability of the ratio of number of atoms striking on the substrate surface and number of atoms sticking to it. This number can be in range of 0 to 1, where 0 is the least probability and 1 is the maximum probability of 0 and 100% of sticking respectively.

After providing all the information required to run MBE process TNL-EpiGrow simulator, users need to click on *Load Source* tab button as shown with red box number 3 at the bottom right of Fig. 2.11. It will load all the data of that cell from the total number of effusion cells in simulator database. If n numbers of effusion cells are chosen, the n times above mentioned six data from ii to vii needs to be provided and similar number of time source data needs to be loaded by pressing this button. Each time the button will be pressed information pop-



up window showing "*Effusion Cell Data Loaded Successfully*". Click on OK button and the information get visible in the input script area shown in Fig. 2.13.



Figure 2.13



2.1.3.2.2 MOCVD Reactor

The **MOCVD** reactor based process inbuilt in TNL-EpiGrow simulator requires gases introduced in the chamber and taking part in the chemical reactions under the influence heat or light etc, are detailed in chemical kinetics section 3.3 in Chapter 3. Most of the gas phase and suface phase reactions for various semiconductor materials systems are inbuilt in the TNL-EpiGrow simulator. It follows the gas phase kinetics and surface limited kinetics and initiated the formation of mono or poly crystalline films on substrate surface which is kept under some thermal conditions. Every MOCVD process requires precursors to transport from the location where the gases are supplied inside reactor chamber and chemical reactions take place, the product reaches over the surface of substrate for deposition process. The difference in the path to choose for the transport mechanism of reactants decides the quality of the film depending on the mechanical and chemical properties. Based on the reactor's geometry, various types of MOCVD reactors can be categorized e.g. Showerhead MOCVD reactor and Injector MOCVD reactor etc. The current version of the TNL-EpiGrow simulator has inbuilt the two famous 'Showerhead' based and 'Injector based' MOCVD rectors. Fig. 2.14 shows the frame of MOCVD reactors options. The MOCVD reactor option provides reactor's conditions for virtual experiments of atomistic growth simulation.

Reactor	MOCVD	1		MOCVD Precursor source		
Steps Time (Step 1) Time for Roughness Upper layer atoms	1 1 1 1	Barrier Energies (eV) Schwoebel Incorporation Desorption	0.05 0.05 3.0	Chamber Condition Chamber Condition Showerhead Based Injector Based 3	2 ShowerHead/Injector Pa Shower hole's area Chamber Volume (ltrs.)	1.0
Substrate Dimension Orientation	Silicon	No. of Interactive Elemer Atomic Number Neighbouring Energy (eV	nts 1 -		Chamber Pressure Ceiling Height Chamber Temperature (C	140 (torr) 1.0 2) 1000
	111110		Add	Precurssor Condition		
Surface Energy (ev) Temperature (C)	2.0 800			Number of Port Precursor 1	0 🔹 Select Prec 💌	
	Add Step	Reset		Flow Rate	atm cc/s	Load Source

Figure 2.14



MOCVD reactor option can be selected from *Reactor option* (as shown in red box 1 in Fig. 2.14). The simulator is ready with virtual MOCVD reactor which needs reactor's chamber and precursor conditions need to be inputted to proceed further. Information under the *MOCVD Precursor Source* tab (as shown by red box 2 in Fig. 2.14) is very important for running an epitaxial growth experiments. Under *MOCVD Precursor Source* tab there are options for inputting the reactor chamber types and their geometrical as well as other relevant parameters with precursor's parameters are shown. TNL-EpiGrow simulator for MOCVD processes contains two type of reactor chamber options, which are inbuilt in the simulator and appear with their names with check box. At a time, users may select any one of the reactor chamber by just clicking on the checkbox. Selecting a checkbox, simulator will be ready to take input for respective chamber in the fields appears besides that.



2.1.3.2.2.1 Injector Based MOCVD Processes

MOCVD Precursor source	
Chamber Condition	с
Showerhead Based	Injector Parameters
✓ Injector Based	İ Chamber Volume (ltrs.)
	ii Chamber Pressure 140 torr
	iii Ceiling Height 1.0
	iv Chamber Temperature (C) 1000
Precurssor Condition	n
Number of Port	0
Precursor 1	Select Prec
Flow Rate	atm cc/s 💌 Load Source

Figure 2.15

To initiate injector based chamber processes, users need to provide real information as per their hardware reactor used for growth applications. The parameters for the injector based chamber are shown in red roman numbers in Fig. 2.15 and the details are as follows:

- i. *Chamber Volume* : This field is for inputting the value of actual volume of the reactor's chamber in liters.
- ii. *Chamber Pressure* : This field is for inputting the real total pressure of the reactor's chamber during whole time duration of the deposition. The chamber's total pressure remains constant during growth simulation experiments. Various units of the pressure are inbuilt for user's flexibility through the drop-box along with *Chamber Pressure* field. Users may input pressure in well known units i.e. *torr, mbar, atm* and *Pa*.
- *Ceiling Height*: This is for inputting the distance between the ceiling (the opening on top of chamber from where inlet of gases inject) and the substrate. Its unit is in centimeters (cm).
- iv. *Chamber Temperature* : Users may input the temperature of the chamber, which remains constant during whole growth process. It is in unit of Centigrade (°C).



2.1.3.2.2.2 Showerhead Based MOCVD Processes

The *Showerhead Reactor based MOCVD* processes inbuilt in TNL-EpiGrow simulator can be initiated by providing reactor specific parameters. The details of *Showerhead* reactor based chamber are shown with red mark numbers in roman in Fig. 2.16 are as follows.

Showerhead Based	ShowerHead Parameters						
Showerneau based	Shower hole's diameter	1.0					
Injector Based	Chamber Volume (ltrs.)	1.4					
	Chamber Pressure	140	torr 🔻				
	Ceiling Height	<mark>1.0</mark>					
	Chamber Temperature (C)	1000					
Precurssor Condition							

Figure 2.16

- Shower hole's Diameter : The Showerhead reactor is characterized by a showerhead flange and inlets very close to the substrate. The gases are injected vertically from these flanges with many small pores with diameters in order of millimeters towards the substrate. This field contains this value of diameter of each hole of showerhead. User may input the actual data for the same.
- ii. *Chamber Volume* : This field is for inputting the actual volume of reactor's chamber in liters.
- iii. Chamber Pressure : This field is for inputting the total pressure inside the chamber during growth processes. It remains constant during entire process of deposition. Various units of the pressure are inbuilt in TNL-EpiGrow simulator through the drop-box along with this field in torr, mbar, atm and Pa.
- iv. *Ceiling Height* : Users may input real distance between the showerhead (the opening on top of chamber from where inlet of gases inject) and to the substrate. Its unit is taken in centimeters (cm).
- v. *Chamber Temperature* : It is field for inputting the constant temperature inside the chamber during whole growth process. Its unit is in centigrade (°C).



2.1.3.2.2.3 Precursor Condition

Precurssor Condition							
Number of Port	i	0					
Precursor 1	ii	Select Prec					
Flow Rate	iii	atm cc/s Load Source					



In the either type of MOCVD reactor's chamber as described above, precursor gases are required to be filled in with their required flow rates. The precursor gases flow rates, temperature etc conditions determine and decide the chemical kinetics in terms of various reactions probabilities in gas phases and surface phases. The following steps are required to input the various precursor gases can be understood with the help of Fig. 2.17. The steps are as follows:

- i. Users need to select the total number of port from which total precursor gases are injected through transport mechanism in the reactor chamber by using top or bottom arrow under *Number of Port*.
- ii. The *Precursor* option drop-box tab contains name of various gases e.g. TMG, NH₃, H₂ etc. inbuilt in the TNL-EpiGrow simulator.
- iii. The *Flow Rate* field tab option is use to input the flow rate of the precursor gases selected. The drop-box besides this option contains some units of flow rate. User may input flow rate in *cc/s*, *sccm*, *mbar l/s*, *torr-l/s*, *slm*, *Pa m3/s*, *Mole/s* etc.

Select the total number of port/precursor gases, after that users need to provide name of each precursor gas and their flow rate with their required unit and press the '*Load Source*' button every time for each inputted gas inside the chamber. Repeating the click on '*Load Source*' button save the input information of precursor gases inputted in simulator database require for invoking epitaxial growth simulation. The input information will get visible in input script area shown in Fig. 2.18.



Chamber condition
Injector Temperature : 1000.0 Pressure 140 torr Volume : 1.4 It. Ceiling Height : 1.0 cm
Precursor condition
Number of Precursor Cell : 2.0
Precursor Cell port : 1 Gas Name : TMG Flow Rate : 5.0 atm cc/s
Precursor Cell port : 2 Gas Name : NH3 Flow Rate : 20.0 atm cc/s

Figure 2.18



2.1.3.2.3 CVD Reactor Process

CVD reactor processes are implemented in TNL-EpiGrow simulator through a process that involves the reactions of a volatile precursor injected into a chamber (typically under vacuum). The chamber is heated to a reaction temperature that causes the precursor gases to react or break down into the desired coating and adsorb to the substrate's surface. To run a CVD process based epitaxial growth simulation experiment, the chamber and precursor conditions need to be inputted by users. The inputted information in the areas showed in the red boxes in Fig 2.19 depicts the CVD reactor frame inbuilt in TNL-EpiGrow simulator. The CVD reactor can be selected from *Reactor option* (shown in red box 1 in figure 2.19), the simulator is ready with virtual *CVD reactor* processes. It requires reactor's chamber and precursor conditions to proceed further. Real data under the *CVD Precursor Source* tab (red box 2 in figure 2.19) are required to calibrate the CVD based real-time epitaxial growth experiments. Under *CVD Precursor Source* tab, the chamber conditions and their parameter as well as precursors parameters are required as shown below.

Reactor	CVD 🔻	1		CVD Precursor Source		
Steps Time (Step 1)	1 ×	Barrier Energies (eV) Schwoebel Incorporation	0.05	Chamber Condition Temperature (C) Pressure	2 622	torr V
Upper layer atoms	1	Desorption	3.0	Cross Sectional Diameter (cm) Length (cm)	12.0	
Substrate	Silicon	No. of Interactive Elemer		Substrate to Edge distance (cm)	1	
Dimension Orientation	10	Atomic Number Neighbouring Energy (eV	14	Precursor Condition		
	111110		Add	Number of Precursor	2	Solid Source
Surface Energy (ev) Temperature (C)	2.0 800			G Source 1 Select Source	S So Weig	ource 1 (Select So 💌
	Add Step	Reset		Load Da	ta	

Figure 2.19



2.1.3.2.3.1 Chamber Condition

Parameters for the CVD chamber need to input as shown with red marked roman numbers in figure 2.20 are as follows.

Chamber Condition		
Temperature (C) i	622	
Pressure ii	0.4	torr
Cross Sectional Diameter (cm)	12.0	
Length (cm)	100	
Substrate to Edge distance $(cm)V$	1	
Drocursor Condition		



- i. *Chamber Temperature*: The users can input the value of temperature inside the chamber; it remains constant during whole process. It is in unit of centigrade (°C).
- ii. *Chamber Pressure*: This field is use to input the total pressure of the chamber and it remains constant during whole time of the deposition. Various units of the pressure are in the drop-box along with this field (torr, mbar, atm and Pa).
- iii. *Cross sectional diameter*: This field is use to input the cross-sectional diameter of the tube used through which gases diffuses inside the CVD chamber. It is in unit of centimeters (cm).
- iv. *Length*: This field is use to input the total length of the chamber tube in centimeters (cm).
- v. *Substrate to Edge distance*: This is use to input the distance between the gas inlet in the chamber and point where substrate is placed.



2.1.3.2.3.2 Precursor Condition

Precursor	Condition			
Number of I	Precursor	i		
📃 Gas Sou	urce	i	📃 Solid Sou	rce
G Source 1	iii Select S	ource 💌	V S Source 1	Select So 🔻
Flow Rate	iv 0	Unit 💌	Vİ Weight (mg)	0
		load Source) vii	

Figure 2.21

Under *Precursor Condition* tab the information regarding chamber precursor gases are input with their required flow rates. The precursor gases flow rates, temperature etc conditions determine and decide the chemical kinetics in terms of various reactions probabilities in gas phases and surface phases. The details of chemical reactions are detailed in *Chemical Kinetics* section 3.3 of chapter 3.

The CVD reactor chamber inbuilt in TNL-EpiGrow simulator has flexibility to input each precursor sources either in gas phase or in solid phase or combination of both phases. Under gas phase the precursor sources are in the gaseous phase, whereas in solid phase remain in form of metal chunk (eg. Ga for growth of gallium III oxide). These can be injected inside CVD reactor chamber in solid phase through thermal evaporation mechanism. The solid precursor will convert into vapor phase under the influence of required temperature of chamber. Users need to decide first the total number of precursors its name and type of phases (Gas or Solid), they may select precursors one by one in steps. Steps as shown in Fig. 2.21 instruct about the inputting method for the gas or solid phase information as follows:

- i. Input the total number of *Precursors* in field required to grow a crystal on substrate after choosing the gas and surface phase reactions from Chemical Kinetic section for particular material system as given in Chapter 3.
- ii. Select one of the two check-boxes named *Gas Source* and *Solid Source* for every precursor.
- When users select *Gas Source* in point ii, then select one various gases (TMG, TBAs, H₂, AlCH₃, NH₃, O₂, Ar, N₂, SiH₄, WH₆, Si₂H₆, GeH₄, SiCl₄, C₃H₈, SiH₂Cl₂, etc.) from the dropbox named under *G Source*.



- iv. The *Flow Rate* of the gases is selected to input under this field. The drop-box besides it contains some well known inbuilt units of *Flow Rate* (atm cc/s, sccm, mbar l/s, torr l/s, slm, Pa m3/s, Mole/s etc.).
- v. In case users select *Solid Source* as shown by point ii, users need to select one of the metal names from the drop-box named *S Sources*.
- vi. The field contains weight of the metal chosen in point V as shown in Fig. 2.21, weight of the *Solid Source* has has unit in milligrams (mg).

Select the total number of port/precursor gases, then provide name of each gas or solid source and their flow rate or weight respectively with their required unit and press the 'Load Source' button every time upto total number of precursor information are inputted. 'Load Source' button writes the input information of precursor sources in TNL-EpiGrow simulator database and get the things ready for simulation. The input information will get visible in input script area shown in Fig. 2.22.



Figure 2.22



2.1.3.3 Reset

Reset option has been included in the TNL-EpiGrow simulator in case information loaded in simulator needs to be filled from initial or bydefault values. As discussed in earlier sections that two button 'Add Step' and 'Load Source' button are two initialization events from where Substrate/Step information and reactor chamber condition loads in simulator respectively. These two informations can be reseted by method discussed below

- 1. As shown in red circle 1 of figure 2.23, Edit menu has two sub-menus *Reset All* and *Reset Chamber*.
 - Reset All: This command is use to reset all the information loaded with Add Step and Load Source buttons i.e. reactor, time, steps, substrate properties, energies, chamber and source conditions.
 - Reset Chamber: This command is use to give option to reset only MBE, CVD or MOCVD reactor's chamber and input source information by selecting any one of the names in sub-menu.

File Edit Simulate Hel	, 1		
Reset Chamber Steps Thee (Step 1) Time for Roughness Upper layer alone	MBE CVD 1 MOCVD 1	Barrier Energies (eV) Schroebel Incorporation Desorption	0.05 0.05 3.0
Substrate Dimension Orientation Surface Energy (ev) Temperature (C)	Silicon Image: Constraint of the second	No. of Interactive Elemen Atomic Number Neighbouring Energy (eV	nts 1 + 1 + 0 0.05 Add
Output	Add Step	Reset	

Figure 2.23

 Reset button shown in red circle 2 in Fig. 2.23 is the other method to Reset all the information i.e. reactor, time, steps, substrate properties, energies, chamber and source conditions.



2.1.3.4 Start Simulation

After filling all the input information described in previous sections, any type of reactor and its chamber conditions chosen as discussed in the sections 2.1.3.1 and 2.1.3.2, the Epi-Grow simulator is ready for invoking the specific reactor based epitaxial growth experiments. Starting simulation can be done in three ways:

- i. Go to the 'Simulate' menu in menu bar at top, it has '*Run*' sub menu.
- ii. A '*Run*' button in the bottom right of the main frame.
- iii. A shortcut key combination of *Shift+F6*.

Trying any one from these options will prompt to show a pop-up frame named '*Save*' option and users can choose desire path or location in their local machine and name of the project input deck. All the inputted information for invoking simulation will be saved at that particular location. After completion of the simulation all the output files associated with simulation will also be saved under the project name provided by users at the desired path or location, as shown in Fig 2.24



Figure 2.24



CHAPTER 3 Physics & Chemistry TNL-EpiGrow Simulator





3.1 Introduction

The epitaxial growth of thin films of materials for a wide range of applications in electronics and optoelectronics is a critical activity in many industries. There are various growth techniques but most research into and (increasingly) much of the production of electronic and optoelectronic devices now centers on chemical vapor deposition (CVD), it's variant metalorganic chemical vapor deposition (MOCVD) and effusion method based molecular beam epitaxy (MBE) techniques. These techniques are more versatile than other growth techniques (although the equipment is more expensive), and they can readily produce multilayer structures with atomic-layer control, which has become more and more important in the type of nanoscale engineering used to produce device structures in as-grown multi layers. For only few materials's system epigrowth technologies have been successfully developed but for which still several issues and challenges associated with these growth techniques need to be addressed. The various physical parameters and quality of thin film grown decide the application of particular thin film.

The numerical computational techniques can help in providing a particularly important solution for the proper theoretical understanding of the microscopic issues and challenges associated with these reactors based epitaxial growth techniques at atomistic scale. The modeling of the chemical vapor phase and effusion method based epitaxial deposition techniques at atomistic scale, including a large number of competing chemical reactions in gas & surface phases along with kinetic Monte Carlo (kMC) algorithms based adsorption, diffusion, desorption events which are inbuilt in TNL-EpiGrow simulator, can provide valuable deeper insight of epitaxial growth mechanisms. The capabilities of TNL-EpiGrow simulator include extraction of the accurate predictive growth rate, strain, roughness, information regarding various types of defects etc. and optimum conditions for epitaxial growth to achieve high quality crystalline thin films successfully. The beauty of TNL-EpiGrow simulator is that each atom and molecule inside particular reactor geometry is traceable at any instant during simulation time. The mapping of various types of defects qualitatively and quantitatively is the essential feature of TNL-EpiGrow simulator. The predictive rate of growth of the film, distinction between the type of defects with location on the lattice, mapping strain in each monocrystalline layer and capturing the morphology of the surface as a function of reactor conditions i.e. pressure, temperature, flow



rates etc can be modeled through TNL-EpiGrow simulator. The lattice parameters can also be extracted and calibrated against XRD obtained lattice parameters of the real thin films.

This chapter covers these basic techniques, chemical kinetics, kMC technique implemented inside TNL-EpiGrow simulator on which epitaxial growth is dependent. **TNL-EpiGrow simulator** provides flexibility to users to choose monocrystalline lattice substrate of cubic, tetragonal, hexagonal symmetries with various crystal orientations to generate the actual environment for operations performed by the atoms inside the reactor. Atoms are assigned bonding possibilities for possible particular hybridization configurations e.g. sp³, sp² etc. In TNL-EpiGrow simulator, atoms make bonds with other atoms only for available appropriate bonding position. This self-assembly of adatoms allows any kind of structure to be grown on appropriate substrate.

The complete flow chart of algorithms implemented inside **TNL-EpiGrow simulator** with flexibilities to choose MBE, MOCVD and CVD reactors for the numerical modeling of thin film epitaxial growth over appropriate substrate are given in reference [49].



3.2 Reactors

Before going into details of TNL-EpiGrow simulator, the three major epitaxial growth processes and reactor's brief information is necessary for users. These processes are extensively in use to produce layers of material for electronic, optical and optoelectronic applications. These processes are chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). We will also consider their main variants.



TNL

3.2.1 Chemical Vapor Deposition (CVD)

This section is intended to provide a comprehensible introduction to how chemical vapor deposition (CVD) processes and reactors work. The experts in the field are already aware about its working but the users, those are new to CVD and who have practiced the art without an opportunity to understand how it works require some brief introduction. The CVD reactor based epitaxial deposition processes are used for nano and microelectronic manufacturing. It works on the principles of heat and mass transport, chemistry, and plasma generation which are applicable to all CVD processes. Every CVD process involves reactions. Certain features are always present in CVD reactor: a source of gases or vapors, a reaction chamber, and a place for the exhaust gases to go [8 - 11].



Various different configurations and chemistries can be existed inside the deposition chamber, but most of them share certain common features,

- Reactant gases the precursor gases must be injected into the chamber and make their way to the substrate, possibly undergoing desirable and undesirable reactions on the way.
- The substrate temperature must almost always be accurately controlled.
- Chemical reactions occur in gas phases to define the kinetics.
- Chemical reactions at the surface form the desired film.
- Byproducts of the reactions must be removed from the chamber.

The detailed CVD deposition process mechanism implemented in TNL-EpiGrow simulator is given latter in the chapter.



3.2.2. Metalorganic Chemical Vapor Deposition (MOCVD)

The MOCVD technique was first introduced by Manasevit and Simpson for the deposition of compound semiconductors thin film in the late 1960s from the vapor phase. MOCVD became a significant thin film production technique for high quality epitaxial layers productions on lattice-matched substrate. The high-quality epitaxial nature of the films was emphasized by changing the name of the growth method to metalorganic vapor phase epitaxy (MOVPE) or organometallic VPE (OMVPE). All of these variants of the name can be found in the literature and in most cases they can be used interchangeably. The basic technique of MOCVD makes it suitable for homoepitaxy and heteroepitaxy. It can be used for growth of narrow bandgap semiconductors e.g. the infrared detector materials $Cd_xHg_{1-x}Te$ and GaInSb and for wide bandgap semiconductors e.g. GaN and ZnO. The below figure is self explanatory and provides details of working principles of MOCVD reactor processes [14 – 18].



3.2.3 Molecular Beam Epitaxy (MBE)

The simplest route for epitaxial growth is MBE process and due to its simplicity makes it powerful technique. The elemental effusion sources are heated to produce neutral atomic and molecular beams under a refined form of vacuum evaporation. The atomic and molecular beams move forward due to the thermal velocities on a heated substrate under ultrahigh vacuum (UHV) without any interaction or collisions between them. In MBE process, only the beam fluxes and the surface reactions influence the growth, extending unparalleled control and reproducibility. The complex structures can be grown atomic layer by atomic layer through MBE process. This process has precise control over thickness, alloy composition and intentional impurity (doping) level. The advantage of UHV conditions provides further cleanliness, as the impurities partial pressures remain so low. The proper understanding of the surface reaction kinetics is always essential [12 - 13].





3.3 Chemical Reactions Kinetic

The chemical reactions kinetics explains the possibilities and probabilities of various chemical reactions in gas phase or surface phase in epitaxial deposition processes. Here, users must aware about the distinction between vapor phase deposition mechanisms i.e. CVD, MOCVD and effusion based mechanism i.e. MBE. During vapor phase deposition processes, the gas phase and surface limited reactions are responsible for deposition on substrate whereas in MBE process atomic or molecular beams impinge on the surface of substrate with any collision i.e. dictated by surface phase reactions mechanisms [45 - 46].

Basically, the probability of any chemical reaction can be decided by involvement of one or several vapor phase reagents inside reactor. The outcome of chemical reaction is intermediate reactants which further react with other reactants; results in a solid reaction product may be used for achieving the deposition of a particular elemental or compound material. However, there are many reactions of limited usefulness where the substrate reacts undesirably with either some of the reactant species (or even with the deposit), the substrate is melted or sublimated, or the deposit is contaminated by some reactive or nonvolatile reaction products [45 - 46].

The chemical processes can be classified according to the nature of the chemical reaction and given as follows:

- (1) Decomposition (pyrolysis)
- (2) Reduction
- (3) Oxidation
- (4) Hydrolysis
- (5) Disproportionation
- (6) Chemical transport
- (7) Nitride formation
- (8) Carbide formation
- (9) Synthesis
- (10) Combined reactions

Users may find more details about above mentioned types of reaction in reference [][][]



The thermodynamic analysis is the essential criteria to consider any vapor phase deposition based reactors. Equilibrium thermodynamic calculations pave ways for a better understanding of chemical processes events along with the facilities to allow optimizing the experimental variables for preparing a desired product. A chemical thermodynamic study of vapor phase epitaxy can help in extracting both qualitative and quantitative data about the particular reaction process. Indeed, under given experimental conditions (starting concentrations of reactants, system temperature and pressure) it is possible to predict theoretically both the feasibility of the process and the nature (as well as the amount) of the solid and gaseous species.

The theoretical initiation of any reaction can be considered based its feasibility if the reaction is thermodynamically possible or not. The feasibility test is always based on reliable thermodynamic data in form of two terms:

- 1. The reaction is more favored when the Gibbs free energy change exhibits greater (negative) values;
- The reaction is possible if the calculated concentrations (partial pressures) of the reactants under conditions of chemical equilibrium are less than their specified initial concentrations.

The sign of the Gibbs free energy of reaction, ΔG_R decides whether the reaction is thermodynamically feasible or not. A negative value of ΔG_R indicates that the reaction may occur, however, a positive ΔG_R indicates that the reaction should not occur. In presence of several thermodynamically feasible reactions, the most negative ΔG_R will be the dominating reaction, as it will lead to the most stable products. The relation between Gibbs free energy and the enthalpy can be defined through ΔG_R , and entropy, ΔS_R , of the reaction at the absolute temperature by using the equation:

$$\Delta G_R = \Delta H_R - T \Delta S_R \tag{3.1}$$

Values for ΔH_R can readily be calculated from published values of the enthalpies of formation ΔH_f using the equation:

$$\Delta H_R = \sum \Delta H_f (products) - \sum \Delta H_f (reactants)$$
(3.2)

Similarly,



$$\Delta S_R = \sum \Delta S_f (products) - \sum \Delta S_f (reactants)$$
(3.3)

$$\Delta G_R = \sum \Delta G_f \ (products) - \sum \Delta G_f \ (reactants) \tag{3.4}$$

The changes in the Gibbs free energy help in calculating the equilibrium constant K_T of the reaction, which is related to the partial pressures (P_f) of reactants in the system:

$$\log K_T = -\frac{\Delta G_R}{4.6T} \tag{3.5}$$

$$K_T = \frac{\prod_{i=1}^{n} P_i(products)}{\prod_{i=1}^{n} P_i(reactants)}$$
(3.6)

The values of enthalpy of formation, entropy of formation and Gibbs (free) energy of formation along with other physical thermodynamics based parameters for various reactants (gases, solids and liquid phases) are well tabulated and obtained from **NIST Chemical Kinetics Database** [50]

link; https://kinetics.nist.gov/kinetics/index.jsp



3.3.1 Reaction Rates

A reaction has many steps or paths in most of the cases. Some reaction paths may be slower than the others and show dominance in determining the rate of reaction. As a consequence, the rate expression, k, of reaction is dependent on the concentrations of reactants and products. The order of the rate expression is defined through the sum of the exponents on the concentrations. A linear rate shows first order, a quadratic dependence shows second order and so on. The reaction can be of several orders depending on the concentrations and the values of the constants k.

Consider a general reaction for example; $A + B \leftrightarrow AB$

$$\frac{d[AB]}{dt} = \frac{k_1[A][B]^2}{1 + k_2[A] + k_3[B]^{1/2}}$$
 I hird order
(depending upon
the values of k

TT1 1 1

The coefficients k's are usually elaborate reaction rates in forward and reverse directions and can be computed from an Arrhenius equation.

$$k = AT^n \exp\left(-\frac{E_a}{RT}\right)$$

where, E_a (calorie) is the activation energy and is often identifiable with the energy barrier for some actual process, e.g. breaking of a bond, to occur. The coefficient A is known as pre frequency factor and dependent on entropy of formation. The prefactor A (unit is dependent on the order of reaction), also include information regarding random motion of molecules as they vibrate, rotate and translate inside reactor space and take part in computation of thermal energy of the molecules. The operating temperature is defined through T, n is exponent of temperature and R is the universal gas constant.

The various data set for A, n and E_a for computation of forward and reverse reaction rates occurring in gas phase and surface phases associated with various reactants are tabulated in Table 3.1 and inbuilt in TNL-EpiGrow simulator through graphical user interface GUI based features.

In many cases, the real microscopic reaction pathways are extremely complex, such that there is no alternative to using lumped kinetic parameters that may actually represent a large number of basic reaction steps. One extreme approach is to simply replace the true reactions with effective



ones that are meant solely to mimic experimentally measured growth rates. Although this approach can be used to predict how substrate topography is covered by the growing film. Fortunately, a few cases do exist for which there is a substantial body of microscopic measurements and predictions for the individual reactions that control film growth.

3.3.1.1 Transition States

In principle, one can determine the mechanism of a chemical reaction by following the motions of all the atoms involved throughout the reaction. However, it is often simpler to think of the reaction as being relatively independent of the exact path, but involving the passage from the reactant state through a transition state: the lowest-energy "pass" through the configuration space to the products. In an association reaction (that is, a reaction whose net effect is the joining together of two formerly separate molecules) the two molecules might strike each other in the gas phase to form a temporary complex, $A + B \sim AB^*$

In order to conserve energy, we are forced to convert much of the kinetic energy of the reactants into internal energy of the transition state: this energy will usually cause the reactants to dissociate again, unless a third atom or molecule (often denoted as M), collides with the transition state and takes some of the energy away, allowing association to occur: $AB^* + M \sim C$

3.3.1.2 Types of Chemical Reactions

Before, proceeding to run epitaxial growth deposition with initiation of chemical reactions implemented in the TNL-EpiGrow simulator. Users need to distinguish between gas phase and surface phase reactions.

In CVD and MOCVD processes, the precursors interact with each other in gas phase and surface phase reactions whereas in MBE process, effusors only interact in surface limited regime. The separate gas phase reactions and surface phase reactions database for various materials system are by defaults inbuilt in the TNL-EpiGrow simulator database. Users have flexibility to change values of A, n and E_a according to their own reaction recipes and paths available with them along with facilities to accommodate user's define chemical reactions.

Various compounds chemistry has been added by default in TNL-EpiGrow simulator. The gas phase mechanism and surface phase mechanisms are listed separately.



There are different precursors sources for *Si*, *SiC* and *SiGe* in the epitaxy process such as SiCl₄ (Silicon tetrachloride), SiHCl₃ (TCS), SiH₂Cl₂ (DCS), SiH₄ (Silane), Si₂H₆ (Disilane) and Si₃H₈ (Trisilane), GeH₄ (Germene),

• <u>Si_{H4} (Silane)/_{H2} System [51]</u>

Gas phase reaction (G) and surface phase reaction (A) rates are in mol/cm³-s and mol/cm²s respectively. *=adsorbed species, σ =free surface site

Phase	Reaction	Α	n	Ea (calorie/mole)
G-1	$SiH_4 \leftrightarrow SiH_2 + H_2$	3.09×10 ⁹	1.7	54710
G-2	$Si_2H_6 \leftrightarrow SiH_4 + SiH_2$	1.82×10^{10}	1.7	50200
G-3→	$HSiSiH_3 + SiH_4 \leftrightarrow Si_2H_6 + SiH_2$	1.74×10^{14}	0.4	8900
G-4	$Si_2H_6 \leftrightarrow H_2 + HSiSiH_3$	9.12×10 ⁹	1.8	54200
G-5	$HSiSiH_3 \leftrightarrow H_2SiSiH_2$	2.51×10 ¹³	-0.20	5380
G-6	$HSiSiH_3 + H_2 \leftrightarrow SiH_2 + SiH_4$	9.33×10 ¹³	0	4092
A-1	$SiH_4 + 2\sigma \leftrightarrow SiH^* + H^*$	1.15×10 ¹⁹	0.5	3000
A-2	$SiH_3 + \sigma \leftrightarrow SiH^* + H^*$	4.37×10 ¹⁷		27000
A-3	$2\mathrm{SiH}^* \leftrightarrow 2\mathrm{SiH}^* + \mathrm{H}_2$	2.40×10 ²⁴		45000
A-4	$SiH_2 + \sigma \leftrightarrow SiH^*$	5.75×10 ¹¹	0.5	0
A-5	$SiH^* \leftrightarrow Si(s) + 1/2H_2 + \sigma$	7.94×10 ¹¹	_	47000
A-6	$2H^* \leftrightarrow H_2 + 2 \sigma$	1.29×10 ²²		43000
A-7	$H_2 + 2\sigma \leftrightarrow 2H^*$	2.29×10 ¹¹	0.5	17250



• <u>GeH₄ (Germene)/H₂ System [52]</u>

Ge₂H₆ (Digermene), Ge₃H₈ (Trigermene)

Gas phase reaction (G) and surface phase reaction (A) rates are in mol/cm³-s and mol/cm²s respectively. *=adsorbed species, σ =free surface site

Phase	Reaction	Α	n	Ea (calorie/mole)
G-1	$GeH_4 - GeH_3 + H$	4.15×10 ¹⁴	2.46	85803
G-2	$GeH_4 - GeH_2 + H_2$	3.01×10 ¹⁴	0.272	53035
G-3	$GeH_2 - GeH + H$	1.95×10 ¹⁵	-0.369	71821
	$GeH_2 - Ge + H_2$	1.91×10 ¹³	0.203	38958
G-4	$Ge_2H_6 \leftrightarrow H_2 + HGeGeH_3$	9.12×10 ⁹	1.8	41490
G-5	$HGeGeH_3 \leftrightarrow H_2GeGeH_2$	2.51×10 ¹³	-0.20	-7330
G-6	$HGeGeH_3 + H_2 \leftrightarrow GeH_2 + GeH_4$	9.33×10 ¹³	0	-8618
A-1	$GeH_4 + 2\sigma \leftrightarrow Ge + 2H_2$	1.15×10 ¹⁹	0.5	2300
A-2	$GeH_2 + \sigma \leftrightarrow Ge + H_2$	5.75×10 ¹¹	0.5	0
A-3	$2H^* \leftrightarrow H_2 + 2 \sigma$	1.29×10^{22}	—	43000
A-4	$H_2 + 2s \leftrightarrow 2H^*$	2.29×10 ¹¹	0.5	17250



• <u>SiCl₄ (silicon tetracloride)/C3H8/H2 System [53]</u>

S and B designate surface species and bulk species, respectively. σ_{Si} and σ_{C} represent Si and C surface sites, respectively. Subscripts C and Si indicate a molecule absorbed on C or Si sites.

	Reaction	Α	n	Ea (calorie)		
G1	$SiCl_4 + H \leftrightarrow SiCl_3 + HCl$	3.031×10^{10}	1.45	1273.02		
G2	$SiHCl_3 \leftrightarrow SiCl_3 + H$	4.319×10 ¹³	0.46 5	5558.65		
G3	$SiHCl_3 \leftrightarrow SiCl_2 + HCl$	1.205×10^{13}	0.48	4537.34		
G4	$SiHCl_3 + HCl \leftrightarrow SiCl_4 + H_2$	3.915×10 ³	2.66	2745.42		
G5	$SiHCl_3 + H \leftrightarrow SiCl_3 + H_2$	2.303×10 ⁹	1.62	198.00		
G6	$SiHCl_3 + H \leftrightarrow SiHCl_2 + HCl$	6.097×10 ⁹	1.46	1341.20		
G7	$SiHCl_2 \leftrightarrow SiCl + HCl$	2.262×10^{12}	0.49	3316.65		
G8	$SiHCl_2 \leftrightarrow SiCl_2 + H$	7.194×10 ¹²	0.35	2774.36		
G9	$SiHCl_2 + H \leftrightarrow SiH_2Cl_2$	4.687×10^{13}	0.52	5489.97		
G10	$SiHCl_2 + HCl \leftrightarrow SiCl_3 + H_2$	2.441×10^{3}	2.56	1829.65		
G11	$SiH_2Cl_2 \leftrightarrow SiCl_2 + H_2$	1.479×10^{12}	0.59	4703.89		
G12	$SiH_2Cl_2 \leftrightarrow SiHCl + HCl$	3.699×10 ¹²	0.59	4637.60		
G13	$SiH_2Cl_2 + HCl \leftrightarrow SiHCl_3 + H_2$	4.041×10^{3}	2.57	2389.05		
G14	$SiH_2Cl_2 + H \leftrightarrow SiH_2Cl + HCl$	3.059×10 ⁹	1.5	1345.73		
G15	$SiH_2Cl_2 + H \leftrightarrow SiHCl_2 + H_2$	1.281×10 ⁹	1.64	200.26		
G16	$SiH_2Cl \leftrightarrow SiCl + H_2$	5.171×10 ¹¹	0.58	3131.36		
G17	$SiH_3Cl \leftrightarrow SiH_2Cl + H$	4.541×10 ¹³	0.56	5458.90		





G18	$SiH_2Cl + HCl \leftrightarrow SiHCl_2 + H_2$	2.883×10^{3}	2.49	1670.78
G19	$SiH_3Cl \leftrightarrow SiHCl + H_2$	2.179×10 ¹²	0.54	4048.51
G20	$SiH_3Cl + H \leftrightarrow SiH_2Cl + H_2$	1.645×10 ⁹	1.66	205.80
G21	$SiH_3Cl + HCl \leftrightarrow SiH_2Cl_2 + H_2$	7.735×10^{3}	2.49	2090.42
G22	$SiH_2Cl \leftrightarrow SiHCl + H$	6.928×10 ¹²	0.43	3470.87
G23	$SiHCl + HCl \leftrightarrow SiCl_2 + H_2$	1.901×10^{3}	2.52	142.40
G24	$SiHCl \leftrightarrow SiCl + H$	3.599×10 ¹¹	0.71	4425.01
G25	$Si + HCl \leftrightarrow SiCl + H$	1.096×10 ⁹	1.63	662.17
G26	$SiH_3Cl \leftrightarrow SiH_2 + HCl$	3.581×10 ¹²	0.66	4757.48
G27	$SiH_4 + HCl \leftrightarrow SiH_3Cl + H_2$	7.926×10^4	2.48	2363.39
G28	$SiCl_2 + H \leftrightarrow SiCl + HCl$	1.676×10 ⁹	1.47	891.74
G29	$SiHCl + H \leftrightarrow SiCl + H_2$	2.320×10 ⁹	1.58	39.75
C20		4 73 0 4 0		
G30	$S_1Cl_3 + H \leftrightarrow S_1Cl_2 + HCl$	$4.538 \times 10^{\circ}$	1.36	51.83
G30 G31	$SiCl_3 + H \leftrightarrow SiCl_2 + HCl$ $SiH_2Cl + H \leftrightarrow SiHCl + H_2$	4.538×10° 3.156×10 ⁸	1.36 1.67	51.83 278.50
G30 G31 Surfa	$S_{1}Cl_{3} + H \leftrightarrow S_{1}Cl_{2} + HCl$ $SiH_{2}Cl + H \leftrightarrow SiHCl + H_{2}$ <i>ince Phase Reactions</i>		1.36 1.67 n	51.83 278.50 E _a
G30 G31 Surfa A1	$S_{1}Cl_{3} + H \leftrightarrow S_{1}Cl_{2} + HCl$ $SiH_{2}Cl + H \leftrightarrow SiHCl + H_{2}$ <i>ace Phase Reactions</i> $CH4 + \sigma_{Si} \rightarrow C(S) + 2H_{2}$	$ \begin{array}{r} 4.538 \times 10^{6} \\ \hline 3.156 \times 10^{8} \\ \hline \mathbf{A} \\ \hline 2.4 \times 10^{9} \\ \end{array} $	1.36 1.67 n 0.5	51.83 278.50 E _a 0.00
G30 G31 Surfa A1 A2	$S_{1}Cl_{3} + H \leftrightarrow S_{1}Cl_{2} + HCl$ $SiH_{2}Cl + H \leftrightarrow SiHCl + H_{2}$ ace Phase Reactions $CH4 + \sigma_{Si} \rightarrow C(S) + 2H_{2}$ $CH3 + \sigma_{Si} \leftrightarrow CH(S) + H2$	$ \begin{array}{c} 4.538 \times 10^{6} \\ \hline 3.156 \times 10^{8} \\ \hline \mathbf{A} \\ \hline 2.4 \times 10^{9} \\ \hline 8.5114 \times 10^{11} \\ \end{array} $	1.36 1.67 n 0.5 0.5	51.83 278.50 E _a 0.00 0.00
G30 G31 Surfa A1 A2 A3	$S_{1}Cl_{3} + H \leftrightarrow S_{1}Cl_{2} + HCl$ $SiH_{2}Cl + H \leftrightarrow SiHCl + H_{2}$ $CH4 + \sigma_{Si} \rightarrow C(S) + 2H_{2}$ $CH3 + \sigma_{Si} \leftrightarrow CH(S) + H2$ $CH2 + \sigma_{Si} \rightarrow C(S) + H2$	$ \begin{array}{c} 4.538 \times 10^{6} \\ \hline 3.156 \times 10^{8} \\ \hline \mathbf{A} \\ \hline 2.4 \times 10^{9} \\ \hline 8.5114 \times 10^{11} \\ \hline 8.913 \times 10^{11} \\ \end{array} $	1.36 1.67 n 0.5 0.5 0.5	51.83 278.50 E _a 0.00 0.00 0.00
G30 G31 A1 A2 A3 A4	$\begin{array}{l} \text{SiCl}_{3} + \text{H} \leftrightarrow \text{SiCl}_{2} + \text{HCl} \\\\ \text{SiH}_{2}\text{Cl} + \text{H} \leftrightarrow \text{SiHCl} + \text{H}_{2} \\\\ \text{ice Phase Reactions} \\\\ \text{CH4} + \sigma_{\text{Si}} \rightarrow \text{C(S)} + 2\text{H}_{2} \\\\ \text{CH3} + \sigma_{\text{Si}} \leftrightarrow \text{CH(S)} + \text{H2} \\\\ \text{CH2} + \sigma_{\text{Si}} \rightarrow \text{C(S)} + \text{H2} \\\\ \text{CH2} + \sigma_{\text{Si}} \rightarrow \text{CH(S)} \\\\ \end{array}$	4.538×10^{6} 3.156×10^{8} A 2.4×10^{9} 8.5114×10^{11} 8.913×10^{11} 9.12×10^{11}	1.36 1.67 n 0.5 0.5 0.5 0.5	51.83 278.50 E _a 0.00 0.00 0.00
G30 G31 Surfa A1 A2 A3 A4 A5	$\begin{array}{l} \text{SiCl}_{3} + \text{H} \leftrightarrow \text{SiCl}_{2} + \text{HCl} \\\\ \text{SiH}_{2}\text{Cl} + \text{H} \leftrightarrow \text{SiHCl} + \text{H}_{2} \\\\ \text{ince Phase Reactions} \\\\ \text{CH4} + \sigma_{\text{Si}} \rightarrow \text{C(S)} + 2\text{H}_{2} \\\\ \text{CH3} + \sigma_{\text{Si}} \leftrightarrow \text{CH(S)} + \text{H2} \\\\ \text{CH2} + \sigma_{\text{Si}} \rightarrow \text{C(S)} + \text{H2} \\\\ \text{CH2} + \sigma_{\text{Si}} \rightarrow \text{C(S)} + \text{H2} \\\\ \text{CH} + \sigma_{\text{Si}} \rightarrow \text{CH(S)} \\\\ \text{C2H5} + 2 \sigma_{\text{Si}} \rightarrow \text{C(S)} + \text{CH(S)} + 2\text{H2} \\\end{array}$	$ \begin{array}{c} 4.538 \times 10^{6} \\ 3.156 \times 10^{8} \\ \hline A \\ 2.4 \times 10^{9} \\ 8.5114 \times 10^{11} \\ 8.913 \times 10^{11} \\ 9.12 \times 10^{11} \\ 5.7544 \times 10^{20} \\ \end{array} $	1.36 1.67 n 0.5 0.5 0.5 0.5	51.83 278.50 E _a 0.00 0.00 0.00 0.00
G30 G31 A1 A2 A3 A4 A5 A6	$SiCl_{3} + H \leftrightarrow SiCl_{2} + HCl$ $SiH_{2}Cl + H \leftrightarrow SiHCl + H_{2}$ $CH2 + \sigma_{Si} \rightarrow C(S) + 2H_{2}$ $CH3 + \sigma_{Si} \leftrightarrow CH(S) + H2$ $CH2 + \sigma_{Si} \rightarrow C(S) + H2$ $CH2 + \sigma_{Si} \rightarrow C(S) + H2$ $CH + \sigma_{Si} \rightarrow CH(S)$ $C2H5 + 2 \sigma_{Si} \rightarrow C(S) + CH(S) + 2H2$ $C2H4 + 2 \sigma_{Si} \rightarrow 2C(S) + 2H2$	$\begin{array}{c cccc} 4.538 \times 10^{6} \\ \hline 3.156 \times 10^{8} \\ \hline A \\ \hline 2.4 \times 10^{9} \\ \hline 8.5114 \times 10^{11} \\ \hline 8.913 \times 10^{11} \\ \hline 9.12 \times 10^{11} \\ \hline 5.7544 \times 10^{20} \\ \hline 9.3325 \times 10^{17} \end{array}$	1.36 1.67 n 0.5 0.5 0.5 0.5 0.5	51.83 278.50 E _a 0.00 0.00 0.00 0.00 0.00
G30 G31 Surfa A1 A2 A3 A4 A5 A6 A7	$\begin{array}{l} \operatorname{SiCl}_{3} + \operatorname{H} \leftrightarrow \operatorname{SiCl}_{2} + \operatorname{HCl} \\\\ \operatorname{SiH}_{2}\operatorname{Cl} + \operatorname{H} \leftrightarrow \operatorname{SiHCl} + \operatorname{H}_{2} \\\\ \begin{array}{l} \text{ice Phase Reactions} \\\\ \operatorname{CH4} + \sigma_{\mathrm{Si}} \rightarrow \operatorname{C}(\mathrm{S}) + 2\operatorname{H}_{2} \\\\ \operatorname{CH3} + \sigma_{\mathrm{Si}} \leftrightarrow \operatorname{CH}(\mathrm{S}) + \operatorname{H2} \\\\ \operatorname{CH2} + \sigma_{\mathrm{Si}} \rightarrow \operatorname{C}(\mathrm{S}) + \operatorname{H2} \\\\ \operatorname{CH2} + \sigma_{\mathrm{Si}} \rightarrow \operatorname{C}(\mathrm{S}) + \operatorname{H2} \\\\ \operatorname{CH4} + \sigma_{\mathrm{Si}} \rightarrow \operatorname{CH}(\mathrm{S}) \\\\ \operatorname{C2H5} + 2 \sigma_{\mathrm{Si}} \rightarrow \operatorname{C}(\mathrm{S}) + \operatorname{CH}(\mathrm{S}) + 2\operatorname{H2} \\\\ \operatorname{C2H4} + 2 \sigma_{\mathrm{Si}} \rightarrow \operatorname{2C}(\mathrm{S}) + 2\operatorname{H2} \\\\ \operatorname{C2H3} + 2 \sigma_{\mathrm{Si}} \rightarrow \operatorname{C}(\mathrm{S}) + \operatorname{CH}(\mathrm{S}) + \operatorname{H2} \end{array}$	$\begin{array}{c c} 4.538 \times 10^{6} \\ \hline 3.156 \times 10^{8} \\ \hline A \\ \hline 2.4 \times 10^{9} \\ \hline 8.5114 \times 10^{11} \\ \hline 8.913 \times 10^{11} \\ \hline 9.12 \times 10^{11} \\ \hline 5.7544 \times 10^{20} \\ \hline 9.3325 \times 10^{17} \\ \hline 5.8884 \times 10^{20} \end{array}$	1.36 1.67 n 0.5 0.5 0.5 0.5 0.5 0.5	51.83 278.50 E _a 0.00 0.00 0.00 0.00 0.00 0.00

A9	$SiHCl3 + 2 \sigma_{Si} + 2 \sigma_{C} \rightarrow SiCl(S) + H(S) + 2ClSi(S)$	2.63×10^{16}	0.5	0.00
A10	$SiH2Cl2 + \sigma_{Si} + 3 \sigma_C \rightarrow SiCl(S) + 2H(S) + ClSi(S)$	3.8×10^8	0.5	0.00
A11	$SiCl4 + 2 \sigma_{Si} + 2 \sigma_{C} \rightarrow SiCl(S) + ClC(S) + 2ClSi(S)$	2.34×10^{16}	0.5	0.00
A12	$SiCl2 + 2 \sigma_C \leftrightarrow SiCl(S) + ClC(S)$	3.09×10^{19}	0.5	0.00
A13	$SiCl2 + \sigma_{Si} + \sigma_{C} \leftrightarrow SiCl(S) + ClSi(S)$	3.09×10^{19}	0.5	0.00
A14	$SiCl + \sigma_C \rightarrow SiCl(S)$	4.17×10^{11}	0.5	0.00
A15	SiHCl + 2 $\sigma_{\rm C} \rightarrow$ SiCl(S) + H(S)	3.31×10^{20}	0.5	0.00
A16	$SiHCl + \sigma_C \rightarrow Si(S) + HCl$	4.17×10^{12}	0.5	0.00
A17	$ClC(S) \rightarrow Cl + \sigma_C$	1×10^{17}	0	0.00
A18	$ClSi(S) \rightarrow Cl + Si(\$)$	1×10^{17}	0	0.00
A19	$2H(S) \rightarrow H2 + 2 \sigma_C$	1×10^{17}	0	0.00
A20	$SiCl(S) + C(S) \rightarrow SiC(B) + \sigma_{Si} + \sigma_{C} + Cl$	1×10^{17}	0	0.00
A21	$SiCl(S) + CH(S) \rightarrow SiC(B) + HCl + \sigma_{C} + \sigma_{Si}$	1×10^{17}	0	0.00
A22	$Si(S) + C(S) \rightarrow SiC(B) + \sigma_C + \sigma_{Si}$	1×10^{17}	0	0.00
A23	$Si(S) + CH(S) \rightarrow SiC(B) + \sigma_C + \sigma_{Si} + H$	1×10^{17}	0	0.00
A24	$HCl + SiC(B) \rightarrow SiCl + CH$	3.55×10^{10}	0.5	0.00



• Trimethyl gallium (TMG- (CH3)3Ga) / Dimethyl gallium (DMG- (CH3)2Ga) / monomethyl gallium (MMG- (CH3)Ga) / NH3 / CH3 [54]

Interaction among CH3, H2 and H; and finally, the pyrolysis reaction for adducts. TMG and MMG decompose slowly because of their large activation energy barriers; however, the pyrolysis reaction of DMG to MMG is rapid. Therefore, the conversion of TMG to MMG is rapid at high temperatures, and the concentration of MMG is expected to be high at higher temperatures. Therefore, MMG and MMG:NH3 are expected to be the dominant gallium-containing precursors at high temperatures, whereas TMG and TMG:NH3 are expected to contribute to deposition at low temperatures [54].

						Ea
Phase	Reactions			А	n	(Cal)
G1	TMG	\leftrightarrow	DMG + CH3	1.00×10^{47}	-9.18	76,996
G2	DMG	\leftrightarrow	MMG + CH3	7.67×10^{43}	-9.8	34,017
G3	MMG	\leftrightarrow	Ga + CH3	1.68×10^{30}	-5.07	84,030
G4	TMG + NH3	\rightarrow	TMG:NH3	2.28×10^{34}	-8.31	3115
G5	TMG + NH3	\rightarrow	DMG:NH2 + CH4	$1.70 imes 10^4$	2	19,969
G6	DMG + NH3	\rightarrow	DMG:NH3	4.08×10^{31}	-7.03	3234
G7	DMG + NH3	\rightarrow	MMG:NH2 + CH4	5.30×10^{5}	1.56	20,744
G8	MMG + NH3	\rightarrow	MMG:NH3	7.95×10^{24}	-5.21	2094
G9	MMG + NH3	\rightarrow	GaNH2 + CH4	8.10×10^{5}	1.3	17,722
G10	NH3 + CH3	\rightarrow	NH2 + CH4	3.31×10^{3}	2.51	9859
G11	CH3 + H2	\rightarrow	CH4 + H	1.20×10^{12}	0	12,518
G12	TMG + H	\rightarrow	DMG + CH4	5.00×10^{13}	0	10,036
G13	DMG + H	\rightarrow	MMG + CH4	5.00×10^{13}	0	10,036
G14	TMG:NH3	\rightarrow	MMG + 2CH3 + NH3	1.33×10^{44}	-8.24	77,791
G15	CH3 + M + H	\rightarrow	CH4 + NH3	2.40×10^{22}	-1	0
G16	2CH3	\leftrightarrow	С2Н6	2.00×10^{13}	0	0
G17	2H + M	\leftrightarrow	H2 + M	2.00×10^{16}	0	0

Where,

TMG \rightarrow (CH3)3Ga DMG \rightarrow (CH3)2Ga MMG \rightarrow (CH3)Ga


Surface-phase mechanism

<u>Path 1</u>				Α	n	Ea
A1	MMG + N(S)	\rightarrow	MMG(S)	1.16×10^{5}	2.98	0
A2	MMG(S)	\rightarrow	MMG + N(S)	1.12×10^{14}	0.55	107,673
A3	NH3 + MMG(S)	\rightarrow	COMPM1(S)	3.35×10^{7}	3.33	0
A4	COMPM1(S) + NH3	\rightarrow	MMG(S)	$5.70 \ge 10^{13}$	-0.16	8146
A5	MMG + COMPM1(S)	\rightarrow	CH4 + COMPM2(S)	1.23×10^{10}	3.22	23,446
A6	NH3 + COMPM2(S)	\rightarrow	COMPM3(S)	3.35×10^{7}	3.33	0
A7	COMPM3(S)	\rightarrow	NH3 + COMPM2(S)	5.70×10^{13}	-0.161	8146
A8	MMG + COMPM3(S)	\rightarrow	CH4 + COMPM4(S)	1.23×10^{10}	3.22	23,446
A9	NH3 + COMPM4(S)	\rightarrow	COMPM5(S)	3.35×10^{7}	3.33	0
A10	COMPM5(S)	\rightarrow	NH3 + COMPM4(S)	5.70×10^{13}	-0.161	8146
A11	COMPM5(S)	\rightarrow	CH4 + RINGM1(S)	1.23×10^{7}	3.22	23,446
A12	Ga(S) + RINGM1(S)	\rightarrow	RINGM2(S) + N(S)	3.35×10^{7}	3.33	0
A13	RINGM2(S)	\rightarrow	3H2 + 3GaN(B) + Ga(S)	3.68×10^{9}	2.05	59,610
<u>Path 2,</u>				Α	n	Ea
A14	CH3 + Ga(S)	\rightarrow	MMG(S)	1.76×10^{9}	1.39	0
A15	MMG(S)	\rightarrow	CH3 + Ga(S)	4.54×10^{13}	0.0346	79,480
A16	NH2 + Ga(S)	\rightarrow	NH2(S)	3.17×10^{8}	1.83	0
A17	GaNH2 + N(S)	\rightarrow	GaNH2(s)	2.27×10^{6}	2.247	0
A18	GaNH2(S)	\rightarrow	GaNH2 + N(S)	4.83×10^{13}	0.614	83,881
A19	COMPMM1(S)	\rightarrow	CH4 + GaNH2(S)	1.49×10^{11}	0.609	25,950
A20	MMG + GaNH2(S)	\rightarrow	COMPMM1(S)	1.16×10^{5}	2.98	0
A21	NH3 + COMPMM1(S)	\rightarrow	COMPMM2(S)	3.35×10^{7}	3.33	0
A22	COMPMM2(S)	\rightarrow	CH4 + COMPMM3(S)	1.49×10^{11}	0.609	25,950
A23	MMG + COMPMM3(S)	\rightarrow	COMPMM4(S)	1.16×10^{5}	2.98	0
A24	NH3 + COMPMM4(S)	\rightarrow	COMPMM5(S)	3.35×10^{7}	3.33	0
A25	COMPMM5(S)	\rightarrow	CH4 + RINGM1(S)	1.49×10^{11}	0.609	25,950
A26	NH2(S)	\rightarrow	NH2 + Ga(S)	1.45×10^{14}	0.09	59,786
A27	COMPMM1(S)	\rightarrow	MMG + GaNH2(S)	1.00×10^{14}	0.55	42,819
A28	COMPMM2(S)	\rightarrow	NH3 + COMPMM1(S)	5.70×10^{13}	-0.1	8146
A29	COMPMM4(S)	\rightarrow	MMG + COMPMM3(S)	1.00×10^{14}	0.55	42,819
A30	COMPMM5(S)	\rightarrow	NH3 + COMPMM4(S)	5.70×10^{13}	-0.1	8146
A31	Ga + N(S)	\rightarrow	Ga(S)	1.00×10^{11}	1.5	0
A32	Ga(S) + NH2(S)	\rightarrow	GaNH2 + Ga(S)	1.00×10^{25}	0	0
A33	Ga(S)	\rightarrow	Ga + N(S)	1.00×10^{13}	0	45,168
A34	6CH3 + RINGM2(S)	\rightarrow	COM1(S)	7.55×10^{7}	2.31	0
A35	COM1(S)	\rightarrow	6CH3 + RINGM2(S)	1.00×10^{13}	0.71	45,506
A36	COM1(S)	\rightarrow	6CH4 + 3GaN(B) + Ga(S)	4.00×10^{12}	0	49,675
<u>Path 3</u>				Α	n	Ea
A37	TMG + N(S)	\rightarrow	TMG(S)	1.16×10^{5}	2.98	0
A38	NH3 + TMG(S)	\rightarrow	TCOM1(S)	3.35×10^7	3.33	0



A39	TCOM1(S)	\rightarrow	CH4 + TCOM2(S)	1.49×10^{11}	0.609	32,785
A40	Ga(S) + TCOM2(S)	\rightarrow	TCOM3(S) + N(S)	3.35×10^{7}	3.33	0
A41	TCOM3(S)	\rightarrow	2CH4 + GaN(B) + Ga(S)	1.49×10^{11}	0.609	49,675
A42	TMG(S)	\rightarrow	TMG + N(S)	1.12×10^{14}	0.55	49,675
A43	TCOM1(S)	\rightarrow	NH3 + TMG(S)	5.70×10^{13}	-0.161	11,922
A44	TMG:NH3	\rightarrow	TCOM1(S)	1.16×10^{5}	2.98	0
A45	TCOM1(S)	\rightarrow	TMG:NH3	1.12×10^{14}	0.55	49,675
A46	TCOM1(S)	\rightarrow	2CH3+MMG(S)+NH3+N(S)	1.12×10^{14}	0.55	107,673
A47	MMGNH3 + N(S)	\rightarrow	COMPM1(S)	1.16×10^{5}	2.98	0
A48	COMPM1(S)	\rightarrow	MMG:NH3	1.12×10^{14}	0.55	107,673
A49	MMG:NH3+COMPM1(S)	\rightarrow	CH4 + COMPM3(S)	1.23×10^{10}	3.22	23,446
A50	MMG:NH3+COMPM3(S)	\rightarrow	CH4 + COMPM5(S)	1.23×10^{10}	3.22	23,446
A51	MMG:NH3+GaNH2(S)	\rightarrow	COMPMM2(S)	1.16×10^{5}	2.98	0
A52	MMG:NH3+COMPMM3(S)	\rightarrow	COMPMM5(S)	1.16×105	2.98	0

Here,

COMPM1(S)
COMPM2(S)
COMPM3(S)
COMPM4(S)
COMPM5(S)
RINGM1(S)
RINGM2(S)
COMPMM1(S)
COMPMM2(S)
COMPMM3(S)
COMPMM4(S)
COMPMM5(S)
TCOM1(S)
TCOM2(S)
TCOM3(3)
COM1(S)

NH3•MMG(S) Ga•NH2•MMG(S) NH3•Ga•NH2•MMG(S) Ga•NH2•Ga•NH2•MMG(S) NH3•Ga•NH2•Ga•NH2•MMG(S) NH2•Ga•NH2•Ga•NH2•Ga(S) (S)NH2•Ga•NH2•Ga•NH2•Ga(S) MMG•GaNH2(S) NH3•MMG•GaNH2•Ga(S) NH2•Ga•NH2•Ga(S) MMG•NH2•Ga•NH2•Ga(S) NH3•MMG•NH2•Ga•NH2•Ga(S) NH3•TMG(S) NH2•DMG(S) (S)NH2•DMG(S) RINGM2(S)•CH3 complex



Intentionally left Blanck for adding more material systems chemical reactions equations.



3.4 Physics of CVD Reactor

The CVD technique implemented in TNL-EpiGrow simulator, the basic mechanisms of the flow of precursors and carrier gases inside reactor and their chemical kinetics are included. The chemical reactions and decomposition in the gas phase are initiated with probabilities of various kinetic reactions paths. The intermediate atoms or molecules in gas phase strike and adsorb to the substrate surfaces and responsible for surface phase reactions [8 - 11].

In **TNL-EpiGrow simulator** CVD reactor is implemented through a process that involves the reaction of a volatile precursor which is injected into a chamber (typically under vacuum). The chamber is heated to a reaction temperature that causes the precursor gas to react or break down into the desired coating and bond to the material surface. Over time the coating material builds on the surface and creates a coating throughout the exposed part's surface. Precursor gases (often diluted in carrier gases) used in **TNL-EpiGrow simulator** is delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase which are deposited onto the substrate. The substrate temperature is critical and can influence what reactions will take place.

The chemical kinetics studies based on rigorous thermodynamics principles can provide useful information regarding chemical reactions data of particular gas phase reaction in terms of activation energy and limiting steps of surface phase reactions which are essentially important for the proper understanding of deposition processes. However, rigorous kinetic analysis with several reaction paths is crucial for better understanding of the chemical vapor deposition processes including adsorption and desorption events over substrate surface. The chemical reaction kinetics determines the rate at which a phase will form and whether its formation is limited by any step in the process. The chemical kinetics algorithms include seven basic steps for proper understanding of chemical reactions take place inside reactor during the chemical vapor deposition process can be understood from below figure.





The steps details are;

- 1. Reactant gases transportation into the reaction chamber
- 2. Formation of intermediate reactants from reactant gases
- 3. Reactant gases diffusion through the gaseous boundary layer to the substrate
- 4. Absorption of gases onto the substrate surface
- 5. Single or multi-step reactions at the substrate surface
- 6. Desorption of product gases from the substrate surface
- 7. Forced exit of product gases from the system

The probabilities of occurrence of above steps determine whether the process is mass transport limited or surface reaction limited. The surface reaction limited adsorption process is dominating mechanism at lower temperatures whereas, with increase in temperature, the surface reaction rate rises exponentially, resulting in a mass transport limited because transport becomes the slowest step in the series of deposition steps.

The reactant flux according to Fick's law, can be written as,

$$J_A = -\frac{D_{A_B}}{RT} \frac{dc_A}{dx} \tag{3.7}$$

where J_A is the diffusion flux of specie A, D_{A_B} is the diffusivity of the bulk stream reactants, c_A is the concentration of species A, x is the direction perpendicular to the substrate surface, R is the gas constant, T is the absolute temperature. The concentration gradient can be approximated as,

$$\frac{dc_A}{dx} \approx \frac{\Delta c_A}{\Delta x} = \frac{c_{A_B} - c_{A_S}}{\delta}$$
(3.8)

where c_{A_B} and c_{A_S} are the bulk stream concentration and surface concentration of species A respectively. δ is the boundary layer thickness. The reactant diffusion through the boundary layer is computed as,

$$J_A = -\frac{D_{AB}}{RT} \left[\frac{c_{AB} - c_{AS}}{\delta} \right]$$
(3.9)



The binary diffusivity, D_{AB} , of the reactants dependent on Leonard-Jones parameters (σ , Ω) is calculated through the Chapman-Enskog theory [8 - 11],

$$D_{A_B} = 0.0018583 \frac{\sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B}\right)}}{p\sigma_{AB}^2 \Omega_{D,AB}}$$
(3.10)

where *T* is the absolute temperature, *M* is the molecular weight, *p* is the pressure, σ_{AB} is the collision diameter, and $\Omega_{D,AB}$ is the collision integral and dependent on temperature and intermolecular potential. Multi-precursors system in proposed method is handled by considering an effective binary diffusivity for each species through the gas mixture. The reactant diffusivity in gas mixture is determined from a mass fraction as,

$$\frac{1-x_i}{D_{im}} = \sum_{j=2}^{n} \frac{x_j}{D_{ij}}$$
(3.11)

where x_i is the mole fraction of the ith species, D_{im} is the effective binary diffusivity for the diffusion of i in a mixture, and D_{ij} is the binary diffusivity for the diffusion of i in j. The laminar gas flow is taken in CVD reactor. The reactant concentrations and gas velocity are taken zero at the substrate surface and increase to the bulk concentration and bulk stream velocity at some distance, δ , from the substrate surface is given by [8 - 11]

$$\frac{\delta}{x} = \frac{5.00}{\sqrt{Re}} \tag{3.12}$$

The average boundary layer thickness, δ , is computed by integrating eqn (3.12) over the length of the substrate and dividing the output by the length of the substrate,

$$\bar{\delta} = \frac{10}{3} \sqrt{\frac{\mu_{mix}L}{\rho U}} \tag{3.13}$$

Here L is the length of the substrate, ρ is the gas density, μ_{mix} is the viscosity of the gas mixture, and U is the free stream velocity. In case when the gases are well mixed at minimal temperature gradients, the diffusion path is determined by the concentration boundary layer, δc , which is related to the momentum boundary layer. It is characterized by a Schmidt number of unity as,

$$Sc^n = \frac{\delta}{\delta_c} = 1 \tag{3.14}$$

The viscosity of a gas mixture, μ_{mix} , is computed as,



$$\mu_{mix} = \sum_{i=1}^{n} \frac{x_{i}\mu_{i}}{\sum_{j=1}^{n} x_{i}\Phi_{ij}}$$
(3.15)

where,
$$\mu_i = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega_{\mu}}$$
 and $\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{1}{4}} \right]^2$ (3.16)

where n is the number of chemical species, and x_j are the mole fractions of species i and j, M is the molecular weight, T is the absolute temperature, σ is the collision diameter and Ω_{μ} is the collision integral for viscosity, x_i and x_j are the mole fractions of species i and j, M_i and M_j are the molecular weights of i and j respectively.

The kinetics of thin film growth is basically dependent on temperatures. A CVD reaction is divided into either surface kinetic or mass transport control. It can be well understood through chemical reactions in gas and surface phases. Suppose C_g is the concentration of the bulk gas and C_s is the concentration of reactants at the substrate interface. The concentration of the reactants drops from the bulk to the substrate surface and the corresponding mass flux is given by,

$$J_{gs} = h_g \left(C_g - C_s \right) \tag{3.17}$$

where h_g is the gas mass transfer coefficient and is insensitive to variations in temperature. The flux consumed at the surface of the thin film growth and can be approximated as first order by,

$$J_s = k_s(C_s) \tag{3.18}$$

where k_s is the slowest surface reaction rate constant. At steady state conditions when $J_{gs} = J_s$,

$$C_s = \frac{C_g}{1 + \frac{k_s}{h_g}} \tag{3.19}$$

If $k_s \gg h_g$, the system is dictated by mass controlled where low gas transport rate through the boundary layer limits the rapid surface reaction. Surface reaction control dominates when $h_g \gg k_s$ (C_s approaches C_g), the surface reaction is slow even through sufficient reactant gas is available. Additionally, h_g increases with increasing pressure and decreasing temperature and k_s follows the Arrhenius equation.

The sequential physical and chemical steps that occur inside **TNL-EpiGrow simulator** CVD process are summarized with simple fluid euations as follows:



• Fluid Flow equations used: Assume "laminar flow" i.e., smooth flow with no turbulence. Force F on the fluid:

$$F = \mu \frac{d\nu}{dz} \tag{3.20}$$

Here: v = velocity of fluid

z = distance from the surface

 μ = viscosity of fluid

• Fluid flow is often measured by Reynolds number (Re).

$$Re = \frac{dv\rho}{\mu} \tag{3.21}$$

Here: d = length of system (diameter of pipe)

 $\rho = density of fluid$

v = velocity

• Laminar Boundary thickness varies as distance from flow start

$$\delta = \frac{l}{\sqrt{Re}} \tag{3.22}$$

Here: Re = Reynolds number

l = distance from the substrate



3.5. Physics of MOCVD Reactor

The data base for various precursors' gases and the carrier gases with their chemical reaction rates as described in the chemical kinetics section are available in the **TNL-EpiGrow simulator** database. A mathematical model is implemented in the **TNL-EpiGrow simulator** for the complicated chemical mechanisms and simplified it through rate of production (ROP) analysis for optimization of chemical reaction mechanisms enabling the accurate prediction of growth rates for thin film [14 - 18].

Users have flexibilities to use their own gas-phase and surface reactions in the **TNL-EpiGrow simulator** by providing the A values which is the pre-exponential factor, n values which is the temperature exponent, E_a values which is the activation energy.

In TNL-EpiGrow simulator, the MOCVD reactor processes are dependent on the molecular flux interacting with the substrate atoms at substrate surface. The number of molecules that will stick to the surface after striking can be calculated as follows. This process is called Physisorption. Physisorption events follow a thermal or barrier less reaction model based on the fundamental kinetic theory of gases which is given by the following rate equation.

$$r_{a,i} = J_i s_c N_a \sigma \tag{3.23}$$

Where J_i is the flux of gas-phase radical i, s_c is the local sticking coefficient, N_a is the Avogadro number, and σ is the average area per surface site. Further, J_i can be calculated by

$$J_i = \eta_i u_i \tag{3.24}$$

while

and

 $\eta_i = \frac{p_i}{RT}$

$$u_i = \sqrt{\frac{8k_b T}{\pi m_i}}.$$
(3.26)

where η_i is the number density of radical i, u_i is the mean radical velocity, p_i is the partial pressure of radical i, R is the gas constant, T is the temperature, k_B is the Boltzmann constant, and m_i is the molecular weight of radical i. So the final equation for atoms is

$$r_{a,i} = \frac{p_i}{RT} \sqrt{\frac{8k_b T}{\pi m_i}} s_c N_a \sigma.$$
(3.27)

Here, k_B is the Boltzmann constant, and m_i is the molecular weight of radical i.



(3.25)

The sticking coefficient play important role in deciding the adsorption of molecules on the substrate surface and is implemented by the equation as;

$$s_c = A(1-m)\sum_{n=0}^{\infty} h_n^{hop}$$
(3.28)

Here, A is the adsorption probability, m is the occupied site on the lattice and n is the available vacant site on the lattice over which hopping or diffusion probabilities are dependent.



3.3 Physics of MBE Reactor

In **TNL-EpiGrow simulator**, Molecular Beam Epitaxy (MBE) reactor is used for the deposition of thin film compound semiconductors, metals or insulators that allows a precise control of compositional profiles by using a process far from the thermodynamic equilibrium. In **TNL-EpiGrow simulator**, MBE reactor can use one or more thermal particles and ordered crystalline substrate to form a thin layer whose crystallinity matches that of the substrate even though the composition of the materials may differ (e.g. SiGe/Si, GaAlAs/GaAs, CdTe/GaAs,...), the thermal particles do not interact with each other or with vacuum chamber gases until they impinge on the substrate. This effect is implemented through particle's long mean free paths which are involved in the deposition process [12 - 13].

In **TNL-EpiGrow simulator**, MBE reactor conditions are achieved by the incidence of one or more molecular beams which are generated in effusion cells, upon a substrate material. An effusion cell consists of a heated crucible containing the source material which sublimates or evaporates to form a molecular beam.

At the substrate surface, the arriving atoms or molecules of the source materials can undergo a number of processes, as summarised. Atoms weakly bound to the surface by van der Waals forces are treated physiosorbed, whereas those bound to the substrate by stronger chemical bonds are treated as chemisorbed. To become incorporated into the lattice, an atom must become chemisorbed at an epitaxial site and form bulk-like bonding configurations. The rate at which this occurs is defined through incorporation rate. Atoms and molecules have flexibilities to migrate across the surface, desorb back into the vacuum, or migrate into the crystal itself. Reactions between adatoms can occur as well, and this can be a crucial stage for breaking up large molecules.

In MBE reactor process, elements are heated in a Knudsen cell that is properly described as an isothermal enclosure with an infinitesimally small exit aperture bounded by vanishingly thin walls. A given material will maintain an equilibrium vapor pressure in such a cell because the small exit opening allows very little vapor to escape. The resulting flux of material from the cell has a velocity distribution determined by Maxwell Boltzmann statistics and a spatial distribution given by

$$J = 1.12 \times 10^{22} \frac{ap}{l^{\frac{1}{2}}_{MT} m^{1/2}}$$
(3.29)



Here J is the molecular flux (molecules/cm²-s), p is the vapor pressure (Torr) of the material in the cell, M is the molecular weight of the vapor (amu), T is the cell temperature (K), a is the area of the exit aperture and 1 is the distance from the aperture to the point at which the flux is measured.

Vapor Pressure of a the effuser cell element is calculated using crucible temperature and atomic number. Vapor pressure in the range of 10^{-15} to 10^{-3} atm are covered. The equation is:

 $log(p / atm) = A + B / T + C * log(T) + D / T^{3}$ (3.30)

The equation reproduces the observed vapor pressures to an accuracy of \pm 5 % or better. This equation is used for calculating the vapor pressure of metallic elements in both the solid and liquid state.

In **TNL-EpiGrow simulator**, there is flexibility to study the IV/IV, V/III and VI/II flux ratio and temperature dependences of the island characteristics during MBE epitaxial growth.



3.7 kinetic Monte Carlo (kMC) Technique

Monte Carlo (MC) method is a stochastic technique to solve any problem. MC simulation technique provides means of approximating solutions to problems through statistical sampling experiments based on randomness on a computer. The solution of non-equilibrium and kinetic phenomena through Monte Carlo (MC) methods can help in accurate prediction of the real events. The kinetic phenomena include the exploration of phase space which must be performed along a Markov chain of states such that each state is accessible from the preceding one along the chain, given the available degrees of freedom. The identification of all of the possible events that can occur and the determination of the rates at which these events occur can be extracted successfully with this technique. The kinetic Monte Carlo (kMC) technique has received a great deal of attention for modeling the vapor phase deposition of thin films. At the molecular-scale, surface evolution with involvement of a large number of competing chemical reactions in gas phase and surface phase at vastly different time scales, kMC is an ideal simulation methodology [9], [49].

Epitaxial Deposition occurs on a time scale which is generally not accessible to fully atomistic approaches such as molecular dynamics. An atomistically resolved Monte Carlo method parameterized by accurate chemical kinetic data is capable of exploring deposition over long range of times (min) at large surfaces (mm²). The most challenging problems in modeling of epitaxial growth through vapor phase or through effusion method are the accurate prediction of the rate of growth of the film and to capture the surface morphology as a function of reactor conditions along with defects, strain etc. All of these aspects can be resolved through kMC technique at the atomistic scale. The thin film surface structure evolution is possible through the atomistic deposition during growth; the surface structure and morphology are established and extracted by kinetic process, rather than equilibrium.

There are other approaches such as molecular dynamics (MD) method also able to provide possible solution for the evolution of the surface. However, since typical growth rates in epitaxial deposition techniques are of the order of microns per hour or monolayers per second, even most heroic MD simulations are capable of simulating the deposition of only a very small fraction of a monolayer within reasonable computational times as compared to kMC simulations, which



provide flexibilities to model the deposition of more than thousands of monolayers or even more depending upon the hardware capabilities. The fidelity of kMC simulations depends on the accuracy of relevant reaction rates data. Fortunately, it is much easier to determine chemical reaction rates in gas phase or surface phase from experiments or Arrhenius equation based calculations as compared to MD simulations where the full atom configuration–dependent energy required for the same. [38 - 40]

Kinetic Monte Carlo (KMC) technique implemented in the TNL-EpiGrow simulator for computation of total reaction and rates at the surface of substrate with the help of deposition, diffusion and desorption events. The rates of each event help in calculating total rates and is given as [49]:

$$R = A + H + D \tag{3.31}$$

Here A, H and D are the adsorption, diffusion and desorption rates respectively. The deposition rate or adsorption rate is measured as number of interacting adsorbed atoms per unit site per unit time. Since this rate is identical at every site on the surface, the total absorption rate is thus the number of simulation cells multiplying deposition flux of each cell and is given as [49]

$$A = Flw \tag{3.32}$$

Here A denotes the total absorption rate, F denotes incident atomic or molecular flux, and l and w denote length and width of substrate respectively.

The diffusion rate, or hopping rate (H), is the likelihood of an atom moving to its neighboring site. This is described through an Arrhenius relation;

$$h_j = D_0 exp\left(-\frac{E_j}{k_B T}\right) \tag{3.33}$$

Here h_j is the hopping rate of the jth atom, E_j is the activation energy of the jth atom and its unit is in eV, k_B is the Boltzmann constant in eV and T is the substrate temperature (K). The pre-factor D_0 corresponds to a vibration frequency which can be obtained by application of the equipartition theorem. The characteristic vibration frequency D_0 is given as [49]:

$$D_0 = \frac{2k_B T}{h} \tag{3.34}$$

Where k_B is Boltzmann's constant and h is the Plank's constant.



The desorption rate (D) is sum of different desorption rate of atoms. The one atom desorption rate can be described by Arrhenius relation and given as [49]

$$d_j = D_0 exp\left(-\frac{E_j^{des}}{k_B T}\right) \tag{3.35}$$

Here d_j is the desorption rate of the jth atom, E_j^{des} is the activation energies responsible for desorption of the jth atom and dependent on nearest neighbor energies as well, and T is the substrate temperature (K). The activation energies are generally different for each atom. The calculation of it is based on the assumption that bonds only exist between nearest neighboring atoms. Denoting E_s as the surface diffusion energy barrier, E_n is nearest binding energy and n as the number of nearest neighbors (n-n) on the surface, the total activation energy is thus computed as [49];

$$E_i^{des} = E_s + nE_n \tag{3.36}$$

Except for n-n interaction, other effects which are also responsible for activation energies such as step-edge barriers from descending steps in form of Schwoebel-Ehrlich barrier and ascending steps in form of incorporation barrier, are also relevant in surface diffusion.



3.7.1. Schwoebel-Ehrlich Barrier:

The Schwoebel-Ehrlich barrier—the additional barrier for an adatom to diffuse down a surface step which dictates the growth modes of thin films. For exchange of atoms between two facets, an adatom has to cross over the ridge, effectively diffusing down a surface step of multiple layers; the Schwoebel-Ehrlich barrier is therefore 3D. During a growth process, a facet may not be so flat, and surface steps can be of one, two, or many layers. As a result, the Schwoebel-Ehrlich barrier experiences a gradual transition from 2D to 3D. The impact of Schwoebel-Ehrlich barrier for accurately predicting the activation energy of an atom is given as [55];

$$E_j = E_S + nE_n + E_{shw} \tag{3.37}$$

Here E_{shw} denote the Schwoebel barriers energies.



Fig. 3.1: Side view of Schwoebel barrier



3.7.2. Incorporation Barrier:

Most of the incorporation sites are supplied by steps which result either from two-dimensional nuclei edges or from vicinal surface steps and their number and distribution are important features of the growth front can be accounted in term of incorporation barrier. The effect of incorporation barrier is included in activation energy of an atom as [49];

$$E_j = E_S + nE_n + E_i \tag{3.38}$$

Here E_i denote the incorporation barriers energies.



Fig. 3.2: Side view of incorporation barrier



These two barriers are destination dependent, so the activation energy for the same atom is also dependent on diffusion destination. The total hopping rate is calculated by $H = \sum_j h_j$. Since A is the total absorption rate and H is the total hopping rate, the total transition rate is calculated with eq. (3.31) including the desorption process into the analysis through $D = \sum_j d_j$. The rate of transition is denoted by R, or the times of events per unit time and this event can be either a deposition or diffusion. The time interval of an event, on one hand, is statistically inversely proportional to the total transition rate; on the other hand, is exponentially distributed. Thus the time interval formula is given as [49]:

$$\tau = -\frac{\log\xi}{R} \tag{3.39}$$

where τ denotes the time interval of an event, and ξ is a random number uniformly distributed between 0 and 1.

The event selection is also a random process in kMC and is controlled by a uniformly distributed random number x. If the total transition rate R multiplying x is smaller than the total deposition rate A, i.e.

$$\xi. R < A \tag{3.40}$$

Under above condition, the event is a deposition. If the product in eq. (3.40) is not smaller than A, the event is a diffusion. In case of deposition, since the flux is the same for all sites, we may easily find the deposition site by:

$$j = \sup\left(\frac{lw\xi R}{A}\right) \tag{3.41}$$

where the lateral size of simulation surface 1 and w are measured by unit cell and j reveals the deposition site from one of the lw sites. In case of diffusion, due to the different hopping rates for different atoms, we can only describe the hopping site by:

$$A + \sum_{k=1}^{j-1} h_k < \xi \cdot R < A + \sum_{k=1}^{j} h_k$$
(3.42)

Where j means the diffusing atom is the j^{th} one.



Every atom is ascribed four patches in tetrahedral arrangement, consistent with the Zinc blende symmetry (patches shown by flat dots on circle). An atom makes bond with another atom when its patches lie in a line. The interaction between two atoms depends upon the angle its patches make with each other (figure). The values of Θ_1 and Θ_2 has been computed by adaption of model proposed in reference [48].



Fig.3.3 The model promotes self-assembly of structures to be grown by kMC method

The model promotes self-assembly of structures to be grown by KMC method [48].



CHAPTER 4 OUTPUTS TNL-EpiGrow Simulator



The TNL-EpiGrow simulator provides many other relevant output parameters related to thin films as strain, roughness, defects, lattice parameters etc. It is capable to predict optimum conditions for epitaxial growth based on MBE, CVD and MOCVD reactors processes successfully. It is a user friendly graphical user interface (GUI) based simulator and does not require programming skill to write or coding the inputs. It works on windows platform with full capabilities; with GUI enabled control make it a simpler simulator.

The various atomistic physics based effects in terms of various outputs associated with each monocrystalline layers of the thin film can be traced easily. TNL-EpiGrow simulator has capabilities to trace and write the properties of each atom or molecule during simulation. The outputs details are given in details with physics based logical estimations.



4.1 Lattice Parameters

The important piece of information in terms of lattice parameters a, b, c, associated with the modeling of micro- or nano structure evolution is easily extractable from TNL-EpiGrow simulator. The lattice parameter of thin films as a function of temperature and composition play important role in deciding the crystalline quality of the micro- or nano structure grown through TNL-EpiGrow simulator or by real conditions in the laboratory. The simulated lattice parameters can be calibrated against XRD studies obtained lattice parameters of similar thin film grown in the Lab. Different regions in a solid micro- or nanostructure on the lattice impose mechanical constraint on each other, and thus when the lattice parameters change in any region on the lattice due to temperature or composition variations or due to a structural phase transformation, local elastic strains and stresses are develop, which can profoundly affect the local morphologies and spatial distributions of neighboring domains or atoms and their temporal evolution [56].

The TNL-EpiGrow simulator has capabilities to trace a single atom/molecule and its associated properties inside the reactor during epitaxial growth simulation experiments. The position of each bonded atom over the surface of substrate and beneath layer in terms of lattice parameters a, b and c are saved as output data file. For each monocrystalline layer of thin film, lattice parameters are computed through taking average of each lattice parameter i.e. a_{avg} , b_{avg} , and c_{avg} in the TNL-EpiGrow simulator.

The lattice parameters a, b, and c data saved as output provide valuable information regarding defects (e.g. vacancies), strain and other associated properties of the thin films.



4.2 Strain

The strain is a mechanical property associated with thin films. The ideal monocrystalline layer contains periodic arrangement of atoms on the lattice and atoms are bonded with each other in a regular fashion. In reality, the lattice deformation in the monocrystalline layer is introduced on the lattice in case if these period arrangements of atoms are disturb. There may be several factors and conditions may be responsible for generation of deformation on the lattice during reactor based epitaxial growth of monocrystalline layer [57]. The major factors responsible for generating deformation in the monocrystalline layer are listed below;

- 1. Addition of Impurity
- 2. Vacancy or Void creation during growth
- 3. Piezoelectric effects
- 4. Etc.

The addition of impurities altered the equilibrium positions of atoms in the lattice. The physics of the disorder impact on the band gap can be explained in terms of the atomic radii of the impurity and host atoms in the lattice. For example: the addition of the Cd atom (atomic radius 1.71 A) with ZnO thin film, the Cd atom has the probability of replacing either the Zn (atomic radius 1.39 A) or the O atoms (atomic radius 0.6 A) in the ZnO lattice. In both case the strain is introduce in the ZnO thin film [58].

The vacancies and voids are also responsible for generation of defects and also responsible for strain during epitaxial thin films growth.

Many properties of the material depend also on its polarity, for example, growth, etching, defect generation and plasticity, spontaneous polarization, and piezoelectricity. The piezoelectric effect results from two different contributions of opposite sign, which were referred to as the clamped ion" and "internal strain.

In TNL-EpiGrow simulator, strain may be induced during epitaxial growth over a relaxed virtual substrate with different lattice constant. The strain depends on the mismatch of the lattice constants and on the substrate orientation. The strain in the plane of the homo- and hetero-interface is implemented through the lattice mismatch



$$\epsilon = \frac{a_s - a_0}{a_0} \tag{4.1}$$

Here, a_0 is the lattice parameter of substrate or beneath monocrystalline layer over which deposition is done. a_s is the lattice parameter of the depositing materials. Under ideal situation no strain should be introduced during homoepitaxially growth. However, It is observed under real conditions in intermediate monocrystalline layers of thin film and at top almost the strain is observed to be relaxed.



4.3 Surface Roughness

In an generic epitaxial deposition process based on reactor configuration, thin film properties such as surface roughness and growth rate are highly dependent on macroscopic system inputs such as substrate temperature and inlet gas concentration. The macroscopic scale determines how these input process parameters will affect the overall growth dynamics of a system. In order to obtain precise control of film properties, the microstructure of the surface must also be considered; these properties are functions of much smaller length scales, typically on the order of several atoms. The surface roughness is a measure of thin film quality.

The TNL-EpiGrow simulator computes roughness in terms of the standard deviation of the height, where the height at each lattice point is compared to the average height of all lattice points, or more explicitly:

$$R = \left[\sum_{i}^{N} \sum_{j}^{N} \frac{(h_{ij} - h_{avg})^{2}}{N \times N}\right]^{\frac{1}{2}}$$
(4.2)

where is the total number of lattice points, h is the height at a given lattice point located at position i and j, on the square lattice and h_{avg} is the average height of all lattice points.



4.4 Defects

Based on dimensionality criterion in TNL-EpiGrow simulator, the defects are introduced in thin films during epitaxial growth based on various reactors geometries, can be categorized into four different major categories: zero-, one-, two- and three-dimensional defects. The respective examples are vacancies, dislocations, stacking faults and precipitates [59 - 61].

At high temperatures, the equilibrium concentrations of both vacancies and interstitials may be considerably higher than those at ambient temperature. However, during cool down of the same sample, these point defects could cluster together to form dislocation loops. Additionally, if temperature-gradient-induced stresses prevail during cooling, the loops could also serve as dislocation sources, leading to increased dislocation density. This problem is fairly acute in the case of materials produced from Groups II and VI and III and V of the Periodic Table because they are softer than silicon. During oxidation process if precautions are not taken, the resulting interstitials can cluster together to form extrinsic stacking faults [59 - 61].

Molecular Beam Epitaxy (MBE) process refers to the epitaxial growth of monocrystalline layers of thin films through reaction at substrate surface of molecular beams of the constituent elements with a crystalline surface maintained under ultra-high vacuum (UHV) conditions and at a suitable temperature. UHV condition helps in achieving low oxidation rate and contamination of the species.

The vapor phase growth process includes molecules adsorbed on the substrate surface and their subsequent pyrolysis releases the required atoms at hopping state and combined with each other to form a deposit. However, the atomic surface mobilities of various molecules are dependent on the growth temperature. At low growth temperatures, the surface mobilities are low, hence low point defect densities are observed. However, at high growth temperatures, high point defect densities are observed due to high atomic mobilities and imperfect monocrystalline layers deposited.



4.4.1 Vacancies & Interstitials

In TNL-EpiGrow simulator, the information regarding vacancies is extracted through mapping of each monocrystalline layer of grown thin film. The lattice site at which no atom is found and no bonds are observed at that particular atomic position is termed as vacancies. During the epitaxial growth experiment through TNL-EpiGrow simulator, the number of vacancies is extracted with output atomic growth data and through atoms positions on the lattice's unit cell tracings. The below figure shows the number of vacancies information in the grown thin film through TNL-EpiGrow simulator.

A type of point defect on the lattice during epitaxial growth is generated when an atom occupies a normally unoccupied site which is not preferable for bonding conditions in the lattice structure is known as an **interstitial defect.** The presence of interstitial defects can modify the physical and chemical properties of a material. The interstitials are shown in below figure.

In the TNL-EpiGrow simulator, the intrinsic point defects are introduced simply by virtue of temperature, for at all temperatures above 0 K there is a thermodynamically stable concentration. The mapping of concentrations of vacancy defects are implemented through ratio of defects to the number of occupancy site for atoms, corresponding to the condition of minimum energy is [62];

$$c_0 = exp\left(-\frac{E_f}{kT}\right)$$

where, E_f is the vacancy or interstitial formation energy, k is Boltzmann's constant and T is temperature (K).



4.4.2. Dislocations or Line Defects

Dislocations are the one-dimensional imperfections in the lattice are also known as line defects. The abrupt changes in the periodic arrangements of atoms along a line in the lattice are defined as line defects. Burgers vector (b) is used to characterize these types of imperfections. In TNL-EpiGrow simulator the measurement of direction and magnitude of Burgers vector is done through a loop construction around the disrupted region and noticing the extra inter-atomic spacing needed to close the loop.

In TNL-EpiGrow simulator, two types of *dislocations* are implemented to measure:

- Edge dislocation
- Screw dislocation

Edge dislocation is described as an edge of an extra plane of atoms within a monocystalline layer in the lattice plane. TNL-EpiGrow simulator provides flexibilities to measure density and location of *edge dislocation* generated in the lattice during reactor based epitaxial thin film growth.

Screw dislocation is a spiral ramp with an imperfection line down its axis. *Screw dislocations* result when displacing planes relative to each other through shear. The implementation of measurement of *screw dislocations* generated in the lattice during reactor based epitaxial thin film growth in TNL-EpiGrow simulator is under development and calibration.



4.4.3. Stacking Faults

Stacking faults are the disturbance in the regular stacking of planes and can be classified as intrinsic or extrinsic. The intrinsic faults in regular stacking are defined by absence of certain atomic layers and extrinsic faults are by addition of certain atomic layers in monocrystalling layer of lattice. There are probabilities of presence of some stacking faults in the epitaxial layer even in case of controlled epitaxial growth process. The clustering of point defects and quality of substrate surface pave way for generation of stacking faults. The simplest method for examination of stacking faults of layer surface is optical microscope but in most cases stacking fault are not visible on layer and have to reveal by chemical etching of epitaxial layer surface.

The tracing of *stacking faults* in TNL-EpiGrow simulator is implemented through extraction and mapping of stacking sequences of epitaxial monocrystalline layers in thin film on top of another. Suppose, the first two layers are identical for hcp and fcc, and labelled AB, the ideal stacking should be ABABABAB. As, the *stacking fault* is defined as a local deviation from one of the close-packed stacking sequences to the other one, only one- two- or three-layer interruptions in the stacking sequence are referred to as *stacking faults* e.g. ABABBABA. The density, size and locations of *stacking faults* are easily traceable through TNL-EpiGrow simulator.



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