Surface ordering of MBE grown 001 gallium(05) aluminum(05) arsenic: A theoretical study

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Surface ordering of MBE grown 001 $Ga_{0.5}Al_{0.5}As$: A theoretical study

Trivedi, Rita C., M.S.

University of Nevada, Las Vegas, 1993
SURFACE ORDERING OF MBE GROWN 001

\textit{Ga}_{0.5}\textit{Al}_{0.5}\textit{As} - A THEORETICAL STUDY

by

Rita C. Trivedi

A thesis submitted in partial fulfillment
of the requirements for the degree of

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in

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ABSTRACT

The surface kinetics of MBE growth of 001 Ga$_x$Al$_{1-x}$As is studied theoretically using the stochastic model which is based on the master equation approach and random distribution approximation. The kinetic processes included in the model are adsorption and surface migration. Evaporation is assumed to be negligible in the temperature range of study for both monatomic As and diatomic As$_2$ molecular species are considered. The model parameters such as atomic pair interaction energies, migrational frequency and activation energy were obtained from available experimental and theoretical data. The surface ordering kinetics is studied as function of fluxes, flux ratio and substrate temperature. The growth parameters employed for the monatomic spices As are: fluxes 2$^\circ$A/sec. for cations with the cation to anion flux ratios 1 : 10, and 1 : 20, and the substrate temperature in the range of 760$^\circ$K to 920$^\circ$K. The growth parameter employ for the diatomic spices As$_2$ are: fluxes 2$^\circ$A/sec. for cations with the cation to anion flux ratios 1 : 10, 1 : 20, and 1 : 30, for cations to anions and the substrate temperature in the range of 760$^\circ$K to 880$^\circ$K. The degree of ordering was obtained in terms of short range order (SRO), parameter. The order-disorder temperature is defined as the temperature of the maximum order, above and below which, SRO parameter decreases, was obtained for various growth conditions for both As and As$_2$ species. The order-disorder temperature was found to increase with flux ratio, while the maximum degree of the ordering decreased slightly. The surface or-
dering kinetics observed can be described in terms of effective surface migration rates of cations as follows. Lower temperature higher flux ratio results in smaller effective surface migration rates for cation, and hence lower SRO parameter. Beyond transition temperature the thermal energy, $\kappa_B T$, is large enough to break the $Al - Ga$ bonds and causes thermal randomization of the $Ga - Ga$, $Al - Al$, and $Ga - Al$ bonds resulting in the lesser degree of ordering. The above observations are supported by the dependence of roughness parameter and the isolated terrace adatom (cations and anions) parameters as a function of temperature. Even though, the result of the work qualitatively agree with the experimental work of Kuan et al. [1], there is a quantitative difference between the results in terms of degree of ordering and type of ordering. This discrepancy is attributed to the limitation of the model, and the model parameters.
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Chapter 1

INTRODUCTION

With the advent of ultra-high vacuum technique of Molecular Beam Epitaxy (MBE), heterostructures consisting of dissimilar materials of thicknesses $10^9$Å have been successfully grown and exploited for novel electro-optic and ultra high speed electronic applications. Since the epitaxial layers are grown under non-equilibrium conditions, many surface phenomena which are the result of kinetic effect occur during MBE growth. One such phenomenon which can have positive influence on the device application is the ordering in compound semiconductors [2].

In an ordered alloy AB, the atoms A and B occupy lattice points in a certain periodic arrangement instead of random arrangement. Such a periodic arrangement imposes a mini-periodicity over the already existing periodic crystal potential. Such a periodicity in potential greatly influences the energy gap, phonon modes and mobility of the carriers in the material, and thus has important implications on the device operation and applications.

Experimentally, ordering has been observed in many compound semiconductors, such as GaAsSb [3], InAsSb, GaInAs [4], GaInP [5], and GaAlAs [1]. These compound alloy semiconductors have been successfully prepared by one or more of the following techniques: molecular beam epitaxy(MBE), metal organic chemical vapor deposition(MOCVD), liq-
uid phase epitaxy (LPE), and organometallic vapor phase epitaxy (OMVPE). The presence
of ordering in the epilayers is usually observed using the Transmission Electron Micro-
scope (TEM) through the intensity of superstructure spots.

The ordering phenomenon in MBE growth is a surface phenomenon and is found to be
influenced by the epitaxial strain [6], substrate temperature [7], orientation [1], growth rate
[8], flux ratio [5], composition [9] and the growth technique [1].

Both theoretical and experimental models have been proposed to clarify the surface
ordering mechanism based on the energy minimization principle [10], surface reconstruc-
tion effect [13], bond length effect [13], strain effect [6], and kinetic effects such as the
exchange of atoms on the surface [14]. None of the above models explores the interplay of
thermodynamics and kinetics in detail.

The theoretical approaches reported in the literature to study the kinetics of MBE
growth are Monte Carlo simulations [16], [15], Molecular dynamic simulations [17], [18].
Rate equation model [19], and Stochastic modeling [20]. Each of these models have some
advantages and limitations. Both the Monte Carlo (MC) and Molecular Dynamic (MD)
simulations are size limited, but keep track of useful microstructure details of the surface
atomic configuration. The rate equation models and stochastic models are not size limited
but do not keep track of the microstructure details, instead they compute the probability
of surface atomic configurations using random distribution approximations.

1.1 Overview of the Thesis

This thesis addresses the issue of interplay of thermodynamics and kinetics in the surface
ordering phenomenon in the MBE growth of (100) GaAlAs theoretically using stochastic
modeling and compares it to the experimental work of Kuan et al. [1]. A brief literature
survey, discussing both the experimental and theoretical models for ordering in compound
semiconductors and MBE growth kinetic is presented in Chapter 2. The details of the
stochastic model for alloy studies along with modification for monatomic As and diatomic \( \text{As}_2 \) as molecular beam species are presented in Chapter 3. The results of the surface ordering kinetics study of \( \text{Ga}_{1-x}\text{Al}_x\text{As} \) with As and \( \text{As}_2 \) molecular beam species are discussed and compared with the experimental work of Kuan et al. [1] in Chapter 4. The conclusions are stated in Chapter 5.
Chapter 2

LITERATURE OVERVIEW

Since the first report on ordering in semiconductor alloys, the ordered structures are observed in nearly all the III-V alloy systems under various growth conditions and techniques. Several theoretical models have been developed in order to understand the phenomenon of ordering and its relations to the growth parameters and techniques of growth. In this section, the experimental and theoretical research reported in the literature on the ordering phenomenon in the compound semiconductors are reviewed.

2.1 Experimental Results

2.1.1 Alloy Systems Exhibiting Ordered Structures

The short range order at the lower temperature and long range order at the higher temperature of growth were observed in the MBE grown (001) $\text{GaAs}_{1-x}\text{Sb}_x$ epilayers in the temperature range of $480^\circ\text{C}$ to $580^\circ\text{C}$ [3]. The existence of two different types of domains of ordered structures were suggested to be caused by the surface atomic arrangements of the growing epilayers.

The observation of ordering in the organometallic vapor phase epitaxy (OMVPE) grown
GaAsP alloy at 680°C was reported [21]. The CuPt ($L1_2$ type) structure with the ordering along $<111>$ direction was observed using the transmission electron diffraction (TED) pattern studies at alloy compositions $x=0.3$ and 0.4. Only two of the four CuPt variants were observed. The ordering was explained in terms of surface kinetic model developed by Suzuki[4] and was attributed to the strain (induced stress) generated due to the difference in atomic sizes of As and P atoms.

The CuPt type ordering was observed in organometallic vapor phase epitaxy (OMVPE) grown (001) $InAsSb$ alloy in the temperature range of 375°C - 480°C [21]. Only two of the four variants were formed during the growth. The degree of ordering of these two variants were found to be varying in different growth domains. The degree of ordering was highest at $x = 0.5$ and decreased as $x$ approached to either 0 to 1. The surface kinetic model proposed by Suzuki et al. was found to adequately explain such ordering.

The ordered phases were observed in $Ga_{0.47}In_{0.53}As$ alloy semiconductor grown at 600°C by vapor levitation epitaxy (VLE) with the $<111>$ as the growth direction [22]. Only one of the four variants (the variant only along one of [111] directions) was observed. It was explained to be appearing due to the formations of alternate $In$ and $Ga$ rich (111) planes in the group III sublattice.

The kinetics of ordering in atmospheric pressure organometallic chemical vapor deposition (OMCVD) grown $GaInP$ in the temperature range of 600°C to 750°C was reported [5]. The ordering kinetics were studied by measuring the $GaInP$ energy band gap as a function of growth rate and temperature. The surprisingly complex variation in band gap was observed in five different temperature regions.

Long range order (a periodic composition modulation) was observed in $Al_xGa_{1-x}As$ by Kuan et al[1] in 1985. The $Al_xGa_{1-x}As$ was grown epitaxially on the (110) or (100) oriented substrates in the temperature range of 600°C to 800°C. The ordered structure consisted of alternating monolayers of $AlAs$ and $GaAs$ planes, when viewed along the [001]
direction normal to the growth axis. This ordered structure was identified as \( L1_0 \) or CuAu-I type. The surface diffusion of Ga and Al atoms during the high temperature growth was considered as a possible mechanism for the ordered structure. Degree of ordering was observed to be strong in [110] growth and the strongest ordering was observed at 650°C. The orientation dependence was attributed to the larger diffusion length of cation along [110] growth direction.

The order-disordered transition in the \( Ge_xSi_{1-x} \) strained superlattice grown by MBE on [100] \( Si \) at 500°C was observed by Ourmazd and Bean [6]. It was proposed based on the experimental evidence that the observed order-disordered transition in the Gesi/Si systems is strain driven and stabilized.

### 2.1.2 Role of Kinetics in Ordering

The important kinetic factors such as growth temperature, growth rate, flux ratio, and the substrate orientations play a vital role in determining the type and the extent of ordering.

Several experimental observations on the effect of the kinetic factors are reported in the literature[1][8]. For example, the effect of growth temperature on ordering is indicated by the absence of ordering in (110) oriented \( GaAsSb \) growth experiment at the reduced temperature of 550°C and growth rate of 0.02 \( \mu m \) per mins. [8]. Also, when the growth rate was reduced by a factor of 2 at 550°C, the ordered structure reappeared in (110) oriented \( GaAsSb \), demonstrating the effects of growth rate on the ordering in the material. Similarly, the suppression of ordering was noted in \( Ga_{0.5}In_{0.5}P \) grown at 680°C temperature, and 0.2 \( \mu m \) per mins. growth rate indicating the effect of the growth parameters. The role of kinetic factors was demonstrated in the studies of the effects of step motion on the ordering in OMVPE grown (001) \( GaInP \) at 670°C [8]. The TED studies revealed that the two directions of step motions produces two different ordered variants in (\( \bar{1}11 \)) and (1\( \bar{1}1 \)) directions[19].
Kuan [1] observed the effect of change in the substrate orientations and temperature on the degree of ordering by TEM $Al_xGa_{1-x}As$ grown by MBE. In this study with substrate orientations [110] and [100], the range of composition $x=0.25$ to $0.75$ and temperature range of $600^\circ$C to $800^\circ$C were used. The degree of ordering was the highest for the substrate orientation [110] at the composition $x=0.75$ and $700^\circ$C temperature. The degree of ordering was found to be decreasing otherwise. The orientation dependence was attributed to larger diffusion length of cation along the [110] growth direction.

2.1.3 Influence of Ordering on the Properties of the Alloy Semiconductors

In ordered alloy structures, the absence of random fluctuations result in the elimination of alloy scattering. Thus the free carrier mobility is enhanced in the ordered alloy which makes the structure fabricated out of ordered alloys most suitable for high speed device applications.

The formation of ordered structures also influences the magnitude of the energy band gap in certain materials.[8] The band gap energy of the MOVPE grown (001) $Ga_{0.5}In_{0.5}P$ in the temperature range of $550^\circ$C to $750^\circ$C with the Long Range Order (LRO) has been found to be about $80$ meV lower than that of the random alloys. [23]. Also, In $Ga_{1-x}As_xSb$, the band gap shrinkage caused by ordering is calculated to be $800$ meV, which is quite significant. The band gap shrinkage is highly undesirable in devices like visible light emitting diodes, where the wavelengths in the visible region (shorter) are needed. The shrinkage of band gap may actually prove useful for the infrared emitter and detectors where the longest wavelengths are desired.

Hence in order to produce materials useful for specific applications, the control and thorough understanding of the ordering process in epitaxial semiconductor materials is extremely vital. There are many studies in the literature on the role of thermodynamic
and kinetic factors that play an important role in determining the degree of ordering in materials. [8].

2.2 Theoretical Models for the Ordering in Semiconductor Alloys

The physical origins of stable and metastable ordering in epitaxial and bulk semiconductor alloys is explained thermodynamically by Zunger et al. [10], based on the theory of stability, which included charge transfer, elastic forces and atomic relaxation. The microscopic strain energy associated with the packing on the lattice atoms A and B of dissimilar sizes can lead to [i] mixing enthalpy for disorder phase, $\Delta H^{(D)} > 0$, even if the microscopic interaction between A and B is attractive, and [ii] a preference at low temperatures of ordered (O) over disordered arrangements even if the formation enthalpy of the ordered compounds $\Delta H^{(O)} > 0$. In either case, long range ordered phases which are stable or metastable could exist at sufficiently low temperature, as long as $\Delta H^{(O)} < \Delta H^{(D)} (x = 0.5)$. The ordered phases were observed to occur spontaneously in lattice-matched epitaxial growth experiments.

The bond length model was proposed by Norman et al. [13] to account for the ordering in III-V ternary alloys. The proposed model explains how the minimization of strain energy (generated by the unequal length of the bonds between the Group III-V atoms) results in the favored atomic arrangement, leading to ordering in the material. In MOVPE grown (001) $Ga_{0.5}In_{0.5}As$, the unequal bond lengths of $Ga - As$ and $In - As$ give rise to displacement of the As atoms and strain in the layers. In order to minimize the strain energy at the surface, the $Ga$ and $In$ atoms alternate along the $[110]$ direction. As a result, rows of $Ga$ and $In$ atoms occur along the $[110]$ direction as shown in Figure 2.1. Consequently, when the additional monolayers are grown, the ordering appears along the $(\bar{1}11)$ and $(\bar{1}1\bar{1})$ directions.
The surface reconstruction model proposed by Murgatroyd [13] shows that the ordering may be the direct consequence of the surface reconstruction, leading to lowering of the energy of the growing surface. The epitaxial layers of Ga_{0.5}As_{0.5}Sb with varied compositions were grown by MBE at about 520°C on (001) GaAs substrate. At all compositions, the ordering was observed on (111) and (111) planes but not on the (111) and (111) planes. The ordering was correlated with the corresponding changes in the reconstruction of the dangling bonds at the growing surface during MBE growth.

Ogale and Madhukar [14] have taken a different approach based on the use of interatomic potentials to develop a surface relaxation model. It was shown in the model that the sequential interplay of the processes like adsorption, migration, and dimmerization occurring in the different layers during the MBE growth can lead to ordering in [100] AlGaAs. The surface relaxation controlled mechanism is proposed and substantiated in the model for occurrence of long range ordering in III-V compound semiconductor alloys grown by MBE. It was concluded that the surface reconstruction and its evolution during growth, the nature of cation migration processes, and the anion formative reactions were of central importance.

A kinetic model was proposed by Suzuki [24] to explain the ordering in group III-V ternary and quaternary alloys. The model explains the formation mechanism for the naturally formed monolayer superlattice (SL) on the column III sublattice in the GaInP grown by the organometallic vapor epitaxy (OMVPE). The mechanism consists of two mechanisms (M1, for intraplane and M2 for interplane) for two different long range orders. The principle of stress reduction gives rise to the site occupation anisotropy for the Ga and In atoms. This anisotropy comes from the following: 1) the dangling bonds directions asymmetry and 2) large bond-length difference between Ga – P and In – P. Hence the driving force for the M1 mechanism. The M2 mechanism is interpreted as the phase-locking mechanism, ascribed to the selective setting of Ga atoms in the specified direction. The kinetic model describes the growth condition dependency of superlattice (SL) formation in GaInP and
has been successfully applied to other alloy systems [24].

2.3 Theoretical Models for the Study of MBE Growth

The theoretical tools employed in the study of growth processes such as MBE, MOCVD, OMVPE are: Monte Carlo simulations (MC), Molecular dynamics (MD), and the stochastic models. This section briefly reviews these models for studying MBE growth.

MC simulations are based on the rigid lattice of finite size, usually 30x30x10. The surface kinetic events, typically, considered in the MC model are incorporation, surface migration, and reevaporation. All of the possible kinetic events at all the lattice sites in the crystal are considered to determine which event occurs and the time at which the event occurs. The probabilities of occurrence of an event is found in terms of the rates of the kinetic events. Rates of surface migration and evaporation are computed using Arrhernius type rate equations involving frequency factors and activation energy for the process. The first and second nearest neighbor pair interaction energies are employed for calculating the binding energies of individual atoms. MC simulations develop the macroscopic understanding of the MBE growth process in relation to growth parameters involving surface kinetic processes. MC simulations study the macroscopic kinetic processes only and do not deal with the atomistic details. The MC simulations are widely used to study MBE growth kinetics of compound semiconductors [15],[16].

The other type of theoretical tool employed in studying MBE growth is MD simulations. In this approach the dynamics of the movement of the atoms is computed based on the Newton’s 2nd law and the experimetally fitted potential energy function for semiconductors. The classical dynamic equations of motion are used to study the surface atomic dynamics involving pico second time scale. MD simulations are employed to study the surface kinetics during the epitaxial growth, the dynamics of strained layer epitaxy, and the evolution of the surface diffusion coefficient. [17],[18]. MD simulations can not be employed for simulating
the surface kinetic processes which occur in the millisecond time scale. It is CPU limited but is very useful for the study of kinetics in the initial stage of the crystal formation and in capturing the atomistic details of surface kinetic processes.

CPU time and the crystal size limitations are major limiting factors for the MC and MD simulations. The dependency of the parameters on the available data also degrades the importance of the MC simulations as a potential theoretical tool.

Venkatasubramanian [20] developed a stochastic model for the growth of compound semiconductors based on the work of Siato et al. [19]. In the modeling, the diamond cubic structure and the two-sublattice nature of the semiconductor crystals were taken into account. The developed model was then extended to accommodate the alloying of the two sublattices. Up to two elements per sublattice can be accommodated. The stochastic model has been successfully employed to study the surface and roughening kinetics in GaAs (100) and Ge (001) respectively. One of the important features of the stochastic model is that it is not limited by the crystal size and can be employed to study the doping kinetics in the crystals. Its major limitation is that it does not keep track of surface atomic configuration. But it can be obtained from the available data using random distribution approximation.
Figure 2.1: A schematic representation of bond length deformation in (001) $Ga_{0.5}In_{0.5}P$. 
Chapter 3

STOCHASTIC MODEL

In this chapter, the stochastic model employed in the [100] MBE growth kinetic studies of compound semiconductors is described [20]. Firstly, the physical basis of the model and the assumptions made are described. Then the time evolution differential equations of macro-variable are presented and the terms in the equations are detailed. The boundary conditions for the coupled non-linear first order differential equation are described. Finally, the computational details for solving the differential equations are presented.

3.1 The Kinetic Model

The surface processes considered in the stochastic model are: adsorption, evaporation, and migration. Two types of surface migration processes, intralayer and interlayer migrations, are considered. These processes are pictorially represented in Figure 3.1.

Adsorption is allowed only at the sites where the surface covalent bonds from the layer below are satisfied. (solid - on - solid restriction, SOS). In other words overhangs of atoms are not allowed. In the case of [100] growth of compound semiconductors which are zinc blende crystals, the modified SOS restriction, MSOS, implies that two nearest neighbor surface atoms be present before an atom gets incorporated at a site in between them at a
layer just above as shown in Figure 3.2. Thus, the rate of adsorption can be written as the product of surface sites satisfying the SOS restriction and the flux rate.

Evaporation of atoms exposed to vapor are considered as these atoms have the lowest binding energy and hence have higher probability of evaporation. Moreover, the SOS restriction requires that only these atoms are conserved. The rate of evaporation is determined as a product of the fraction of a layer exposed to the vapor, the rate of evaporation of an isolated atom, and the term involving the binding energy of the atom. The rate of evaporation of an isolated $a$ type atom is described by Arrhenius type rate equation involving frequency factor and activation energy and for evaporation, the rate is given by:

$$R = R_0 e^{-\frac{E_{act} + K_{aa} + K_{ax}}{kT} p q}$$  \hspace{1cm} (3.1)$$

where $R_0$ is the frequency factor, $E_{act}$ is the activation energy for an isolated atom, $K_{aa}$ and $K_{ax}$ are the pair-interaction energies for $a - a$ and $a - x$ bonds respectively, $p$ is the fraction of $a$ type atom, and $q$ is the fraction of $b$ type atom. The activation energy for evaporation of an isolated atom is equal to that of its binding energy. It is noted that the binding energy is dependent on the surface atomic configuration surrounding the atom under consideration.

The surface migration processes are also allowed only for the atoms exposed to vapor. Rates of intralayer and interlayer migrations are considered equal. Rates of these migrations are described as the product of the sites, atoms available for migration, the rate of migration of an isolated atom, and the binding energy of the atom. The rate of migration of an isolated atom is expressed in terms of Arrhenius type rate equations involving frequency factor and activation energy for surface migration. The activation energy is dependent on the surface
atomic configuration. The rate equation is similar to the Eq. 1.2 except for the fact that $E_{act}$ is smaller for the migration.

In this study for the adsorption process of As, two cases, monatomic ($As$) and diatomic ($As_2$) molecular species, are considered and compared. For the monatomic molecular species, $As$, the incorporation of an $As$ atom at a site satisfying the SOS condition in the $2n + 1^{th}$ layer requires that two nearest neighbor $Ga$ atoms (or one nearest neighbor $Ga = Ga$ pair) be available in the $2n^{th}$ layer. For the diatomic molecular species, $As_2$, the incorporation of two $As$ atoms at two of the nearest neighbor sites satisfying the SOS condition in the $2n + 1^{th}$ layer requires that four $Ga$ atoms be available in the $2n^{th}$ layer.

3.2 The Stochastic Model

The stochastic model is a rate equation model based on the master equation approach, quasi-chemical approximation and the solid on solid (SOS) restriction. The master equation is a gain-loss equation which conserves the macro-variables based on all possible reversible rate processes. Example of the reversible rate processes are: adsorption and evaporation. The time rate of change of the concentration of atoms $C(n)$ and atom-vacancy bonds $Q(n)$ in each layer are described in terms of the transition probabilities of the kinetic processes, such as adsorption, reevaporation and surface migration. The key principle behind the master equation approach is the detailed balancing condition to be satisfied under the dynamic equilibrium condition. The condition of detailed balance is described by:

$$W_R(h_i,h_j)P_{eq}(h_i) = W_R(h_j,h_i)P_{eq}(h_j)$$  \hspace{1cm} (3.2)
where $W_R(h_i h_j)$ and $W_R(h_j h_i)$ define the transition rates for two reversible processes and the respective transition probabilities is given by $P_{eq}(h_i)$. The condition of detailed balancing suggest that rate of reversible processes (adsorption and evaporation) should be equal at equilibrium. In other words, at equilibrium (dynamic), on an average no change in the macro-variables should result.

One of the key assumptions in the model is the quasi-chemical approximation. In this approximation, the number of a particular surface atomic configuration is described in terms of the total number of macro-variables irrespective of the surface atomic configuration, and the probabilities of all possible surface atomic configuration. The probability distribution is assumed to be trinomial. For example, consider a surface atom with co-ordination number four and that the probability for $a$ type atomic neighbor is $p_a$, for $b$ type atomic neighbor, $p_b$, and for vacancy as a neighbor, $p_v$. The probability of presence of such configuration, $P_r(k, l)$, is given by trinomial distribution as:

$$
P_r(k, l) = \binom{4}{k} \binom{4-k}{l} (p_A)^k (p_B)^l (p_V)^{4-k-l}
$$

(3.3)

where $\kappa$ is the number of $a$ neighbors, $l$ is the number of $b$ neighbors, and $4 - k - l$ is the number of vacancies. With the probability for a certain surface atomic configuration known, the binding energy of the central atom in that configuration can be computed based on the number of its neighbors as:

$$
E_{binding} = E_{binding,iso} + \kappa E_{aa} + l E_{ab}
$$

(3.4)
where \( k \) is the number of \( a \) neighbors, and \( l \) is the number of \( b \) neighbors. This information is required for computing the evaporation and migration rates.

The additional assumption built in the model is the rigid lattice model with the nearest neighbor pair interactions within the growing plane. Due to the SOS restriction, the interactions of all the atoms with the lower layer are assumed to be identical.

It is noted that the effects of epitaxial strain, and surface reconstruction on the kinetics are not considered; Also the anti-site defect, (i.e.), anion present in the cation sublattice and vice versa is not allowed. This is typical of the Monte Carlo simulations. But it limits the scope of the model to studies with defects kinetics.

### 3.2.1 Macrovariables

Zinc blende crystals have two sublattices, cation and anion sublattices. Therefore, two sets of macro-variables, one for each sublattice, should be defined. In the case of \( Ga_{0.5}Al_{0.5}As \), the cations (\( Ga \) and \( Al \)) are assumed to belong to the even sublattice and anion (\( As \)) to the odd sublattice. The macrovariables that can be defined for the \( 2n^{th} \) layer are: concentration variables, \( C_{Ga}(2n) \), and \( C_{Al}(2n) \), the second nearest neighbor atom-vacancy bond densities, \( Q_{Ga}(2n) \), and \( Q_{Al}(2n) \), the second nearest neighbor atom-atom bond densities, \( \tilde{N}_{Ga,Al}(2n) \), \( \tilde{N}_{Ga,Al}(2n) \), and \( \tilde{N}_{Al,Al}(2n) \). These above described variables involve only one layer. In other words, the bonds used in the description of the above variables are inplane.

Of the seven variables described, only five are independent due to the following relations:

\[
\tilde{N}_{Ga,Ga}(2n) = 2C_{Ga}(2n) - \frac{1}{2}Q_{Ga}(2n) - \frac{1}{2}\tilde{N}_{Ga,Al}(2n)
\]
for Ga–Ga bond density.

\[ \tilde{N}_{\text{AlAl}}(2n) = 2 C_{\text{Al}}(2n) - \frac{1}{2} Q_{\text{Al}}(2n) - \frac{1}{2} \tilde{N}_{\text{GaAl}}(2n) \]

for Al–Al bond density and

\[ \tilde{N}_{\text{VV}}(2n) = 2 (C_V(2n) - \frac{1}{2} Q(2n)) \]

(3.5)

for vacancy-vacancy bond density.

The vacancy density, \( C_V(2n) \) used in Eq. (1.5) is given by:

\[ C_V(2n) = (1.0 - C(2n)) \]

and

\[ C(2n) = C_{\text{Ga}}(2n) + C_{\text{Al}}(2n) \]

and

\[ Q(2n) = Q_{\text{Ga}}(2n) + Q_{\text{Al}}(2n) \]

(3.6)

Similar set of equations can be written for the anion sublattice, (i.e.), As. In the derivation of the Eqs.(3.5)-(3.6), the inplane coordination number is assumed to be four.

In this study only the cation sublattice is alloyed, (i.e.), there are two kind of atoms, Ga and Al present in the cation sublattice, and only one kind of atom, (i.e.), As, in the anion sublattice. Thus, five independent macrovariables for cation sublattice and two independent macrovariables for the anion sublattice should be considered to study the kinetics of MBE growth of \( \text{Ga}_x\text{Al}_{1-x}\text{As} \). The independent variables considered are : \( C_{\text{Ga}}(2n) \), \( C_{\text{Al}}(2n) \), \( Q_{\text{Ga}}(2n) \), \( Q_{\text{Al}}(2n) \), \( \tilde{N}_{\text{GaAl}}(2n) \), \( C_{\text{As}}(2n + 1) \), and \( Q_{\text{As}}(2n + 1) \).
3.2.2 Time Evolution Equations

In this section, the time evolution equations for the compound semiconductor alloy with the monatomic As are presented and described in terms of various surface kinetic processes.
The time evolution equation for \( C_a(2n) \) is given by [20]:

\[
\frac{dC_a(2n)}{dt} = \frac{1}{\tau_r} \left( \left[ \frac{\tilde{N}_{bb}(2n-1)}{2} - C_a(2n) \right] e^{L_a} \right.

- \left[ C_a(2n) - 2C_b(2n+1) + \frac{\tilde{N}_{bb}(2n+1)}{2} \right] \left[ \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^2

+ \frac{4}{\tau_d} \left( \left[ \frac{\tilde{N}_{bb}(2n-1)}{2} - C_a(2n) \right] e^{L_{oo}} \right)

- e^{L_{ps}} \left[ C_a(2n) - 2C_b(2n+1) + \frac{\tilde{N}_{bb}(2n+1)}{2} \right] \left[ \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^2
\]
where \( e^{L_{oa}} \), \( e^{L_{pa}} \), are given by:

\[
e^{L_{oa}} = \sum_{-\infty}^{\infty} \left( \frac{C_{a}(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\bar{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2}\bar{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2}Q_a(2n)}{2C_a(2n)} \right]^4,
\]

and

\[
e^{L_{pa}} = \sum_{-\infty}^{\infty} \left[ \frac{\bar{N}_{cc}(2n-1)}{2} - C(2n) \right] \neq 1,
\]

where \( e^{L_{oa}} \), \( e^{L_{pa}} \), are given by:

\[
e^{L_{oa}} = \sum_{-\infty}^{\infty} \left( \frac{C_{a}(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\bar{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2}\bar{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2}Q_a(2n)}{2C_a(2n)} \right]^4,
\]

and

\[
e^{L_{pa}} = \sum_{-\infty}^{\infty} \left[ \frac{\bar{N}_{cc}(2n-1)}{2} - C(2n) \right] \neq 1,
\]
where \( \frac{La}{ra} \) is the flux of atoms in atoms/site sec., and \( 2Ka_\alpha \) and \( 2Ka_x \) are the \( \alpha - \alpha \) and \( \alpha - x \) pair interaction energies, respectively. The coordination number is assumed to be four in the above equations.

Term A1 describes the rate of gain of \( C_\alpha(2n) \) due to adsorption of the atoms in terms of number of sites available and the flux rate. Term A2 describes the rate of loss of \( C_\alpha(2n) \) due to the evaporation of the \( Ga \) atoms in terms of the fraction of the \( 2n^{th} \) layer exposed (allowed to evaporate), rate of evaporation of an isolated atom and the various possible surface atomic configurations and their binding energies. The intralayer surface migration does not change the configuration of the \( Ga \) atoms in any layer and therefore, no such term is present in the Eqs. A2. Term C1 describes the rate of gain and loss of \( Ga \) atoms in the \( 2n^{th} \) layer due to \( Ga \) atoms migrating in and out of the \( 2n^{th} \) layer, from and to other layers. The gain term is described in terms of available sites in the \( 2n^{th} \) layer, the rate of migration of an isolated \( Ga \) atom, the number of atoms exposed to vapor in the other layers, the possible surface atomic configuration and the binding energy of exposed atoms. Similarly the loss term is also defined.
The time evolution equation for $Q_a(2n)$ is given by [20]:

\[
\frac{dQ_a(2n)}{dt} = \frac{4}{\tau_{ra}} \left( \left[ \frac{\bar{N}_{cc}(2n-1)}{2} - C(2n) \right] e^{\ell_{a}} \left[ \frac{\bar{N}_{vv}(2n) - \frac{1}{2} Q_a(2n)}{2C_v(2n)} \right] \right.

- \left( \frac{C_a(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\bar{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \bar{N}_{a\pi}(2n)e^{-2k_{a\pi}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^4

\times \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} - \frac{1}{2} Q_a(2n)}{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \bar{N}_{a\pi}(2n)e^{-2k_{a\pi}} + \frac{1}{2} Q_a(2n)} \right] \left[ \frac{\bar{N}_{cc}(2n+1)}{2} \right]

- \frac{4}{\tau_{rx}} \left( \left[ \frac{\bar{N}_{cc}(2n-1)}{2} - C(2n) \right] e^{\ell_{x}} \left[ \frac{1}{2} Q_x(2n) \right] \right.

\left. \times \left[ \frac{\bar{N}_{xx}(2n)e^{-2k_{xx}}}{\bar{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \bar{N}_{a\pi}(2n)e^{-2k_{a\pi}} + \frac{1}{2} Q_x(2n)} \right] \right)

\left. \left[ \frac{\bar{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \bar{N}_{a\pi}(2n)e^{-2k_{a\pi}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right]^4 \right)

\]
\[ + \frac{3}{\tau_d^{\text{intra}}} \left[ \frac{\tilde{N}_{cc}(2n-1)}{C_v(2n)} - \frac{C_a(2n)}{2} \right] Q_a(2n) \]
\[ \times \left( \frac{C_a(2n)}{C(2n)} \right) \left[ \frac{C(2n) - 2C(2n + 1) + \tilde{R}_{cc}(2n+1)}{C_a(2n)} - \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} - \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right] \left[ \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \tilde{N}_{aa}(2n) e^{-2k_{aa}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^3 \]
\[ \times \left[ \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \tilde{N}_{aa}(2n) e^{-2k_{aa}} + \frac{1}{2} Q_a(2n)}{2C_v(2n)} + \frac{\tilde{N}_{vv}(2n) - \frac{1}{2} Q_a(2n)}{2C_v(2n)} \right] \]
\[ + \frac{3}{\tau_d^{\text{intra}}} \left[ \frac{\tilde{N}_{cc}(2n-1)}{C_v(2n)} - \frac{C_f(2n)}{2} \right] Q_f(2n) \]
\[ \times \left( \frac{C_a(2n)}{C(2n)} \right) \left[ \frac{C(2n) - 2C(2n + 1) + \tilde{R}_{cc}(2n+1)}{C_a(2n)} - \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \tilde{N}_{aa}(2n) e^{-2k_{aa}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^3 \]
\[ \times \left[ \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \tilde{N}_{aa}(2n) e^{-2k_{aa}} + \frac{1}{2} Q_a(2n)}{2C_v(2n)} + \frac{\tilde{N}_{vv}(2n) - \frac{1}{2} Q_a(2n)}{2C_v(2n)} \right] \]
\[ + \frac{16}{r_{\text{intera}}^2} \left[ \frac{\bar{N}_{cc}(2n-1)}{2} - C(2n) \right] e^{L_{ps}} \left[ \frac{\bar{N}_{vv}(2n) - \frac{1}{2} Q_{a}(2n)}{2C_{v}(2n)} \right] \]
\[ + e^{L_{ps}} \left( \frac{C_{a}(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\bar{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \bar{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_{a}(2n)}{2C_{a}(2n)} \right]^4 \]
\[ \times \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} - \frac{1}{2} Q_{a}(2n)}{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \bar{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_{a}(2n)} \right] \]
\[ - \frac{16}{r_{\text{intera}}^2} \left[ \frac{\bar{N}_{cc}(2n-1)}{2} - C(2n) \right] \]
\[ \times \left( \frac{C_{a}(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\bar{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \bar{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_{a}(2n)}{2C_{a}(2n)} \right]^4 \]
\[ \times \left[ \frac{\bar{N}_{aa}(2n)e^{-2k_{aa}} - \frac{1}{2} Q_{a}(2n)}{\bar{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \bar{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_{a}(2n)} + \frac{\bar{N}_{vv}(2n) - \frac{1}{2} Q_{a}(2n)}{2C_{v}(2n)} \right] \]
\[ + \frac{16}{\tau_d \text{inter}} \left( \left[ \frac{\tilde{N}_{cc}(2n - 1)}{2} - C(2n) \right] e^{\text{los}} \left[ \frac{\tilde{N}_{uv}(2n) - \frac{1}{2} Q_a(2n)}{2C_v(2n)} \right] \right) \\
+ e^{L_{px}} \left( \frac{C_x(2n)}{C'(2n)} \right) \left[ C(2n) - 2C(2n + 1) + \frac{\tilde{N}_{cc}(2n + 1)}{2} \right] \left[ \frac{\tilde{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right]^4 \\
\times \left[ \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} \right] \left[ \frac{\tilde{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right] \left( \frac{\tilde{N}_{cc}(2n - 1)}{2} - C(2n) \right) \\
\times \left( \frac{C_x(2n)}{C'(2n)} \right) \left[ C(2n) - 2C(2n + 1) + \frac{\tilde{N}_{cc}(2n + 1)}{2} \right] \left[ \frac{\tilde{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right]^4 \\
\times \left[ \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} \right] \left[ \frac{\tilde{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} + \frac{\tilde{N}_{uv}(2n) - \frac{1}{2} Q_a(2n)}{2C_v(2n)} \right] \]
where $e^{L_{oa}}$, $e^{L_{ox}}$, $e^{L_{pa}}$, and $e^{L_{px}}$ are given by:

$$e^{L_{oa}} = \sum_{-\infty}^{\infty} \left( \frac{C_a(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n + 1) + \frac{N_{cc}(2n + 1)}{2} \right] \left[ \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2}\tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2}Q_a(2n)}{2C_a(2n)} \right]^4,$$

$$e^{L_{ox}} = \sum_{-\infty}^{\infty} \left( \frac{C_x(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n + 1) + \frac{N_{cc}(2n + 1)}{2} \right] \left[ \frac{\tilde{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2}\tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2}Q_x(2n)}{2C_x(2n)} \right]^4,$$

$$e^{L_{pa}} = \sum_{-\infty}^{\infty} \left[ \frac{N_{cc}(2n - 1)}{2} - C(2n) \right] \neq 1,$$

and

$$e^{L_{px}} = \sum_{-\infty}^{\infty} \left[ \frac{N_{cc}(2n - 1)}{2} - C(2n) \right] \neq 1,$$

respectively.
The change in $Q_a(2n)$ due to adsorption is described by the term $A_2$ for the $a$ atoms in terms of the fraction of a layer available for adsorption, rate of adsorption of an isolated atom, and the change in the surface atomic configuration due to adsorption of an $a$ atom in the layer. The change in $Q_a(2n)$ due to evaporation of an $a$ atom is described by the term $B_2$, in terms of the fraction of the layer exposed to vapor, i.e., allowed to diffuse or evaporate, the rate of evaporation of an isolated $a$ atom, and the change in the surface atomic configuration due to the evaporation of an $a$ atom. Terms $C_2$ and $D_2$ correspond to change of $Q_a(2n)$ due to adsorption and evaporation of $x$ atoms. $E_2$ and $F_2$ describe change of $Q_a(2n)$ due to intralayer migrations of $a$ and $x$ atoms respectively. $G_2$ and $H_2$ describe change of $Q_a(2n)$ due to interlayer migration of $a$ atoms in and out of $2n^{th}$ layer. $I_2$ takes care of double counting involved in $G_2$ and $H_2$. $J_2$ and $K_2$ describes $Q_a(2n)$ change due to interlayer migration of $x$ atoms in and out of the $2n^{th}$ layer and $L_2$ takes care of the double counting involved in $J_2$ and $K_2$. 
The time evolution equation for $\tilde{N}_{ax}(2n)$ can be written as [20]:

$$
\frac{d\tilde{N}_{ax}(2n)}{dt} = \frac{4}{\tau_{ra}} \left( \left[ \frac{\tilde{N}_{cc}(2n-1)}{2} - C(2n) \right] e^{L_0} \left[ \frac{1}{2} Q_a(2n) \right] 
- \left( \frac{C_a(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\tilde{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\tilde{N}_{aa}(2n)e^{-2k_{aa}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right] \right)
\times \frac{1}{\tau_{rx}} \left( \left[ \frac{\tilde{N}_{cc}(2n-1)}{2} - C(2n) \right] e^{L_x} \left[ \frac{1}{2} Q_x(2n) \right] 
+ \left( \frac{C_x(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\tilde{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\tilde{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right] \right)
\times \frac{1}{\tau_{ix}} \left[ \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} \right] \left[ \frac{1}{2} \tilde{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n) \right] \right)
$$


\[
- \frac{3}{r_{\text{d,intra}}} \left( \frac{\hat{N}_{\text{cc}}(2n-1) - C_a(2n)}{C_v(2n)} \right) Q_a(2n)
\times \left( \frac{C_a(2n)}{C(2n)} \right) \left[ \frac{C(2n) - 2C(2n + 1) + \frac{\hat{N}_{\text{cc}}(2n+1)}{2}}{C_a(2n)} \right] \left[ \frac{\hat{N}_{\text{aa}}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{\text{ax}}(2n)e^{-2k_{xx}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^3
\times \left[ \frac{\frac{1}{2} \hat{N}_{\text{ax}}(2n)e^{-2k_{xx}}}{\hat{N}_{\text{ax}}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{\text{ax}}(N)e^{-2k_{xx}} + \frac{1}{2} Q_a(2n)} - \frac{1}{2} Q_a(2n) \right] \left( \frac{\hat{N}_{\text{xx}}(2n) - C(2n)}{2C_v(2n)} \right) Q_x(2n)
\times \left( \frac{C_x(2n)}{C(2n)} \right) \left[ \frac{C(2n) - 2C(2n + 1) + \frac{\hat{N}_{\text{cc}}(2n+1)}{2}}{C_x(2n)} \right] \left[ \frac{\hat{N}_{\text{xx}}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{\text{ax}}(2n)e^{-2k_{xx}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right]^3
\times \left[ \frac{\frac{1}{2} \hat{N}_{\text{ax}}(2n)e^{-2k_{xx}}}{\hat{N}_{\text{xx}}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{\text{ax}}(2n)e^{-2k_{xx}} + \frac{1}{2} Q_x(2n)} - \frac{1}{2} Q_x(2n) \right] \left( \frac{\hat{N}_{\text{xx}}(2n) - C(2n)}{2C_v(2n)} \right) Q_x(2n)
\]
\[
\frac{16}{\tau_d \text{ intera}} \left( \frac{\hat{N}_{cc}(2n - 1)}{2} - C(2n) \right) e^{L_{po}} \left( \frac{1}{2} Q_a(2n) \right) \\
- e^{L_{po}} \left( \frac{C_a(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n + 1) + \frac{\hat{N}_{cc}(2n + 1)}{2} \right] \left[ \frac{\hat{N}_{aa}(2n)e^{-2k_{ax}} + \frac{1}{2} \hat{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^4 \\
\times \left[ \frac{1}{2} \frac{\hat{N}_{aa}(2n)e^{-2k_{ax}} + \frac{1}{2} \hat{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right] \\
- \frac{16}{\tau_d \text{ intera}} \left( \frac{\hat{N}_{cc}(2n - 1)}{2} - C(2n) \right) \\
\times \left( \frac{C_a(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n + 1) + \frac{\hat{N}_{cc}(2n + 1)}{2} \right] \left[ \frac{\hat{N}_{aa}(2n)e^{-2k_{ax}} + \frac{1}{2} \hat{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right]^4 \\
\times \left[ - \frac{1}{2} \frac{\hat{N}_{aa}(2n)e^{-2k_{ax}} + \frac{1}{2} \hat{N}_{ax}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_a(2n)}{2C_a(2n)} \right] \\
\]
\[
+ \frac{16}{r_d^{inter}} \left( \left[ \frac{\hat{N}_{cc}(2n-1)}{2} - C(2n) \right] e^{L_{ox}} \left[ \frac{1}{2} Q_a(2n) \frac{2}{2C_v(2n)} \right] \right.

+ e^{L_{ps}} \left( \frac{C(z)(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\hat{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\hat{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{az}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right] \right.

\times \left[ \frac{\hat{N}_{ax}(2n)e^{-2k_{ax}}}{\hat{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{az}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)} \right] \left[ \frac{\hat{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{az}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right] \left[

- \frac{16}{r_d^{inter}} \left( \left[ \frac{\hat{N}_{cc}(2n-1)}{2} - C(2n) \right] \right.

\times \left( \frac{C(z)(2n)}{C(2n)} \right) \left[ C(2n) - 2C(2n+1) + \frac{\hat{N}_{cc}(2n+1)}{2} \right] \left[ \frac{\hat{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{az}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right] \right.

\times \left[ \frac{-\frac{1}{2} \hat{N}_{ax}(2n)e^{-2k_{ax}}}{\hat{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{az}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)} + \frac{1}{2} Q_a(2n) \frac{2}{2C_v(2n)} \right] \left[ \frac{\hat{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{az}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)}{2C_x(2n)} \right] \left[ \frac{-\frac{1}{2} \hat{N}_{ax}(2n)e^{-2k_{ax}}}{\hat{N}_{xx}(2n)e^{-2k_{xx}} + \frac{1}{2} \hat{N}_{az}(2n)e^{-2k_{ax}} + \frac{1}{2} Q_x(2n)} + \frac{1}{2} Q_a(2n) \frac{2}{2C_v(2n)} \right] \right.\]
The change in $\tilde{N}_{ax}(2n)$ due to the adsorption and evaporation of the $a$ atoms is described by terms $A3$ and $B3$ respectively. The change in $\tilde{N}_{ax}(2n)$ due to the adsorption and evaporation of the $x$ atoms is described by the terms $C3$ and $D3$ respectively. The change in $\tilde{N}_{ax}(2n)$ due to the intralayer diffusion of the $a$ and $x$ atoms is described by terms $E3$ and $F3$ respectively. The change in $\tilde{N}_{ax}(2n)$ due to the interlayer diffusion of the $a$ atoms into and out of the $2n^{th}$ layer is described by terms $G3$ and $H3$ respectively. The term $I3$ takes care of the double counting involved in the terms $G3$ and $H3$ respectively. The change in $\tilde{N}_{ax}(2n)$ due to the interlayer diffusion of the $x$ atoms into and out of the $2n^{th}$ layer is denoted by the terms $J3$ and $K3$ respectively. The term $L3$ takes care of the double counting involved in terms $J3$ and $K3$ respectively.

It is noted that the time evolution equations (3.6)-(3.8) are suitable for monatomic As species only. As the case of diatomic molecular species, $As_2$, is also used in this study, the terms corresponding to the adsorption process in the equations (3.6)-(3.8) are modified as follows: The probability, $P_1$, that there exists a surface $Ga$ adatom pair in the $2n^{th}$ layer is given by:

$$P_1 = \frac{\tilde{N}_{GaGa}(2n)}{2C_{Ga}(2n)}$$  \hspace{1cm} (3.15)

where $\tilde{N}_{GaGa}(2n)$ is the $Ga-Ga$ second nearest neighbor bond density. In case of diatomic spices four $Ga$ atoms (or three nearest neighbor pairs) are required to form the surface $Ga$ adatom arrangement. Therefore, the probability $P_s$ that there exist surface atomic arrangement given by:

$$P_s = P_1^3$$  \hspace{1cm} (3.16)

The concentration of $Ga$ atoms having such nearest neighbor arrangements is given by:

$$C_s(2n) = C_{Ga}(2n)P_s$$  \hspace{1cm} (3.17)
Thus, for $\text{As}_2$ incorporation in the $2n + 1^{th}$ layer, the concentration of sites available in the $2n^{th}$ layer is given by the following modification.

$$\left[\frac{\Delta \gamma_{bb}(2n - 1)}{2} - \gamma_a(2n)\right] - [C_t(2n) - C_{As}(2n + 1)]$$  \hspace{1cm} (3.18)

In this study, $a$, $x$, $b$, $y$ are assumed to be $Ga$, $Al$, $As$, and $As$ respectively.

### 3.2.3 Boundary Conditions

The boundary conditions for the growth of the compound semiconductor alloy $GaAlAs$ is discussed in this section. It is assumed that the substrate is flat and that it consists of four layers- the first two layers of the cation ($ax$) and the other two, anion ($by$) sublattices. The initial conditions for the independent macrovariables are given by:

$$C_{Ga}(2n) = \begin{cases} 1.0 & n = 1 \ldots 2 \\ 0.0 & n = 3,4 \ldots \infty \end{cases}$$

$$C_{Al}(2n) = \begin{cases} 1.0 & n = 1 \ldots 2 \\ 0.0 & n = 3,4 \ldots \infty \end{cases}$$

$$C_{As}(2n + 1) = \begin{cases} 1.0 & n = 1 \ldots 2 \\ 0.0 & n = 3,4 \ldots \infty \end{cases}$$

$$Q_{Ga}(2n) = 0.0 \quad n = 1 \ldots \infty$$  \hspace{1cm} (3.19)
and

\[ Q_{Al}(2n) = 0.0 \quad n = 1, \ldots, \infty \]

and

\[ Q_{Al}(2n+1) = 0.0 \quad n = 1, \ldots, \infty \]  \hspace{1cm} (3.20)

\[ \tilde{N}_{GaAl}(2n) = 4p - 4p^2 \quad n = 1, \ldots, \infty \]

\[ = 0.0 \quad n = 3, 4, \ldots, \infty \]  \hspace{1cm} (3.21)

where \( p \) is the fraction of the Al atom which for this study is 0.5.

### 3.3 Computational Details

To study the kinetics of growth of \( n \) monolayers, \( 7n \) coupled nonlinear differential equations (\( n \) for each of the 7 macrovariables) together with the boundary conditions described in section 1.2.3 should be considered. The coupled nonlinear differential equations given by Eqs. (3.6)-(3.8) along with the boundary conditions given by Eqs. (3.13)-(3.15) were solved numerically. By trial and error, it was found that it is sufficient to consider 30 layers to get numerically correct results. The CRAY YMP 2/216 of NSCEE was used for the Numerical Solution. Average CPU time for a typical growth of 13 monolayers was about 4 hrs.
Figure 3.1: A schematic representation of atomistic picture of all the kinetic processes that are considered for the simulation: (1) incorporation, (2) surface migration, (3) reevaporation.
Figure 3.2: A pictorial representation of the MSOS restrictions.
Chapter 4

RESULTS AND DISCUSSIONS

In this chapter, the model parameters for the surface kinetic study of the MBE growth of $Ga_{1-x}Al_xAs$ alloy are discussed in Section 4.1. The growth parameters, such as the instantaneous roughness parameter (IRP), short range order (SRO) parameter, isolated terrace cation parameter (ITCP), and isolated terrace anion parameter (ITAP) are defined in Section 4.2. The results of the ordering study are presented in sections 4.3 and 4.4 for monatomic and diatomic molecular $As$ species respectively. The comparisons of results for both the monatomic and diatomic species, are presented in section 4.5.

4.1 The $Ga_{1-x}Al_xAs$ Alloy System and The Model Parameters

The model parameters for the present study of the MBE growth of $Ga_{1-x}Al_xAs$ are obtained from the literature and the MBE growth parameters of Ref. [1].

The material parameters such as the $Ga - Ga$, $Al - Al$, and $Ga - Al$, second nearest neighbor pair interaction energies were obtained from the first principle calculation results of Krishnamurthy et al [25] as:
\[
\begin{align*}
V_{Ga-Ga} &= 0.000 \text{ eV} \\
V_{Al-Al} &= 0.000 \text{ eV} \\
V_{Ga-Al} &= 0.124 \text{ eV} \\
V_{As-As} &= 0.325 \text{ eV}
\end{align*}
\]

The activation energy, \( E_{act} \), of the surface migration for isolated \( Ga \), \( Al \) and \( As \) atoms are assumed to be 1.3 eV [26]. The frequency factor for surface migration is assumed to be \( 1.0 \times 10^{13} \) / sec. Evaporation rate for \( Ga \), \( Al \), and \( As \) are assumed to be negligible. The MBE growth parameters for this study are obtained from the experimental data given in Ref. [1]. The growth parameters employed for the monatomic species are: flux rate, \( J_c \), of cation equal to \( 2A^0/\text{sec.} \); cation to anion flux ratios 1 : 10. and 1 : 20; and substrate temperatures in the range of 760°K to 920°K. The growth parameters for the diatomic species are: flux rate, \( J_c \), of cation is \( 2A^0/\text{sec.} \); cation to anion flux ratio 1 : 10, 1 : 20 and 1 : 30; and substrate temperatures in the range of 760°K to 880°K. The substrate is assumed to be [100] and flat. The material and the growth data discussed above are employed to calculate the model parameters. The flux parameter, \( e^L \), is obtained from the flux rate \( J \), and the relaxation time constant \( \tau_r \). The value of relaxation time constant, \( \tau_r \), was arbitrarily assumed to be \( 1 \times 10^{10} / \text{sec.} \) for \( Ga \), \( Al \), and \( As \) as evaporation is assumed to be the negligible. The diffusion time constant, \( \tau_d \), is obtained in terms of the frequency factor and the activation energies. In this study, the rate of intralayer and interlayer diffusions are assumed to be same.

### 4.2 Data Analysis Parameter

In order to compare the growth data obtained from the stochastic model with the experimental results [2], the growth parameters, such as the instantaneous roughness parameter (IRP), short range order (SRO) parameter, isolated terrace cation parameter (ITCP), and isolated terrace anion parameter (ITAP) are defined as follows [27]:
The instantaneous growth surface roughness can be described in terms of the atom-vacancy bond densities, \(Q_{Ga}(2n), Q_{Al}(2n)\) and \(Q_{As}(2n+1)\), as:

\[
IRP(T) = \sum_{i=3}^{i=\infty} [Q_{Ga}(i)(t) + Q_{Al}(i)(t) + Q_{As}(i+1)(t)]
\] (4.1)

The time averaged surface roughness parameter, \(TRP(t)\), is given by

\[
TRP(T) = \frac{1}{t_{gro}} \int_{t=0}^{t=t_{gro}} [IRP(t)dt]
\] (4.2)

The short range order (SRO) parameter is obtained from the growth data as follows [28]:

\[
SRO = \sum_{i=3}^{i=\infty} \left[ \frac{\tilde{N}_{Ga-Ga}(2n) + \tilde{N}_{Al-Al}(2n) - \tilde{N}_{Ga-Al}(2n)}{2C(2n)} \right]
\] (4.3)

Where \(\tilde{N}_{Ga-Ga}(2n)\), \(\tilde{N}_{Al-Al}(2n)\), and \(\tilde{N}_{Ga-Al}(2n)\) are the second nearest neighbor atom-atom bond densities and \(C(2n)\) is the cation concentration variable, which is the sum of \(C_{Ga}(2n)\) and \(C_{Al}(2n)\).

The SRO parameter defined in Eq. 4.3 is 0.0, 1.0, and 2.0 for completely segregated, completely random, and completely ordered alloys, respectively. Other useful parameters which describe the roughness of the surface are the instantaneous isolated terrace cation and anion concentrations, \(ITCP(T)\), and \(ITAP(T)\) respectively. Observing that the isolated terrace adatom has 4 vacancy neighbors and 0 atom neighbors, the \(ITCP(T)\) can be obtained using the trinomial distribution from the growth data as follows:

\[
ITCP(T) = \sum_{n=3}^{n=\infty} C_{Ga}(2n) \begin{pmatrix} 4 \\ 0 \end{pmatrix} \left( \frac{\tilde{N}_{Ga-Ga}(2n)}{2C_{Ga}(2n)} \right)^0 \left( \frac{Q_{Ga}(2n)}{2C_{Ga}(2n)} \right)^4 \left( \frac{\tilde{N}_{Ga-Al}(2n)}{2C_{Ga}(2n)} \right)^0
\]

\[
+ \sum_{n=3}^{n=\infty} C_{Al}(2n) \begin{pmatrix} 4 \\ 0 \end{pmatrix} \left( \frac{\tilde{N}_{Al-Al}(2n)}{2C_{Al}(2n)} \right)^0 \left( \frac{Q_{Al}(2n)}{2C_{Al}(2n)} \right)^4 \left( \frac{\tilde{N}_{Ga-Al}(2n)}{2C_{Al}(2n)} \right)^0
\] (4.4)
The time averaged isolated terrace cation parameter, \( TITC P(T) \), can be obtained as follows:

\[
TITC P(t) = \frac{1}{t_{gro}} \int_{t=0}^{t=t_{gro}} [ITCP(t) \, dt] \tag{4.5}
\]

Similarly for the anion, \( ITAP(T) \), can be obtained from the growth data as follows:

\[
ITAP(T) = \sum_{n=3}^{n=\infty} C_{Ar}(2n+1) \left( \frac{\hat{N}_{Ar-\hat{Ar}}(2n+1)}{2C_{Ar}(2n+1)} \right)^{0} \left( \frac{Q_{Ar}(2n+1)}{2C_{Ar}(2n+1)} \right)^{4} \tag{4.6}
\]

The time averaged isolated terrace anion parameter, \( ITAP(t) \), can be obtained as follows:

\[
TITAP(T) = \frac{1}{t_{gro}} \int_{t=0}^{t=t_{gro}} [ITAP(t) \, dt] \tag{4.7}
\]

### 4.3 Results of Diatomic Molecular Species \( As_2 \)

A plot of SRO parameter versus temperature is shown in Figure 5.1., in the temperature range of \( 760^0K \) to \( 880^0K \). The SRO parameter for all flux ratios increases till a temperature with increase in temperature. Thus, the temperature at which the SRO parameter attains its maximum is called the kinetic order - disorder temperature or the transition temperature. It is found to be \( 760^0K \), \( 800^0K \) and \( 810^0K \) and are obtained as the transition temperatures for the flux ratios \( 1 : 10 \), \( 1 : 20 \) and \( 1 : 30 \) respectively. For the \( As_2 \) source, the maximum degrees of ordering observed for flux ratios \( 1 : 10 \), \( 1 : 20 \), and \( 1 : 30 \) are \( 85\% \), \( 84\% \) and \( 83\% \) respectively. The temperature dependence of the SRO parameter can be explained by the following surface kinetic mechanism.
In the low temperature regime, the effective migration rate of cation (Ga and Al) is small, therefore, cation gets adsorb at the sites in and around the site of their arrival, limiting the chance of sampling many different surface atomic configuration. As the arrival of the atom is random, they incorporate on the lattice randomly, which results in a complete random distribution of the Ga–Ga, Al–Al and Ga–Al surface bonds leading to smaller SRO parameter. As the temperature increases, the effective migration rate increases, resulting in more chances for cations to sample various nearest neighbor configurations. The process of sampling enables cations to end up with energetically most favorable nearest neighbor configuration, which in this case is Ga having Al and Al having Ga atoms as their nearest neighbors. Thus, as the temperature increases the SRO parameter increases.

At and above the transition temperature, the thermal energy is large enough to break the stronger Ga–Al bonds. Thus, the thermal randomization of the surface atomic configuration sets in leading to a more random arrangements of the Ga and Al atoms, resulting in decrease in the SRO parameter with the temperature.

The transition temperature dependence on flux ratio can be explained as follows. As the flux ratio increases, the surface migration rate for cation decreases because the interval between the time of arrival of the cation on the surface to the time of adsorption of anion on it, decreases. Therefore, in order to achieve the same effective migration rates, extra thermal energy is needed for higher flux ratios. Therefore, the transition temperature increases with the flux ratio.

The plot of time averaged roughness parameter, TRP, versus growth temperature is as shown in Figure 5.2. for the flux ratios 1 : 10, 1 :20 and 1 : 30. The surface roughening parameter is observed to be decreasing with increase in temperature, till the minimum
temperature (called transition temperature) and increases thereafter for all flux ratios. The dependence of the roughness parameter with the temperature can be explained as follows. At low temperatures, the surface migration is less and the surface smoothing effect is less, resulting into higher value of roughening parameter. At higher temperatures, the intralayer and interlayer surface migration aids in atoms reaching energetically more favorable sites, thus lowering the value of the roughening parameter. At higher temperatures, breaking of $Ga - Al$, $Ga - Ga$ and $Al - Al$ bonds by the thermal energy results in the rougher surface and higher roughness parameter. Even though the transition temperature observed for the roughness parameter is in the same temperature range as that of the SRO parameter, there is no observed dependence of it on the flux ratios. This can be attributed to less resolution in the data or to the intensity of TRP to flux rate. The lower values of roughness parameter at the higher flux ratios can be attributed to the increase in the effective surface migration rates at the higher flux ratios and the decrease of the SRO parameter.

A plot of the time averaged Isolated Terrace Cation Parameter versus growth temperature is as shown in Figure 5.3. The value of TITCP, increases with temperature for the flux ratios $1 : 10$, $1 : 20$, and $1 : 30$. The transition temperature is identified from the temperature dependence of TITCP and is close to $760^\circ K$ which is consistent with the results of Figure .. For temperatures, above the transition temperature, the thermal randomizing effects dominate the surface kinetics resulting in the higher concentrations of isolated terrace cations at the surface. This physical explanation of the thermal randomizing effect also correlates well with the results of the SRO and roughness parameters.

A plot of the time averaged Isolated Terrace Anion Parameter versus growth temperature is as shown in Figure 5.4. In the low temperature range, the TITAP, is observed to be very
high, implying the presence of large number of anions on the growing surface. In the intermediate temperature range, the intralayer and the interlayer migration rates of anions increase with the increase in the temperature, aiding the formation of larger surface islands and hence lowering the value of time averages. In the higher temperature range, the thermal energy is large enough to break the $\text{As} - \text{As}$ bonds, and also thermal evaporation of $\text{As}$ at the surface aids in to breaking up of the islands, thereby, increasing the number of isolated anions on the surface, and higher values of TITAP at higher temperatures.

4.4 Results of Monatomic Molecular Species $\text{As}$

A plot of SRO parameter is shown in Figure 5.5. in the temperature range of 760°K to 920°K. The kinetic order-disorder temperature are 773°K and 823°K for the flux ratios 1 : 10 and 1 : 20 respectively. For the $\text{As}$ source, the maximum degrees of ordering observed for flux ratios 1 : 10, and 1 : 20 are 79%, and 80% respectively.

Trends similar to that observed for the $\text{As}_2$ is observed for the dependence of SRO parameter on the growth temperature and flux ratios. The surface kinetic mechanism similar to that in section 4.3 apply.

The plots of time averaged roughness parameter, TRP, versus growth temperature is as shown in Figure 5.6. for the flux ratio 1 : 10 and 1 : 20. The surface roughening parameter is observed to be gradually decreasing with the increase in temperature for both flux ratios. The variations of the roughness parameter with temperature are similar to that observed for the roughness parameter of the diatomic, $\text{As}_2$, in section 4.3. and hence similar explanations apply.

The plots of isolated terrace cation parameter, TITCP, versus growth temperature is as
shown in Figure 5.7. The value of TITCP increases with the temperature for the flux ratios 1:10 and 1:20. The transition temperatures identified are the same and are as 773°K and 823°K for the flux ratios 1:10 and 1:20 respectively. The results of isolated terrace cation parameter, TITCP, are comparable for both As and As₂ species.

The plots of isolated terrace anion parameter, TITAP, versus growth temperature is as shown in Figure 5.8. The plots are observed to be identical to the plots of TITAP for the diatomic As₂ species. Hence similar explanations analyzing behavior of TITAP with the can be written.

4.5 Comparison of As and As₂ Results and The Experiments

The results of SRO parameter, time averaged roughness, isolated terrace cation, and anion parameters were observed to be comparable for both diatomic and monatomic species except that for As, the transition temperatures are larger by a few degrees. These results were compared with the experimental work reported in Ref.[1]. In this study, the temperature for most pronounced ordering is found to be increasing with increase in the flux ratio, indicating the agreement with the experimental observations. The ordering observed in terms of SRO parameter is also found to be growth temperature dependent, as observed experimentally. The qualitative agreement between this study and the experimental observations for the dependence of the SRO parameter on the temperature was found to be excellent.

The concentration profiles for various growth temperatures and flux ratios are obtained for the monatomic and diatomic species. Concentration versus time plots are shown for the temperature 773°K and 823°K in Figures 5.18-19, and 5.20-21, respectively, for the
flux ratios 1 : 10 and 1 : 20 for the As molecular species. For the $As_2$ molecular species, the plots are shown for the temperatures 773°K and 823°K in Figure 5.12-14, 5.15-17 for the flux ratios 1 : 10, 1 : 20, and 1 : 30 respectively. It is observed that the time delay between the growth of Ga and subsequent As layers decreases with the flux ratio, for both molecular species in the temperature range used. The above observation about the time evolution of the concentration profiles can be explained as follows. The growth of the As layer is controlled by the surface processes, adsorption and evaporation. In this study, the evaporation of the surface As is considered negligible. Higher the flux ratio, higher the rate of arrival of As, and therefore faster incorporation which results in shorter time between the growth of the Ga layer and the subsequent As layer. Also, there is a perceptible time difference between the As and $As_2$ ($As_2$ being larger) for the same flux ratio and temperature. This is attributable to the slower formation of 4 Ga cluster for $As_2$ incorporation as compared to 2 Ga cluster for As incorporation.

One major difference between the results is the type of ordering reported in Ref. [1] for the MBE growth of (100) $Ga_{1-x}Al_xAs$. Experimentally, $L1_0$ type ordering is observed. In this study, the order structure observed is such that Ga atoms are surrounded by the Al atoms and vice versa which is not $L1_0$ type ordered structure. The reasons for this difference can be explained as follows. Firstly, the $L1_0$ type ordering results from the difference between the bulk-surface and surface-surface pair interaction energies of atoms which are not accounted for in the stochastic model used in this study. Also, the averaged out values of the atom pair interaction energies for both, sigma and pi bonds are used in this study. The other difference is that they observed very weak ordering in [100] and strong ordering in along [110]. This study did not concern 110 growth but observed strong ordering...
along 100. The discrepancy related to surface reconstruction limitation of the model.

The ordering observed in this study is comparable to the ordering observed along the (111) planes in Ga$_{0.5}$In$_{0.5}$As Ref.[22], as shown in Figure 4.19. The periodicity along the [111] direction is doubled because of alternating (111)In and (111)Ga planes.
Figure 4.1: For the molecular species $\text{As}_2$, a plot of SRO parameter versus temperature for flux ratios: (a) 1 : 10, (b) 1 : 20, (c) 1 : 30.
Figure 4.2: For the molecular species \( As_2 \), a plot of roughness parameter versus temperature for flux ratios: (a) 1:10, (b) 1:20, (c) 1:30.
Figure 4.3: For the molecular species $As_2$, a plot of isolated terrace cation parameter versus temperature for flux ratios: (a) 1 : 10, (b) 1 : 20, (c) 1 : 30.
Figure 4.4: For the molecular species $As_2$, a plot of isolated terrace anion parameter versus temperature for flux ratios: (a) 1 : 10, (b) 1 : 20, (c) 1 : 30.
Figure 4.5: For the molecular species As, a plot of SRO parameter versus temperature for flux ratios: (a) 1 : 10, (b) 1 : 20.
Figure 4.6: For the molecular species As, a plot of roughness parameter versus temperature for flux ratios: (a) 1 : 10, (b) 1 : 20.
Figure 4.7: For the molecular species As, a plot of isolated terrace cation parameter versus temperature for flux ratios: (a) 1 : 10, (b) 1 : 20.
Figure 4.8: For the molecular species As, a plot of isolated terrace anion parameter versus temperature for flux ratios: (a) 1 : 10, (b) 1 : 20.
Figure 4.9: For the molecular species $As_2$, a plot of concentration versus time for temperature $773^\circ K$, and flux ratio $1 : 10$. 
Figure 4.10: For the molecular species $\text{As}_2$, a plot of concentration versus time for temperature 773$^\circ$K, and flux ratio 1 : 20.
Figure 4.11: For the molecular species $As_2$, a plot of concentration versus time for temperature $773^\circ K.$ and flux ratio $1 : 30$. 
Figure 4.12: For the molecular species $As_2$, a plot of concentration versus time for temperature 873°K, and flux ratio 1 : 10.
Figure 4.13: For the molecular species $As_2$, a plot of concentration versus time for temperature $873^\circ K.$ and flux ratio $1:20.$
Figure 4.14: For the molecular species $\text{As}_2$, a plot of concentration versus time for temperature 873°K, and flux ratio 1 : 30.
Figure 4.15: For the molecular species As, a plot of concentration versus time for temperature 779 K, and flux ratio 1:10.
Figure 4.16: For the molecular species $As$, a plot of concentration versus time for temperature 773 K, and flux ratio 1 : 20.
Figure 4.17: For the molecular species As, a plot of concentration versus time for temperature 873°K, and flux ratio 1 : 10.
Figure 4.18: For the molecular species As, a plot of concentration versus time for temperature 873°K, and flux ratio 1 : 20.
Figure 4.19: A schemforic diagram showing a $L1_0$ ordered structure.
Chapter 5

CONCLUSION

The surface kinetics of MBE growth of (100) $Ga_xAl_{1-x}As$ was studied theoretically using the stochastic model for various growth conditions. The degree of ordering obtained in terms of the short range order (SRO) parameter. The order-disorder temperature is defined as the temperature of maximum ordering after which the SRO parameter begins to decrease. The temperature range used for As species is $760^0K$ to $920^0K$, with the flux ratios 1 : 10, and 1 : 20. The temperature range used for the $As_2$ species is $760^0K$ to $880^0K$ for the flux ratios 1 : 10, 1: 20, and 1 : 30. For monatomic As source, the order-disorder temperature was found to be $773^0K$ and $823^0K$ with the flux ratios 1 : 10 and 1 : 20 respectively. The maximum degree of ordering of 79% and 80% is observed for the flux ratio 1 : 10 and 1 : 20, respectively. For diatomic $As_2$ source, the order-disorder temperature was found to be $760^0K$, $800^0K$ and, $810^0K$ for the flux ratios 1 : 10, 1 : 20, and 1 : 30. The maximum degree of ordering observed for the flux ratio is 1 :10, 1 : 20, and 1 : 30 is 85%, 84%, and 83%, respectively. The results of SRO parameter as a function of temperature are in good qualitative agreement with experiments. The surface ordering kinetics observed can be described in terms of the dependence of the effective migration rates for the cations. The key difference between the experiments and our study is in the type of ordering and the
degree of ordering observed. The difference is attributed to the indistinguishability between various kinds of second nearest neighbor bonds, (i.e.), surface-surface bonds, surface-bulk, and the sigma, and pi bonds, in the present stochastic model. The discrepancy in the degree of ordering can be attributed to the limitations of the model and model parameters.

Based on the present work, and as a continuation of this work, the following studies are recommended. The stochastic model for [110] and [111] can be developed to study the ordering in $Ga_{0.5}Al_{0.5}As$. The SOS restriction can eliminated from the stochastic model thereby increasing the accuracy of the model. The interplane interactions can be included in the model. Finally, the model can be employed to study other material systems.
Bibliography


