Low-temperature molecular beam epitaxy of gallium arsenide Antisite incorporation and Rheed oscillations: A theoretical study

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LOW TEMPERATURE MOLECULAR BEAM EPITAXY OF $GaAs$:
ANTISITE INCORPORATION AND RHEED OSCILLATIONS
- A THEORETICAL STUDY

by

Natarajan Krishnan

Bachelor of Engineering
Annamalai University, Tamilnadu, India
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of the requirements for the degree of

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in

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Dean of the Graduate College
ABSTRACT

Low Temperature Molecular Beam Epitaxy of Ga As: Antisite Incorporation and RHEED Oscillations - A Theoretical Study

by

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Surface dynamics dominate the incorporation of charged and neutral antisite arsenic and the temporal variation of reflection high energy electron diffraction (RHEED) intensity in the low temperature (LT) molecular beam epitaxy (MBE) of (100) gallium arsenide (GaAs). A comprehensive rate equation model is proposed based on the presence and dynamics of a physisorbed arsenic (PA) riding the growth surface which dictates the incorporation and concentration of antisites and the RHEED oscillations (ROs) behavior. The dependence of antisite concentrations on growth parameters can be explained based on the saturation of the PA layer coverage at a monolayer and the competing rate processes such as the incorporation into and evaporation of antisite arsenic from the crystalline surface. The RHEED intensity is computed based on kinematical theory of electron diffraction with different interplanar distances for the PA layer (2.48Å) and the crystal (1.41 Å). At temperatures and beam equivalent pressures (BEP)s when the surface coverage is 0.5, the resulting RHEED reflection contributions from both surfaces covered by the PA layer and the crystal interfere destructively to result in no ROs.
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CHAPTER 1

INTRODUCTION

Molecular beam epitaxy (MBE) is a versatile film growth technique for growing thin epitaxial structures made of semiconductors, metals or insulators. In this technique, the atomic or molecular beams are thermally evaporated onto a heated substrate in an ultra-high vacuum. The ultra-high vacuum allows monitoring of the growth with \textit{in situ} tools like reflection high-energy electron diffraction (RHEED). There has been a great interest in the past in understanding the properties of low-temperature-grown GaAs (LT-GaAs) grown by MBE at substrate temperatures of 200-400°C, generally followed by annealing at a higher temperature. The material is highly non-stoichiometric with a large excess As incorporated into GaAs in the form of point defects. When annealed at a temperature above 500°C, the material becomes semi-insulating [1] crystal if the thickness is limited to a critical value, with the excess As precipitating to form semi-metallic clusters [2] and the lattice mismatch of the substrate vanishes. The semi-insulating property is an important technological innovation observed first in 1978 since it is useful for fabrication of devices, such as semi-insulating buffer layers for GaAs metal-semiconductor field-effect transistors (MESFET) to eliminate the problem of side-gating [3] and for ultra-high photodetectors. The point defects are present in the form of antisites arsenic, As$_{Ga}$, arsenic interstitials, As$_{i}$ [4] and gallium vacancies, V$_{Ga}$ [5] causing the epilayer to dilate [4]. Of the point defects, As$_{Ga}$ is accepted as the dominant defects [6]. The amount of excess arsenic can be controlled with the substrate temperature and beam equivalent pres-
sure (BEP) during MBE. A considerable amount of $As_{Ga}$ is in the positively charged state [7] and hence antisites are distinguished as neutral, $As_{Ga}^0$, and charged, $As_{Ga}^+$, antisites. To maintain the charge neutrality of the material, gallium vacancies are present as triple acceptors, $V_{Ga}^{3-}$. The ultra-fast trapping characteristics of carriers in these materials which are useful for photoswitching applications have been correlated to the presence and concentration of $As_{Ga}^+$ [8]. It is shown that doping the material with Be increases the $As_{Ga}^+$ concentration from 10% to more than 50% to develop a thermally stable GaAs with subpicosecond lifetimes [9]. A stochastic model of growth has been utilized to investigate the LT MBE GaAs growth [18,68]. In the study, a weakly bound physisorbed As (PA) layer is included whose dynamics is essential to explain the experimental observation of temperature and BEP dependencies of $As_{Ga}$ concentration. This study did not include the incorporation of gallium vacancies, $V_{Ga}$ and charged antisites, $As_{Ga}^+$.

RHEED oscillations (ROs) observed during MBE growth are periodic step density oscillations corresponding to monolayer deposition time [10,11,12,13]. ROs have been observed only at high temperatures around 600°C with an $As_4$ to $Ga$ flux ratio of at least 5:1 until recently when Ibbetson et al [14] observed at low temperatures as low as 200°C under strict stoichiometric conditions. In a subsequent Monte Carlo study [15], they suggested that even with very small surface migration rate for $Ga$, one can achieve enough step density oscillations to obtain ROs. Pamula et al [16] used a stochastic model of growth allowing for a physisorbed layer of As. It was shown that the ROs were enhanced by the temporal oscillations of the PA layer coverage which exposed the crystal periodically to RHEED beam. Recently Shen et al [17] have shown that stoichiometric condition is not a prerequisite for the RO observation and that the ROs can be observed over a wide range of BEP ratios and temperatures. They also observed that the ROs are suppressed over a temperature window at a
fixed BEP and over a BEP ratio window at a fixed temperature.

The aim of this thesis is to modify the stochastic model of Ref.[18] to make it a comprehensive model which will capture not only the physics of antisite arsenic incorporation but also the RO behavior. Additionally the model shall include both neutral and charged $\text{As}_{\text{Ga}}$ incorporation. The results of the model will be compared to various experimental results [17,19]. Then the model will be employed to theoretically study the growth mechanisms and to identify the dominant mechanism which controls the incorporation of $\text{As}_{\text{Ga}}^{0}$ and $\text{As}_{\text{Ga}}^{+}$ and also the behavior of the specular ROs as a function of growth conditions, specifically the influences of growth parameters such as temperature, flux ratio and growth rate.

1.1 Organization of the thesis

A brief overview of MBE of LT GaAs is presented in chapter 2. The details of the comprehensive rate equation model developed to study the antisite incorporation and ROs in the LT MBE is presented in chapter 3. The details of the physics of the surface mechanisms included and the formulation of the kinetic rate equation model are presented in section 3.1. The computational details are presented in sections 3.2. Results and discussions are presented in section 4. Finally, conclusions and recommendations are presented in chapter 5.
CHAPTER 2

OVERVIEW

Crystal growth technology is one of the fast advancing fields related to fabrication of integrated circuits in the recent years. Epitaxy is a growth process of a solid film on a crystalline substrate in which the atoms of the growing film mimic the crystalline arrangement of the atoms of the substrate. Hence, the epitaxially grown layer, usually, exhibits the same crystal structure and the same orientation as the substrate. By present day epitaxial growth techniques, layers of the order of 5 Å to 20 μm of single crystal material can be deposited upon the surface of a single crystal substrate. The development and production of the next generation of high speed discrete and IC devices is inextricably linked to the ability to grow highly complex device structures epitaxially. MBE is distinguished from other vacuum deposition techniques because of its significantly more precise control of the beam fluxes and growth conditions and hence the composition and the thickness of the epilayers. MBE, used at first for studying semiconductor surfaces [20], now has found practical applications in the fabrication of conventional and novel ultrafast quantum devices. The low growth rate of 1μm/hr. (≈1 monolayer/sec.) at low temperatures and ultra high vacuum conditions (UHV) ensures accurate control of stoichiometry, crystallinity, layer thickness and interface abruptness to the level of interatomic dimensions. It is also possible to grow artificial crystals with periodic variation in compositions which are not available in nature. Exploiting the unique advantage of UHV conditions, the growth is controlled in-situ by surface diagnostic methods such as RHEED, Auger Electron Spectroscopy.
(AES) and Scanning Tunneling Microscopy (STM). These powerful analytical tools for control and analysis enable the fabrication of sophisticated device structures using MBE. Epilayers of many materials have been grown by MBE. But III-V semiconductor compounds, in general, and GaAs, in particular, have received the most attention [21]. Of interest to this thesis work is the MBE growth of low temperature (LT) GaAs. The experimental and theoretical studies on LT GaAs are summarized in this chapter.

2.1 Molecular Beam Epitaxy

MBE is a sophisticated crystal growth process in which molecular beams of constituent elements of the epilayer flow towards the heated substrate under ultra high vacuum levels of the order of $10^{-8}$ Torr. The molecular beams are generated under UHV conditions normally from Knudsen-effusion-cells containing the constituent elements whose temperatures are accurately controlled to enable a good flux stability. Computer controlled temperatures of the substrate and each of the sources, and operation of shutters dictate the desired chemical composition and doping of the epitaxial films. The molecules of different species of beams have no collisions or interactions before reaching the surface of the substrate as the mean free path of the molecules is very long. Epitaxial growth occurring on the substrate surface involves a series of surface processes like adsorption of the atoms on the substrate surface, surface migration of the adsorbed atoms, incorporation of the atoms into the crystal lattice and thermal desorption of the species. The crystal surface has crystal lattice sites created by the surface dangling bonds and is characterized by its individual chemical activity. The surface processes are characterized by relevant kinetic parameters. The flux of the incoming species is the number of atoms or molecules impinging on an unit area of the surface per second. Not all the atoms arriving at the surface stick to
the surface by condensation. The ratio of number of atoms adhering to the surface to the number of atoms arriving there is called sticking coefficient of the species.

Though MBE growth of II-VI and IV-IV semiconductor compounds as well as of metals, insulators and Si is common, the growth of III-V materials and structures has become more important because of the superior high frequency properties and unique optical properties of the III-V semiconductors as compared to Si. Good compositional control of the growing alloy film is achieved by supplying excess group V species and adjusting the flux densities of the impinging group III beams. Thermal stability of the less stable of the two III-V compounds limits the growth of ternary III-III-V alloys by MBE. At high temperatures, preferential desorption of the more volatile group III element occurs. Thus, the surface composition of the alloy reflects the relative flux ratio of the group III elements only, if the growth is carried out at temperatures below which GaAs is thermally stable [22]. The growth rate is determined almost by the flux rate of group III element.

The group III elements produce monoatomic beams, whereas, the group V elements usually produce dimers or tetramers [23]. The established growth models are not unique to GaAs but valid for other binary III-V compounds such as AlAs [20] and InP [24]. In-situ doping of the material is possible. Typically, for III-V compounds, Be is used for p-type doping and Si for n-type. The typical conditions for MBE of high-quality GaAs are a substrate temperature of 600°C, a beam equivalent pressure (BEP) ratio of 15-20, and an extremely low growth rate of 1μm/hr. [20]. The BEP is the ratio of the flux of the group V element i.e., As to the flux of the group III element i.e., Ga. The BEP is measured with an ion guage at the growth position. With the Ga effusion furnace at a temperature near 900°C to obtain a 1μm/hr. growth rate, every Ga atom that impinges on the substrate at a temperature of 600°C has enough thermal energy to find a lattice site. The arsenic molecules, originating from an ef-
fusion furnace at a temperature of about 250°C, will only result in the incorporation of an arsenic, As, atom if there is a surface Ga atom to bond to. This results in the growth of stoichiometric material. The possibility of growing high-quality epitaxial layers of different materials on lattice mismatched semiconductor substrates is a topic of considerable interest in MBE for many years. The range of useful devices available with a given substrate is considerably enhanced by this method.

The growing surface is accessible to observation using powerful real-time surface-science diagnostics which require high-vacuum. Hence RHEED is routinely used to monitor the crystal structure and microstructure of growing surfaces. Reflection mass spectrometry (REMS) and modulated beam mass spectrometry (MBMS) are used to monitor the chemistry of growing surfaces, and reflectance difference spectroscopy (RDS) is used to monitor the composition and optical properties of growing surfaces. In a nutshell, the device engineer can control and produce the state of the surface including the composition, crystal structure and smoothness and subsequently, the quality of the material very precisely and the surface scientist can study, directly, the real-time evolution of surface structure, microstructure and composition. The advantages of the MBE systems over the conventional systems can be summerized as:

- The growth process is controlled to atomic scales of the order of 5Å due to low growth rates to create smooth and perfect surfaces.

- The low temperature environment, preventing the mixing of multilayered structures, and the beam nature of sources help to grow heterointerfaces.

- Clean growth environment.

- The fluxes are controlled precisely by computerized systems. Coupled with low growth rates, the composition of the growing epilayer can be modulated within a monolayer scale.
• Constant *in-situ* monitoring and control of growth is possible using analytical tools like RHEED.

• Compatibility with other high vacuum thin-film processing methods such as ion implantation.

2.2 Low Temperature MBE growth of GaAs

The substrate temperature is a critical parameter in determining the crystal quality of semiconductor films grown by MBE or other epitaxial methods. The growth of high quality epitaxial GaAs layers with low concentration of deep traps by MBE is usually performed in the temperature range of 550 to 650°C [20]. It is also known that growth at temperatures lower than 500°C lead to a very high concentration of deep traps [25] and low carrier mobilities due to the compensating crystal effect. Detrimental effects like diffusion and segregation occur at this high temperatures when high doping is to be done for certain applications like the base region of heterojunction bipolar transistor (HBT). Because the rate of solid-state diffusion decreases exponentially with decreasing temperature, growth of GaAs at low substrate temperatures would be advantageous if high-quality films could be obtained. Such growth would be expected to produce more abrupt doping profiles, reduce outdiffusion of impurities from the substrate into active regions and decrease interdiffusion of atoms at heterojunction interfaces. In 1978, Murotani *et al* [1] first observed the crystallinity and semi-insulating properties of non-stoichiometric Low Temperature grown GaAs, even when doped heavily at 400°C. After 10 years, Smith *et al* [3] showed that the material remained crystalline even at 200°C. Later, even at 140°C, GaAs epitaxy was observed [26]. It was also observed that only within a critical thickness, which is a function of amount of excess arsenic incorporated, the material remained single crystalline. The crystal defects formed because Ga and As atoms adsorbed on the
substrate from the vapor phase are incorporated into the growing film before they reach appropriate lattice sites by surface diffusion. The defect concentration can be decreased by increasing the temperature or by decreasing the growth rate [27].

It was shown that backgating and light sensitivity in metal-semiconductor field-effect transistors (MESFET) could be eliminated by growing a semi-insulating GaAs buffer layer at 200°C and annealing at 600°C [3]. In short channel FETs, the parasitic source to drain current through the buffer-substrate region is minimized due to the semi-insulating property [28]. MESFET with better forward and breakdown voltages has become possible with LT GaAs [29]. It was also shown [30] that if grown on LT GaAs buffer layers, the high electron mobility transistors (HEMT) have the benefit of having the diffusion of impurities from the substrate to the active layers slowed down. Lin et al [31] showed the elimination of side-gating in HEMTs but observed outdiffusion of defects from the buffer layer to the active regions, resulting in degradation of the high-frequency performance and minimized the effect by using a multi-substrate temperature procedure during MBE of the buffer regions.

Solomon et al [32] demonstrated the reduction in back-gating in GaAs semiconductor-insulator-semiconductor FETs (SISFETs). Subramanian et al [33] have shown that the semi-insulating properties can be used for isolation of optical devices by using GaAs:As for isolation between tandem solar cells. It can also be used as a current-blocking layer in diode lasers [34]. LT GaAs has applications as high-speed photoconductor because of its subpicosecond carrier lifetimes and high mobilities. Rahman et al [35] have used LT GaAs:As as the photoconducting switch to launch freely propagating electromagnetic pulses.
2.2.1 Point defects in LT GaAs growth

The incorporation of excess As in the form of point defects, such as arsenic antisites, arsenic interstitials and gallium vacancies, is critical to understand the interesting properties like short carrier lifetimes of LT GaAs. The LT GaAs grown at about 200°C contains upto 1.5% excess As. This excess arsenic dilates the lattice thus straining it [5]. But the structural quality of the epilayer is good [36]. When annealed at 600°C for 10 to 30 minutes, the lattice mismatch caused by the excess As reduces [5]. This strain relaxation is accompanied by conglomeration of the excess arsenic [2]. The amount of excess As can be controlled with the substrate temperature during MBE. The lower the substrate temperature, the greater is the amount of excess arsenic that is incorporated [37]. Melloch et al [38] cycled the substrate temperature to 600°C after a growth of 2µm of material and then brought back to the growth temperature of 250°C thereby, relaxing the strain before the critical thickness is reached and hence showed that LT GaAs with any arbitrary thickness can be grown. The arsenic antisite was observed first in LT GaAs as point defect. Results of electron paramagnetic resonance (EPR) [5] and absorption experiments [39] show the presence of As antisites, although these experiments cannot determine if they are isolated or if they occur primarily in complexes involving other point defects. The antisite concentration varies for different samples and different growth conditions but total measured concentration accounts for most of the deviation from stoichiometry in LT GaAs. The concentration of charged $\text{As}_\text{Ga}^+$ measured by EPR was found to be in the order of $1$ to $5 \times 10^{18} \text{cm}^{-3}$ and neutral antisites, $\text{As}_\text{Ga}^0$, measured by absorption measurements was about $1 \times 10^{20} \text{cm}^{-3}$ for the layers grown at 200°C. As the point defect concentration is more, the material exhibits hopping conductivity with resistivities as low as $10 \Omega \text{cm}$. Upon annealing the resistivity increases dramatically.

The part of excess As which is not observed as antisites exist as Ga vacancies
as evidenced by slow positron annihilation experiments [40] or as arsenic interstitials as evidenced by both rapid diffusion and ion channeling experiments [41]. However, these measurements involve many approximations. Initial theoretical studies [42] on As$_i$ considered only tetrahedral configurations and predicted the concentration to be much less than antisites and vacancies in As-rich GaAs. In addition, As$_i$ were found to be donors and hence was suggested that the dominant acceptors in LT GaAs must be Ga vacancies. Later theoretical investigations on As$_i$ showed that the As$_i$ are not tetrahedral, but split-interstitial configurations [43]. Though it was presumed initially that the concentration of As$_{Ga}^{+}$ is equal to concentration of ionized acceptors, the ionized Ga vacancy, later it was proved that the Ga vacancy is a triple acceptor, V$_{Ga}^{2-}$, by comparing the concentration of As$_{Ga}^{+}$ measured by magnetic dichroism of absorption (MCDA) and V$_{Ga}$ measured by slow positron annihilation [9].

Annealed LT GaAs has its electrical properties dependent on point defects and arsenic precipitates. The defect model [44] correlates the decrease in hopping conductivity to the precipitation of excess As, but, the model assumes that the compensation is provided by residual arsenic antisites and not arsenic precipitates. The model proposed a depletion region around As precipitate and the As precipitates are assumed as an embedded Schottky contact. The material properties are controlled by the defects or the Schottky barriers depending on the relative composition of the defects, which in turn, depends on the anneal temperature which when increased to 600°C will transform the material whose properties are dominated by arsenic precipitates. Ibbetson et al [45] reported that the room temperature conductivity of the material annealed at 600°C for 30 seconds was due to hopping conductivity and for higher-temperature anneals, it was due to a thermally assisted tunneling process caused by arsenic precipitates.

Liu et al [46] studied the structural properties of the LT GaAs by a high-resolution
X-ray diffractometer and measured the concentration of $As_{Ga}^0$ and $As_{Ga}^+$ by optical measurements such as near infrared absorption (NIRA) and magnetic circular dichroism (MCDA) and suggest that the dominant defects are $As_{Ga}$ and $V_{Ga}$ and that the amount of $As_i$ is negligible. Since only the ion channeling experiments supported the presence of $As_i$ as a direct result [47] and as it is believed that the $As$ precipitation upon annealing is attributed to $As_i$. Additionally, the formation energy of $As_i$ is several eVs higher than that of $As_{Ga}$ and $V_{Ga}$, the presence of $As_i$ in LT GaAs is very unlikely. Further, the lattice expansion linearly correlates with the concentration of $As_{Ga}$.

Lagadas et al [48] observed the presence of $As$ precipitates by transmission electron microscopy (TEM) in the material annealed at 600°C and the dependence of excess $As$ incorporation on the growth temperature and BEP. Their theoretical model based on mass balance equation showed that the incorporation of excess $As$ on the surface depends on the growth temperature, BEP and the evaporation of arsenic molecules from the physisorbed state considered in the model.

Luysberg et al [19] studied the growth of LT GaAs by NIRA, MCDA and slow positron annihilation under various growth conditions. They showed that at a fixed temperature, the lattice mismatch increased linearly with BEP up to a critical BEP and then saturated. The saturation value is higher for lower temperatures. They also studied that the concentration of neutral and charged antisites at different growth parameters. At a fixed temperature, the concentration of neutral and charged antisites increased with the increase in BEP up to a critical value of BEP and then saturated. At a higher temperature, the defect concentrations decreased as indicated by the previous results. The concentration of $As_{Ga}^0$ was always an order of magnitude higher than that of $As_{Ga}^+$. Further studies showed that the ultra-fast electron trapping time measured in LT GaAs is related to the presence of $As_{Ga}^+$ [9]. They studied the material
by doping highly with p-type Be to increase the concentration of $As^2_{Ga}$ to improve on the trapping time characteristics.

2.2.2 RHEED

RHEED is the routinely used surface analytical tool to study the dynamics of in situ film growth. In RHEED, a high energy beam of electrons in the range of 5-40 keV is directed towards the surface at a grazing angle of about 1° to 3°. This is ideal for MBE where the molecular beams impinge on the surface at near-normal incidence. The glancing angle reflection geometry exploits the strong forward scattering of high-energy electrons by atoms and leads to a very high surface sensitivity. The de Broglie wavelength of these electrons is in the range of 0.18-0.06 Å. The energy component perpendicular to the surface is around 100 eV. Hence, the penetration of the beam into the surface is low, restricted to the top few atomic layers. The geometrical aspects of the electron diffraction pattern can be explained based on limited penetration and hence by kinematic theory of electron diffraction. The smooth surface with periodic arrangement of atoms acts as a two-dimensional grating and diffracts the incident electron beam. The diffraction pattern is recorded by the fluorescent screen placed diametrically opposite the electron gun.

A plane monochromatic wave incident upon a specimen gives rise to an elementary secondary wave in each element of its volume. The incident wave reaches different points of the volume in different phases and consequently the secondary waves arising from these points also have different phases. The amplitude of scattering in its mathematical form represents a Fourier integral. The required fundamentals of the theory of scattering and of structure analysis can be obtained from the theory of Fourier integrals and from Fourier series. Thus, the relationship between the reciprocal lattice and the planes of the direct lattice for a two dimensional non-orthogonal
cell can be obtained. Using Bragg’s Law and the reciprocal lattice concept, the atom periodicities in the solid surface region can be found by measuring the diffraction spot spacings. The relation between the interplanar distance in the crystal $d$ and the observed diffraction pattern on the fluorescent screen is given by [49]:

$$d = \frac{4\lambda L}{D}$$

(2.1)

where $L$ is the distance between the substrate and the screen and $D$ is the spacing on the screen between beams.

The diffraction is not always a true reflection. If the surface is rough, the pattern is caused by transmission-reflection diffraction and exhibits spotty features. If the surface is smooth, the features look streaky because of the true reflection diffraction [50]. The high specular intensity caused initially is due to the smoothness of the surface.

RHEED Oscillations during MBE

The oscillations of the specular beam intensity as a function of time during MBE was first observed in 1981 [51]. The RHEED oscillations are used to determine growth rates, mole fractions, and quantum well thicknesses. When the growth of the layer is initialized, nucleation occurs and the specular intensity decreases due to destructive interference of the reflected electron beam from the rough surfaces. As the layer fills up, the surface becomes smoother and hence the constructive interference increases which in turn, results in higher specular beam intensity. Layer-by-layer epitaxy with alternate roughening and smoothening of the surface, indicative of significant surface migration, causes RHEED intensity oscillations (ROs) to occur with a period equal to a monolayer deposition time [10,11]. If the migration is limited due to growth conditions, the surface will be rougher which results in decreased amplitude of ROs. The surface migration length changes the period measured due to the competition
between step-flow growth and 2D nucleation, for growth on vicinal surfaces, under constant fluxes. Petrich et al [52] found differences between measured period and growth rate when Ga diffusion length was comparable with the terrace length while calculating expected intensity oscillations during growth on a vicinal surface. Resh et al [53] found that the differences are much more when they added nucleation to this model.

Numerical simulations were carried out by Shitara et al [54] and showed that the intensity oscillation period varied with growth temperature. Sudijono et al [55] reported that the ROs disappear above the temperature at which the growth proceeds by step flow, in which the step density on the growing surface remains constant. Dabirian et al [56] reported that at a constant Ga flux, the period of RHEED oscillations during GaAs growth on an As-stabilized (111) B surface depends on As flux. Since migration length of Ga decreases with decrease in temperature, it was believed that the growth of the crystal is not possible at low temperatures and hence no ROs were expected at low temperatures. Ibbetson et al [14] reported the occurrence of ROs at low temperatures with near stoichiometric flux ratios and suggested that the growth is a layer-by-layer process. They proposed that the process is very sensitive to BEP and that the ROs were observed only under stoichiometric conditions with no excess As present. Recently, Shen et al [17] reported the observance of ROs, over a wide range of BEPs from 12 to 100 at a fixed temperature of 300°C and over temperatures ranging from 150 to 750°C at a fixed BEP of 40, suggesting that the stoichiometric condition is not mandatory for the occurrence of ROs. The theoretical model of Vamsee et al [16] explained the cause of the ROs based on a physisorbed state of As lying above the growing surface and loosely connected to the surface dictating the incorporation of As. They reported that the coverage of this PA layer varied from 0.24 to 0.72.
2.3 Theoretical modeling of MBE growth

Realistic theoretical models of crystal growth by MBE have been developed. Using continuous space models, the assumption of the Hamiltonian is sufficient to describe the physical behavior of the system and are more closer to reality. Conventionally, by discrete models, thermodynamical theories were used to describe processes such as condensation, re-evaporation and incorporation of dislocations. Ab-initio calculations have been made possible with latest computer technologies with realistic interaction potentials. With these microscopic models, the position of the atoms in the growth processes can be simulated in the given conditions and the growth can be better understood. Various theoretical models developed are based on Monte Carlo simulations [57-61], Molecular dynamics [62-64], the stochastic models [18,65-69] and the kinetic rate equation models [16,70].

The widely used technique for modeling MBE processes is Monte Carlo simulation which is done by random sampling [57-61]. The algorithm is based on thermodynamic equilibrium. The properties of the growth system under equilibrium are calculated from its distribution function in the phase space. The size of the growing crystal is taken to be n x n lattice with upto 10 layers building up. The surface processes like incorporation of atoms on the surface, migration and back evaporation from the surface are considered. The system is disturbed by the insertion of a new particle which is incorporated into the growing crystal and then brought to equilibrium until the change in the potential energy by more MC steps is negligible. By repeating this procedure several times, dynamic processes are simulated. Migration and back evaporation processes are taken to be of Arrhenius type with activation energies and frequency factors. MC models represent the substrate and kinetics simply and are easy to implement but consumes more computational time.

Molecular dynamics simulations [62-64] can solve the equation of motion of the
molecules based on Newton's second law of motion and the potential energy functions of semiconductors like Leonard-Jones [62] and Stillinger and Weber functions [71]. The surface kinetics of the atoms in picosecond scales are simulated using the classical dynamical equations of motion. The solution of the coupled equations of motion for any particle of the system in MD restricts the number of particles and also the range of real time simulation because of limitations in CPU time. The specific advantage of MD simulations is that the surface kinetics can be studied to get atomistic details.

Rate equation model [16,70] calculates the time evolution of the change of concentration in each epilayer caused by the surface kinetic processes such as incorporation, migration and evaporation occurring on the surface during growth [70]. The model involves solving simultaneous non-linear differential equations and hence computationally less intensive but does not provide microscopic details of the atoms.

Venkatasubramanian [65] developed a stochastic model for the MBE growth kinetic studies of compound semiconductors based on the work of Saito et al [68]. The model developed at first for diamond cubic lattice and later for the two-sublattice zinc blende structure was based on the master equation approach and modified solid-solid restriction whereby the atom is not absorbed exactly on top of another atom but in a vacant site whose projection falls in between a pair of nearest neighbor atoms. The time evolution of the epilayer is described by the rate of change of a complete set of macrovariables such as coverage of atoms in a layer, atom-atom pair concentration etc. The model was employed to study the surface roughening kinetics in Ge [69]. The kinetics of the LT GaAs were studied using the modified model [16] which in addition to the surface processes like incorporation, evaporation and migration, included the kinetics of the physisorbed layer of As, loosely bound to the surface of the growing crystal by Van der Waal type binding. The thermally activated surface processes are considered rate limiting to dictate the growth of the film. The presence of the PA
layer affects the *in-situ* monitoring of the growth by RHEED. The RHEED beam will interact with both the PA layer and the crystalline surface and the amplitude of the ROs will vary with the coverage of physisorbed arsenic. The model was used to study the RHEED intensity dynamics over a wide range of growth conditions. The model considered the factor that As stayed in the physisorbed state with lifetimes in the range of $10^{-3}$ to $10^{-5}$ s and incorporated only when an appropriate configuration of Ga atoms formed on the surface. The stochastic model is simple, not limited by the crystal size and can be employed to study the doping kinetics in the crystals.

The modified stochastic model [18] developed by Muthuvenkatraman *et al* considers the growth kinetics of the physisorbed arsenic (PA) layer with the inclusion of the chemisorption of As into the surface antisites from the physisorbed state and the evaporation from these surface antisites. The antisite incorporation from the PA layer and the evaporation of the antisites are taken to be temperature dependent and fitted to Arrhenius form of equations with incorporation lifetime $\tau_{in}$ and evaporation lifetime $\tau_{ev}$ factors and activation energies for incorporation and evaporation. The model was employed to study the antisite incorporation in the growth of $LT - GaAs$. The dependences of $As_{Ga}$ and the resultant lattice mismatch on various growth parameters like arsenic flux, temperature and growth rate were explained by this model.
CHAPTER 3

THE RATE EQUATION MODEL FOR GROWTH OF GaAs

3.1 The Kinetic Rate Equation Model

MBE growth involves several surface kinetic processes such as the adsorption and the evaporation, and the surface diffusion processes such as the intralayer diffusion and the interlayer diffusion. The rate of adsorption depends on the flux rate, $J$, and the availability of proper sites on the surface for adsorption. The evaporation and diffusion processes are assumed to be thermally activated and are modelled as Arrhenius type with frequency factor and activation energy given by:

$$ R = R_0 e^{-\frac{E_{\text{act}}}{k_B T}} $$

where $R_0$ is the frequency prefactor, $E_{\text{act}}$ is the activation energy, $k_B$ is the Boltzmann constant and $T$ is the temperature in Kelvin. The atom interactions are assumed pairwise and only up to second nearest neighbor interactions are considered.

The time evolution of the growing epilayer is described through the change of macrovariables resulting from the surface processes. The macrovariables of growth are normalized with respect to the maximum number of possible atoms in the layer. The macrovariables considered are the layer coverage of Ga, As and $A_{\text{Ga}}$ in the layers given as:

$$ C_{\text{Ga}}(2n) : \text{layer coverage of Ga in the } 2n^{\text{th}}\text{ layer} $$
$$ C_{\text{As}}(2n + 1) : \text{layer coverage of As in the } 2n+1^{\text{th}}\text{ layer} $$
$$ C_{A_{\text{Ga}}}(2n) : \text{layer coverage of antisite As in the } 2n^{\text{th}}\text{ layer} $$

(3.2)
where \( n \) is the layer index, with the regular Ga and antisite As belonging to even numbered layers, and the regular As belonging to the odd numbered layers. The layer coverage of atoms is 1, when the layer is completely full and 0, when the layer is completely empty.

Low temperature MBE growth of GaAs will involve additional physics related to possible presence of physisorbed molecules of incoming beams [72,73]. Typically these molecules form a weakly bound precursor state with Van der Waal type binding. This layer of material undergoes two dynamic processes, chemisorption into regular and antisites and desorption [11,68,72,73]. A schematic diagram illustrating the surface dynamic processes of the PA layer and antisite As is shown in Figure 4.1. The processes are thermally activated processes and the time constants for these processes which are inverse of the rate processes are described in the Arrhenius rate form as:

\[
\tau_{\text{in}} = \tau_{0,\text{in}} e^{\frac{E_{\text{in}}}{kT}} \tag{3.3}
\]
\[
\tau_{\text{ev}} = \tau_{0,\text{ev}} e^{\frac{E_{\text{ev}}}{kT}} \tag{3.4}
\]

where \( \tau_{0,\text{in}} \) and \( \tau_{0,\text{ev}} \) are time factor constants, \( E_{\text{in}} \) and \( E_{\text{ev}} \) refer to activation energy for incorporation and evaporation of antisites, respectively, \( k \) is the Boltzman constant and \( T \) is the temperature in K.

The time evolution of the layer coverage of the PA layer, \( \frac{dC_{\text{Phy,As}}}{dt} \), is given by:

\[
\frac{dC_{\text{Phy,As}}}{dt} = \left( J_{\text{As}} - \frac{dC_{\text{As}}}{dt} \right) - \frac{C_{\text{Phy,As}}}{\tau_{\text{eu}}^{\text{Phy,As}}} - \frac{C_{\text{Phy,As}} f_{\text{As}}}{\tau_{\text{in,rec}}^{\text{Phy,As}}} - \frac{C_{\text{Phy,As}} f_{\text{Ga}}}{\tau_{\text{in,an}}^{\text{Phy,As}}} \tag{3.5}
\]

where \( C_{\text{Phy,As}} \) is the PA layer coverage and is equal to 1, when the layer is completely full and is zero, when the layer is completely empty. \( J_{\text{As}} \) is the molecular flux of As coming into the PA state and its units here are in atom/sec. The units of flux is usually in atoms/cm\(^2\).sec. and it can be converted to atom/site.sec which is simply written as atom/sec. The conversion is performed using the effective area per crystalline site which in case of GaAs, with lattice constant \( a=5.6533\AA \), is given by \( a^2/2 \) and is...
equal to 15.97 Å² in the (100) growth direction. \( \frac{dC_{\text{phy, As}}}{dt} \) is the rate of incorporation of As into the epilayer and \( C_{\text{As}} \) is the total concentration of As in all the crystalline layers. Typically, it is equal to the growth rate or the Ga flux rate, \( J_{\text{Ga}} \). In the above equation, the first term denotes the increase in PA coverage due to arrival of As flux into the PA layer. The next three terms denote the net loss of PA layer coverage due to evaporation, chemisorption into regular As site and \( As_{\text{Ga}} \) incorporation into Ga layer, respectively. \( f_{\text{Ga}} \) and \( f_{\text{As}} \) represent the fraction of the available surface Ga sites and are time and temperature dependent. \( \tau \) with respective suffixes represent the corresponding time constants.

The time evolution of the growing epilayer is described through the change of macrovariables resulting from the surface processes. The macrovariables of growth are normalized with respect to the maximum number of possible atoms in the layer. The macrovariables considered are the layer coverage of Ga, As and \( As_{\text{Ga}} \) in the layers given as:

\[
C_{\text{Ga}}(2n) : \text{layer coverage of Ga in the } 2n^{\text{th}} \text{layer}
\]

\[
C_{\text{As}}(2n + 1) : \text{layer coverage of As in the } 2n+1^{\text{th}} \text{layer}
\]

\[
C_{\text{AsGa}}(2n) : \text{layer coverage of antisite As in the } 2n^{\text{th}} \text{layer}
\]

where \( n \) is the layer index, with the regular Ga and antisite As belonging to even numbered layers, and the regular As belonging to the odd numbered layers. The layer coverage of atoms is 1, when the layer is completely full and 0, when the layer is completely empty. The time evolution of the layer coverage of Ga in the \( 2n^{\text{th}} \) layer due to the various surface processes is given by:

\[
\frac{dC_{\text{Ga}}(2n)}{dt} = (\{C_{\text{As}}(2n - 1) - C(2n)\} J_{\text{Ga}}) (A1) + [C_{\text{As}}(2n - 1) - C(2n)]
\]

\[
\times \left( R_0 e^{-\frac{E_\text{a}(2n+2)}{kT}} \left( \frac{C_{\text{Ga}}(2n+2)}{C(2n+2)} \right) [C(2n+2) - C_{\text{As}}(2n+3)]
\]

\[
+ R_0 e^{-\frac{E_\text{a}(2n-2)}{kT}} \left( \frac{C_{\text{Ga}}(2n-2)}{C(2n-2)} \right) [C(2n-2) - C_{\text{As}}(2n-1)] \right) (B1)
\]
\[ - R_0 e^{-\frac{E_d(2n)}{kT}} \left( \frac{C_{Ga}(2n)}{C(2n)} \right) [C(2n) - C_{As}(2n + 1)] \]
\[ \times \left( [C_{As}(2n + 1) - C(2n + 2)] + [C_{As}(2n - 1) - C(2n)] \right) (C1) \]
\[ - R_0 e^{-\frac{E_d(2n)}{kT}} \left( \frac{C_{Ga}(2n)}{C(2n)} \right) [C(2n) - C_{As}(2n + 1)] (D1) \]

(3.7)

where the term A1 denotes the increase in \( C_{Ga}(2n) \), due to adsorption of Ga from the incoming molecular beam. The rate of adsorption is the product of the available sites for Ga incorporation on the surface, \([C_{As}(2n - 1) - C(2n)]\), and the flux of Ga, \( J_{Ga} \). The sticking coefficient of Ga is taken as unity. The term B1 describes the increase in \( C_{Ga}(2n) \) due to migration into the 2n\(^{th}\) layer from adjacent Ga layers indexed (2n+2) and (2n-2) and is proportional to the fraction of available sites for Ga in the 2n\(^{th}\) layer, \([C_{As}(2n - 1) - C(2n)]\). The rate of migration is described by Arrhenius type rate equations with frequency factor, \( R_0 \) and activation energy, \( E_d \). The cation sublattice contains two possible elements, Ga and antisite, \( As_{Ga} \). Thus,

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

Therefore, of the fraction of the (2n+2)\(^{th}\) layer exposed, only a fraction of it is Ga portion. Thus, the fraction \( \frac{C_{Ga}(2n+2)}{C(2n+2)} \) is used to make sure that only the Ga portion is considered for migration. Similar arguments hold for the (2n-2)\(^{th}\) layer also. The activation energy for a particular layer is a function of layer coverage of that layer, the activation energies of isolated atoms, \( E_{d,iso} \), and the second neighbor atom-atom pair interaction energy, \( E_{Ga,Ga} \), with a factor of four as there are four possible neighboring atoms present. In the mathematical form, the activation energy for diffusion for the (2n+2)\(^{th}\) Ga layer is given as:

\[ E_d(2n - 2) = E_{d,iso} + 4E_{Ga,Ga}C_{Ga}(2n - 2) \]

Thus \( E_d(2n) \) is equal to \( E_{d,iso} \) when the coverage is very small, and this is the correct value since there will be no inplane nearest neighbors, and is equal to \( E_{d,iso} + 4E_{Ga,Ga} \)
when the layer is full and is also the correct value in this limit since there will be 4 inplane nearest neighbor atoms. The term C1 denotes the decrease in $C_{Ga}(2n)$ due to migration out of the 2n<sup>th</sup> layer to the adjacent layers, (2n+1) and (2n-3). The description of the rate of this process is similar to term B1, with $E_d(2n)$ being the activation energy for migration from 2n<sup>th</sup> layer, $[C_{As}(2n+1) - C(2n + 2)]$ and $[C_{As}(2n-1) - C(2n)]$ being the fractions available for Ga atoms to migrate in the adjacent layers (2n+1) and (2n-3) respectively and $[C_{As}(2n) - C(2n + 1)]$ being the fraction of Ga atoms in the 2n<sup>th</sup> layer. $\frac{C_{Ga}}{C}$ is the fraction of the 2n<sup>th</sup> layer to which the rate constant is applied. The term D1 describes the evaporation of Ga atoms from the 2n<sup>th</sup> layer resulting in the decrease in $C_{Ga}(2n)$ with activation energy for evaporation, $E_e(2n)$, and the fraction of the 2n<sup>th</sup> layer exposed, $[C_{As}(2n) - C(2n + 1)]$. Note that only the Ga portion of the exposed layer is considered by using the fraction $\frac{C_{Ga}(2n)}{C(2n)}$.

The description of the activation energy for evaporation, $E_e$ is similar to that of $E_d$ and is given as:

$$E_e(2n) = E_{e,iso} + 4E_{GaGa}C_{Ga}(2n)$$

with $E_{e,iso}$ is the evaporation energy for the isolated atom.

The time evolution of the layer coverage of As$_{Ga}$ in the 2n<sup>th</sup> layer is given as:

$$\frac{dC_{As_{Ga}}(2n)}{dt} = ([C_{As}(2n - 1) - C(2n)]J_{Ga}) (A2) + [C_{As}(2n - 1) - C(2n)]$$

$$\times \left( R_0 e^{-\frac{E_d(2n+2)}{kT}} \left( \frac{C_{As_{Ga}}(2n + 2)}{C(2n + 2)} \right) [C(2n + 2) - C_{As}(2n + 3)] 
+ R_0 e^{-\frac{E_d(2n-2)}{kT}} \left( \frac{C_{As_{Ga}}(2n - 2)}{C(2n - 2)} \right) [C(2n - 2) - C_{As}(2n - 1)] \right) (B2)$$

$$- R_0 e^{-\frac{E_d(2n)}{kT}} \left( \frac{C_{As_{Ga}}(2n)}{C(2n)} \right) [C(2n) - C_{As}(2n + 1)]$$

$$\times \left( [C_{As}(2n + 1) - C(2n + 2)] + [C_{As}(2n - 1) - C(2n)] \right) (C2)$$

$$- R_0 e^{-\frac{E_d(2n)}{kT}} \left( \frac{C_{As_{Ga}}(2n)}{C(2n)} \right) [C(2n) - C_{As}(2n + 1)] (D2)$$

(3.8)

Note that Eqn. 3.8 is similar to 3.7 except for the substituion of Ga with As$_{Ga}$.
The activation energies \( E_{d, As_{Ga}} \) and \( E_{e, As_{Ga}} \) are given by:

\[
E_{d, As_{Ga}} = E_{d, As_{Ga}, iso} + 4E_{Ga, As_{Ga}} C_{Ga}
\]

\[
E_{e, As_{Ga}} = E_{e, As_{Ga}, iso} + 4E_{Ga, As_{Ga}} C_{Ga}
\]

The terms A2, B2, C2 and D2 are similar to that of A1, B1, C1 and D1 in description except for the substitution of \( Ga \) with \( As_{Ga} \).

The time evolution of the layer coverage of \( As \) in the \( 2n+1^{th} \) layer, \( C_{As}(2n + 1) \), is written as:

\[
\frac{dC_{As}(2n + 1)}{dt} = ([C(2n) - C(2n + 1)] J_{As}) (A3) + \left[ C(2n) - C(2n + 1) \right]
\]

\[
\times \left( R_0 e^{\frac{-E_{d, (2n+1)}}{kT}} \left( \frac{C_{As}(2n + 3)}{C(2n + 3)} \right) \right) [C(2n + 3) - C(2n + 4)]
\]

\[
+ R_0 e^{\frac{-E_{d, (2n-1)}}{kT}} \left( \frac{C_{As}(2n - 1)}{C(2n - 1)} \right) [C(2n - 1) - C(2n)] (B3)
\]

\[
- R_0 e^{\frac{-E_{d, (2n+1)}}{kT}} \left( \frac{C_{As}(2n + 1)}{C(2n + 1)} \right) [C(2n + 1) - C(2n + 2)] (C3)
\]

\[
\times \left( [C(2n + 2) - C_{Ga}(2n + 3)] + [C(2n) - C(2n + 1)] \right) (C3)
\]

\[
- R_0 e^{\frac{-E_{d, (2n+1)}}{kT}} \left( \frac{C_{As}(2n + 1)}{C(2n + 1)} \right) [C(2n + 1) - C(2n + 2)] (D3)[3.9)
\]

All the terms A3, B3, C3 and D3 can be explained similar to those of Eqn. 3.7.

Thus coupled nonlinear first order differential equations, given by Eqns. 3.7, 3.8 and 3.9, are obtained for the time evolution of all the macrovariables for every layer to be simulated and an additional equation for the PA layer, given by Eqn. 3.5, considered on the surface is also included.

### 3.2 Computational Details

Description of evolution of each bilayer of \( GaAs \) requires 3 first order nonlinear differential equations, one describing the time evolution of each of the normalized macrovariables. In this work simultaneous growth of 80 bilayers and the PA layer are considered requiring a total of 241 (= 80 x 3 + 1) coupled nonlinear first order
differential equations. The system of equations were integrated using a Fourth-order Runge Kutta method with time steps of less than $10^{-6}$ s to get the values of each of the macrovariables as a function of time for a growth time of 20 s. The growths were simulated on the Silicon Graphics supercomputer ORIGIN-2000. The average coverages of $Ga$, $As$ and $As_{Ga}$ in individual layers at the end of growth are obtained from the solution of the differential equations by considering the coverage of a few layers in the bulk, viz., the layers far from the substrate and the surface. A fraction of layer coverages of the particular species is obtained by this method. This fraction is converted to concentration per cm$^3$ using the total number of sites/cm$^3$ in a sublattice, which in the case of GaAs is $2.21 \times 10^{22}$/cm$^3$.

3.3 Conversion of $J_{As}$ to BEP

Experimentally, the As flux is described in terms of BEP for a given Ga flux, whereas our model requires the flux in number of monomer atoms per site per second. The conversion between the two flux definitions is accomplished using the following equation [75]:

$$
\frac{J_{As}}{J_{Ga}} = \frac{P_{As}}{P_{Ga}} \frac{T_{As}}{T_{Ga}} \frac{M_{Ga}}{M_{As}}
$$

(3.10)

where $\frac{P_{As}}{P_{Ga}}$ is the BEP, $J$ is the flux and $T$ is the absolute temperature and $M$ is the molecular weight. $\eta$ is the ionization efficiency for the respective species relative to nitrogen and is given by:

$$
\frac{\eta}{\eta_{N_2}} = \left[ \left( \frac{0.4Z}{14} \right) + 0.6 \right]
$$

(3.11)

where $\eta_{N_2}$ is the ionization efficiency of nitrogen and $Z$ is the atomic number. In this Eqn 3.10, the As is assumed a tetramer. The values used for MBE growth of GaAs are: $Z_{Ga}=31; Z_{As}=4 \times 33; T_{As}=1173K; T_{Ga}=573K; M_{Ga}=69.72$ and $M_{As}=4 \times 74.92$ to obtain the value of $J_{As}$ as 0.2345(BEP)(J$_{Ga}$) monomer/site.sec. $J_{Ga}$ is in $\mu$m/hr. The number of sites per cm$^2$ in case of (100) GaAs is obtained as: $1\mu$m/hr. $= 2.77$
Å/sec.; Since one bilayer of GaAs is half of the cubic lattice constant which is equal to 2.82Å, 0.98 atoms/site/sec. arrive a site for a growth rate of 1μm/hr. The equivalent surface area for a (100) site is $6 \times 10^{-16}$ cm$^2$ and hence, the number of sites per cm$^2$ is obtained as $6.26 \times 10^{14}$. Using the conversion factors described in the above paragraph along with Eqn. 4.2, Eqn. 4.1 can be rewritten as:

$$J_{As}(\text{monomer/cm}^2\cdot\text{sec.}) = 4.0 \times 1.46 \times 10^{14} \times \left(\frac{P_{As}}{P_{Ga}} \text{(BEP)}\right) J_{Ga}(\mu\text{m/hr.}) \quad (3.12)$$

where 4 is used for converting the tetramer to monomer.
CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Neutral and Charged antisite concentrations

The growth direction considered is [100] and the growth rate is \(1 \mu \text{m/hr.}\) for antisite calculations. The growth rate of \(1 \mu \text{m/hr.}\) is equivalent to 0.983 atoms/sec. As is assumed to be a monomer, cracked from either As\(_2\) or As\(_4\). Both Ga and As are allowed to incorporate on the surface sites even when only one of the surface covalent bonds is satisfied. This is equivalent to relaxing the modified solid on solid (MSOS) restriction of the initial model of Ref. [65]. Investigations are performed over a temperature ranging from 423°K to 513°K for the calculations of antisite concentrations over a BEP ranging from 9 to 30.

From the solutions of the differential equations, the coverage of Ga, As and As\(_{Ga}\), viz., \(C_{Ga}\), \(C_{As}\) and \(C_{AsGa}\), in their respective layers of all the 80 bilayers are obtained using the procedure explained in section 3. In the case of even numbered layers, i.e., Ga sublattices, in addition to Ga, As\(_{Ga}\), there are vacancies, \(V_{Ga}\), present. Hence, the coverage of the even numbered layers, \(C(2n)\), is obtained as:

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

(4.1)

And the coverage of \(V_{Ga}\) in the \(2n^{th}\) layer is the sum of all Ga sites not occupied by either Ga or As\(_{Ga}\) and is obtained as:

\[
C_{V_{Ga}} = 1 - C(2n)
\]

(4.2)
since the maximum coverage possible in a layer is 1. The Ga vacancies, $V_{Ga}$, which are present as triple acceptors [9], partially compensate $As_{Ga}$, a part of which is positively charged. Thus, from the charge neutrality equation, the charged antisite $As_{Ga}^+$ coverage is equal to three times that of $V_{Ga}$. Mathematically,

$$3V_{Ga}^{3-} = C_{As_{Ga}}^+$$  \hspace{1cm} (4.3)

So, $V_{Ga}^{3-}$ and hence $C_{As_{Ga}}^+$ can be obtained from the simulation results using Eqns. 4.1-4.3. The total antisite coverage in the 2$n^{th}$ layer which is obtained as part of the results of simulation is the sum of charged and neutral antisites:

$$C_{As_{Ga}}(2n) = C_{As_{Ga}^+} + C_{As_{Ga}^0}$$ \hspace{1cm} (4.4)

Hence, the coverage of neutral antisites $C_{As_{Ga}^0}$ can be obtained by subtracting the coverage of charged antisites, from that of the total antisites $C_{As_{Ga}}$. The layer coverages of antisites for several layers far away from the surface and substrate, i.e., bulk, were found to be uniform for all simulations. These coverages were converted to volume concentrations by using the approach discussed at the end of section 3.2.

Charged and neutral antisite As concentration versus BEP obtained from our simulations were fitted to four experimental data points of Luysberg et al [8] to fix the model parameters accurately. The fixed model parameters for the various surface processes are listed in Table I. Using the fixed model parameters, model predictions for the remaining growth conditions were obtained.

Plots of $As_{Ga}^0$ and $As_{Ga}^+$ versus BEP for 513°K and 473°K obtained using the model are shown along with the experimental data of Luysberg et al [8] in Figure 4.2. The agreement between the results is good. Both $As_{Ga}^0$ and $As_{Ga}^+$ concentrations saturate beyond a BEP of 20 for 513°K and 473°K. The explanation for such a behavior can be given based on the consideration of the PA layer of arsenic. For
a given temperature, as BEP increases, the \( As \) flux in excess of \( Ga \) flux increases, resulting in increase in the PA layer coverage till the coverage reaches its maximum value of unity at a critical BEP [18]. Beyond the critical BEP, any further increase in BEP does not change the PA layer coverage as it has attained its maximum of monolayer coverage. The \( As^0_{Ga} \) and \( As^+_{Ga} \) concentrations incorporated in the crystal are dictated by two competing mechanisms, incorporation of \( As \) from the PA layer and evaporation of \( As_{Ga} \) from the crystal. For a given temperature, the saturation of \( As_{Ga} \) occurs because the incorporation and evaporation lifetimes and the PA layer coverage are all constant beyond the critical BEP. Hence the incorporation of \( As^0_{Ga} \) and \( As^+_{Ga} \) directly depends on the PA layer coverage. The saturation of \( As_{Ga} \) concentration is lower for higher temperature because of higher evaporation rate of \( As_{Ga} \) from the crystal. The decrease in \( As^+_{Ga} \) concentration with increase in temperature is also due to the reason that the migration length of \( Ga \) is more at a higher temperature which decreases the \( Ga \) vacancy concentration and hence decreases the \( As^+_{Ga} \) concentration. Both \( As^+_{Ga} \) and \( As^0_{Ga} \) exhibit the same dependencies on BEP and temperature, but the \( As^0_{Ga} \) is consistently one order of magnitude higher than the concentration of \( As^+_{Ga} \).

3-D plots of the concentration of \( As^0_{Ga} \) and \( As^+_{Ga} \) respectively with respect to the variation of temperature from 423°K to 513°K and BEP from 9 to 30 are shown Figures 4.3 and 4.4. When the temperature is decreased from 513°K the concentrations of both \( As^0_{Ga} \) and \( As^+_{Ga} \) continue to increase until a particular value and then saturate at all BEP values. This result is in agreement the experimental results [74] in which the lattice mismatch proportional to \( As^0_{Ga} \) was measured. In the experimental measurements below 165°C, the layers became polycrystalline and the lattice mismatch could not be determined. As the temperature decreases from 513°K, the evaporation of \( As^0_{Ga} \) from the crystal decreases and becomes negligible at lower temperatures.
Hence, the \( \text{As}_{Ga}^0 \) concentration increases. At low temperatures, the PA layer coverage is more and at a critical temperature it reaches the monolayer coverage which makes the antisite concentration saturate.

A plot of the change in the concentration of \( \text{As}_{Ga}^0 \) for various growth rates in the range of 1-1.5 \( \mu \text{m/hr.} \) at 473°K for various BEP ratios and at 513°K at a fixed BEP of 20 is shown in Figure 4.5. The \( \text{As}_{Ga}^0 \) concentration decreases when the growth rate is increased at all the values of BEP uniformly. When the growth rate is increased, say from 1\( \mu \text{m/hr.} \), the number of \( Ga \) atoms arriving at the surface increases. There is a competition between the arriving \( Ga \) atoms and the antisite \( As \) to occupy the surface cationic sites of the growing crystal. When more number of \( Ga \) atoms arrive at the surface, the incorporation of excess \( As \) in to antisites decreases and hence the \( \text{As}_{Ga}^0 \) concentration decreases. A similar plot for the concentration of \( \text{As}_{Ga}^+ \) with different growth rates at 473°K for various BEP ratios and at 513°K at a fixed BEP of 20 is shown in Figure 4.6. The behavior of \( \text{As}_{Ga}^+ \) concentration and explanation are similar to those of \( \text{As}_{Ga}^0 \).

Since the concentration of \( \text{As}_{Ga}^+ \) was correlated to the short decay times of excess carriers [6], it was suggested that the response times actually correspond to the trapping time of excess electrons, rather than to carrier recombination times. Hence the temporal response of \( LT - GaAs \) can be controlled not only by changing the growth temperature but also by introducing acceptor dopants that allow to increase the concentration of \( \text{As}_{Ga}^+ \). In undoped \( LT - GaAs \), the concentration of \( \text{As}_{Ga}^+ \) was determined mainly by \( V_{Ga} \), the native acceptors of the material. However, the undoped \( LT - GaAs \) is metastable, i.e., thermal annealing above 400°C causes lattice relaxation due to \( As \) outdiffusion and \( As \) precipitate formation. It was found [7] that the ionized antisites are thermally more stable than the neutral antisites. Specht et al [9] investigated the high \( p \)-doping with \( Be \) acceptors to achieve high ionization fraction.
of the antisites. The $Be$ concentrations in the layers were determined by Secondary Ion Mass Spectrometry (SIMS), the concentration of $As_{Ga}^2$ was determined by NIRA, the concentration of $As_{Ga}^4$ by MCDA and that of $V_{Ga}$ by slow positron annihilation. For a $Be$ concentration of $7 \times 10^{19}/cm^3$, the lattice mismatch of the sample grown at $200^\circ C$, was found to decrease. This is due to the fact that the size of $Be$ atom is smaller than that of $As$.

The kinetic rate equation model was used to determine the $Be$ doping kinetics of LT GaAs. Though experimental data are available for $Be$ concentrations, the $Be$ flux is not available without which modeling the doping kinetics with the present model is limited. With the data available, the general trend of the decrease in antisite concentration with increase in $Be$ doping was observed with the model but predictions for different growth parameters could not be performed without the $Be$ flux data.

### 4.2 RHEED Oscillations

The growth direction considered is $[100]$ for RHEED intensity calculations. The range of growth conditions investigated in the study are: temperature in the range of $523-773^\circ K$ and $As$ beam equivalent pressures in the range of $10-40$ at a growth rate of $0.7\mu m/hr$. $As$ is assumed to be a monomer, cracked from either $As_2$ or $As_4$. The presence of the PA layer on the surface influences the in $–$ situ monitoring of the growth rate and the surface quality by RHEED. In the presence of the PA layer, the incident RHEED electron beam interacts with both the crystalline surface of the growing crystal and the surface of the PA layer. Hence the amplitude of ROs is dictated not only by the step density variation, but also by the physisorbed layer coverage variation with time. The crystalline surface of the $GaAs$ exposed to the RHEED beam changes with time with respect to the periodic variation of the surface coverage of the PA layer even if the step density is constant. A schematic picture of the RHEED beam interactions with the two surfaces is illustrated in Figure 4.7.
A 10kV electron beam incident at 1° grazing incidence is considered. The scattering from the two distinct surfaces, the PA surface and the exposed crystalline surface, should be considered and are given by:

$$A_1(t) = \sum_{n=1}^{\infty} (C(2n-1) - C(2n)) (1 - C_{Phy}) \exp \left[ i \left( \frac{2\pi}{\lambda} d - \frac{2\pi}{\lambda} d_{Phy} \right) \right]$$ (4.5)

$$A_2(t) = \sum_{n=1}^{\infty} (C(2n-1) - C(2n)) (C_{Phy}) \exp \left[ i \left( \frac{2\pi}{\lambda} d + d_{Phy} \right) \right]$$ (4.6)

where the term $A_1$ accounts for the scattered wave amplitude from the exposed crystal and $A_2$ for that from the PA layer. $C_{Phy}$ is the surface coverage of the PA layer. $d_{Phy}$ is the interplanar distance from the PA layer to the underlying crystalline layer. $d$ is the interplanar distance of the GaAs crystal. $\lambda$ is the wavelength of incident beam. The resultant specular beam intensity $I$ is given by:

$$I(t) = \sum_{n=1}^{\infty} |A_1(2n) + A_2(2n)|^2$$ (4.7)

Note that the coverage variables are a function of time and hence $A_1(t)$, $A_2(t)$ and $I(t)$ will also be a function of time.

RHEED intensity versus time can be computed using growth data of concentration versus time into Eqns. 4.5 - 4.7 with an $As - As$ interplanar distance of 2.48 Å for physisorbed As layer and a $Ga - As$ interplanar distance of 1.41 Å. The interplanar distances considered are quite reasonable since in the PA layer, atoms are loosely connected by Van der Waal type binding and hence the value should be larger than the crystalline $Ga - As$ bond and close to the gaseous dimer bond length.

Plots of ROs versus time at a BEP of 40 with varying temperatures simulated using our model are shown in Figure 4.8. Comparing the results of Fig. 1 of Ref [Shen] to Figure 4.8, the qualitative agreement between the results is good. At an As BEP of 40, the ROs are prominent for temperature above 673°K and below 573°K with a temperature window between 573 and 623°K in which ROs disappear. This behavior can be explained as follows. The growing $GaAs$ surface is partially covered by a layer of physisorbed $As$ which is bonded to chemisorbed crystalline $As$. Thus, the reflected
RHEED intensity has two components, one from the exposed GaAs crystalline surface and the other from physisorbed As. For low temperatures, the surface is almost covered by the physisorbed As whose step density oscillates periodically with the subsurface crystalline GaAs and hence results in ROs. At high temperatures, the physisorbed As evaporates from the surface and exposes the crystalline GaAs which yields ROs due to periodic step-density oscillations. At intermediate temperatures, the surface is partially covered by the physisorbed As resulting in RHEED intensity from crystalline and physisorbed As surfaces. Due to very different interplanar distances between these layers i.e., \( d_{Ga-As} = 1.41\,\text{Å} \) and \( d_{As-As} = 2.48\,\text{Å} \), complete destructive interference of the two reflected from the PA layer and the crystal results at surface coverage of 0.5 of the PA layer. Thus, there are no ROs in the intermediate temperature range of 573°K and 773°K.

A plot of ROs versus time at 573°K with varying BEPs obtained using the model is shown in Figure 4.9. The results agree qualitatively well with that of Fig. 3 of Ref.[17]. The ROs are seen at a BEP above 40 and below 30 and disappear in the intermediate range. This behavior can be explained based on a reasoning similar to the one presented for the temperature behavior. For high BEPs, the surface is almost covered by the PA layer whose step density oscillates periodically with that of the underlying crystal and hence results in ROs. At low BEPs, due to the reduced overpressure of As, more crystalline surface is exposed to the electron beam which yields ROs due to periodic step density oscillations. At intermediate BEPs, due to the partial surface coverage of the PA layer, the RHEED intensity has both the components interacting with each other. When the PA layer coverage is 0.5, both the reflected beams interfere destructively due to their different interplanar distances to result in no ROs.

ROs versus time obtained by simulation using the model at a growth rate of 1.4\( \mu \text{m/hr} \) at 573°K at various BEP ratios is plotted in Figure 4.10. The results are compared with those of Figure 8 corresponding to a lower growth rate of 0.7\( \mu \text{m/hr} \).
other growth conditions remaining same. It is obvious from the plots that by doubling the growth rate, the number of layers grown is doubled, at any BEP ratio, which can be seen as the number of ROs in the plots. However, the BEP ratio window at which the ROs are suppressed remains the same between 30 and 40. This is due to the reason that the PA layer coverage remains unaffected by the variation of growth rate.

4.3 Advantages and limitations of the model

The kinetic rate equation model developed calculates the change in concentration of elements in each epilayer grown at each interval of time. Since the model is described by a system of differential equations, the calculations can be performed easily with less computational time. The model considers surface kinetic processes like incorporation, evaporation, migration, deposition, nucleation, growth of islands and interlayer and intralayer migration of atoms from the islands. The model is simple and not limited by crystal size. The doping kinetics in the crystal growth can be performed with ease. Any number of elemental sources can be considered with all surface processes applicable.

The main disadvantage of the model is that the microscopic details of the atoms such as size and shape of the islands cannot be obtained. The position of atoms or the energy cannot be determined and hence the sites available for antisites are considered only from the total number of atoms in the layer. The activation energies for evaporation, $E_e$ and migration, $E_d$ considered with four neighbor atoms is only approximate and may not exactly have neighbors as assumed. Those energies may be a different function of the coverage of atoms.
Table I: Model parameters obtained by fitting the simulation results to the experimental data of Luysberg et al. [8] and obtained from Ref.[18].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Model Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{As, Ga_{0, in}}$</td>
<td>prefactor for antisite adsorption</td>
<td>172.0 s</td>
</tr>
<tr>
<td>$\gamma_{Phy, As_{0, in}}$</td>
<td>prefactor for physisorbed As evaporation</td>
<td>$2.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\gamma_{Phy, As_{0, in, re}}$</td>
<td>prefactor for physisorbed As incorporation in regular As site</td>
<td>172.0 s</td>
</tr>
<tr>
<td>$E_{d, iso}^A_{Ga}$</td>
<td>activation energy for diffusion for isolated Ga atom</td>
<td>0.4 eV</td>
</tr>
<tr>
<td>$E_{d, iso}^A_{As_{Ga}}$</td>
<td>activation energy diffusion for isolated As$_{Ga}$ atom</td>
<td>1.45 eV</td>
</tr>
<tr>
<td>$E_{d, iso}^A_{As}$</td>
<td>activation energy for diffusion for isolated As atom</td>
<td>0.8 eV</td>
</tr>
<tr>
<td>$E_{d, iso}^A_{Ga}$</td>
<td>activation energy for evaporation for isolated Ga atom</td>
<td>1.4 eV</td>
</tr>
<tr>
<td>$E_{d, iso}^A_{As_{Ga}}$</td>
<td>activation energy diffusion for isolated As$_{Ga}$ atom</td>
<td>1.3 eV</td>
</tr>
<tr>
<td>$E_{d, iso}^A_{As}$</td>
<td>activation energy for evaporation for isolated As atom</td>
<td>1.5 eV</td>
</tr>
<tr>
<td>$E_{Ga-As}$</td>
<td>$2^{nd}$ neighbor atom-atom pair interaction energy for Ga</td>
<td>0.14 eV</td>
</tr>
<tr>
<td>$E_{As-As}$</td>
<td>$2^{nd}$ neighbor atom-atom pair interaction energy for As and As$_{Ga}$</td>
<td>0.25 eV</td>
</tr>
<tr>
<td>$E_{As-As_{Ga}}$</td>
<td>$2^{nd}$ neighbor atom-atom pair interaction energy for As and As$_{Ga}$</td>
<td>0.25 eV</td>
</tr>
<tr>
<td>$R_{0, d, Ga}$</td>
<td>frequency factor for Ga for diffusion</td>
<td>2537.0 / s.</td>
</tr>
<tr>
<td>$R_{0, e, Ga}$</td>
<td>frequency factor for Ga for evaporation</td>
<td>463970.0 / s.</td>
</tr>
<tr>
<td>$R_{0, d, As_{Ga}}$</td>
<td>frequency factor for As$_{Ga}$ for diffusion</td>
<td>$7.8 \times 10^{14} / s.$</td>
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<tr>
<td>$R_{0, e, As_{Ga}}$</td>
<td>frequency factor for As$_{Ga}$ for evaporation</td>
<td>$1.1 \times 10^{12} / s.$</td>
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<tr>
<td>$R_{0, As}$</td>
<td>frequency factor for As</td>
<td>$4.16 \times 10^{10} / s.$</td>
</tr>
</tbody>
</table>
Figure 4.1: A schematic picture showing the surface processes of the physisorbed and antisite As.
Figure 4.2: A plot of model results of charged and neutral antisite concentrations versus BEP along with the experimental results of Luysberg et al. [8]

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NEUTRAL ANTISITES

Figure 4.3: Model results of neutral antisites concentration versus BEP and Temperature.

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Figure 4.4: Model results of charged antisites concentration versus BEP and Temperature.

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Figure 4.5: Model results of neutral antisites concentration versus BEP at different growth rates.

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Figure 4.6: Model results of charged antisites concentration versus BEP at different growth rates.
Figure 4.7: A schematic picture showing the reflected electron beams from the PA layer and the crystalline surface and the thicknesses of the layers.
Figure 4.8: ROs versus time at 573°C for various BEP ratios at a growth rate of 0.7μm/hr. compared qualitatively with the experimental results of Shen et al: Fig. 1 of Ref. [17].
Figure 4.9: ROs versus time at 40 BEP for various temperatures at a growth rate of 0.7μm/hr. compared qualitatively with the experimental results of Shen et al: Fig. 3 of Ref. [17]
Figure 4.10: Model results of ROs versus time at 573°K for various BEP ratios at a growth rate of 1.4μm/hr.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The low temperature MBE of GaAs, which has received much attention in the recent years due to the semi-insulating nature of the material grown, useful for device applications, was investigated theoretically over various growth parameters such as temperature and BEP ratio to pave way for a better understanding of the incorporation of neutral and charged antisites, $As_{Ga}^0$ and $As_{Ga}^\pm$. A comprehensive kinetic rate equation model is developed based on the surface kinetic processes such as adsorption, evaporation of As and antisites and migration and the kinetics of the physisorbed state of As on the surface of the growing crystal of GaAs to explain both the physics of the incorporation of both charged and neutral antisites and the occurrence of ROs at different growth conditions. The PA layer of As weakly bound at the surface of the growing crystal is responsible for the incorporation of the dominant point defects, $As_{Ga}^0$ and $As_{Ga}^\pm$ and influences the resultant ROs. The model considers the presence of the gallium vacancies, $V_{Ga}^{3-}$ which are dominant acceptors, to calculate the concentration of the $As_{Ga}^\pm$ so that the charge neutrality of the material is maintained. The concentration of $V_{Ga}^{3-}$ which are very small to be measured by any currently available experimental techniques accurately have been calculated theoretically, first time by any of the theoretical studies reported. The results of the model which allows for the temperature dependent incorporation and evaporation of regular As and $As_{Ga}$ agrees well with the experimental observations of Luysberg et al [8] for $As_{Ga}^0$ and $As_{Ga}^\pm$ concentrations and the experimental results of Shen et al [17] for the RHEED behavior.

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The values activation energies obtained are agreeable. The concentrations of \( \text{As}^0_{\text{Ga}} \) and \( \text{As}^+_{\text{Ga}} \) increase with the increase in \( \text{As} \) flux, and then saturate at a critical value. When the temperature is decreased from 523°K, both the concentrations decrease and saturate. The concentration of \( \text{As}^+_{\text{Ga}} \) is always an order of magnitude lower than that of \( \text{As}^0_{\text{Ga}} \). Both \( \text{As}^0_{\text{Ga}} \) and \( \text{As}^+_{\text{Ga}} \) decrease with increase in growth rate as the time for incorporation decreases.

The PA layer has a higher value (2.48 Å) of interplanar distance than the crystal (1.41 Å) because of the weakly bound atoms. Based on the kinematical theory of diffraction, this time evolving physisorbed layer of arsenic affects the RHEED intensities with constructive and destructive interference. At an intermediate temperature of about 573 to 723°K, ROs disappear due to destructive interference between those reflected from the crystalline surface and from the PA layer. Similarly, the suppression of ROs at an intermediate BEP ratio of 30 and 40 is due to destructive interference of the reflected beams from the crystal and the PA layer. The experimental observations of Shen et al [17] agree well qualitatively with the results of the RO behavior obtained. This comprehensive model explains the variation of antisite concentrations with BEP ratio, temperature, growth rate and also the RHEED behavior. Any systematic growth data can be modeled and the developed model can be utilized as a predictive tool.

Theoretical investigation of \( \text{LT- GaAs} \) using the model takes one step further in understanding the surface dynamics. The model can be developed to explain the growth at higher temperatures with some modifications. This model can also be utilized to study other experimental data to build consistency. The model can definitely be used to study doping kinetics especially with \( \text{Be} \) acceptor where much research is performed recently.
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Thesis Title: Low Temperature MBE of GaAs: Antisite Incorporation and RHEED oscillations - A Theoretical Study

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