Development of Strain-Induced Quantum Well Intermixing Technique on InGaP/InAlGaP Laser Structures and Demonstration of First Orange Laser Diode

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ABSTRACT

Development of Strain-Induced Quantum Well Intermixing Technique on InGaP/InAlGaP Laser Structures and Demonstration of First Orange Laser Diode

Ahmad Ali Al-Jabr

Laser Diodes (LD) have numerous applications for industry, military, medicine and communications. The first visible LD was invented in 1962 by Nick Holonyak, emitted at 710 nm (red). In 1990s, Shuji Nakamura invented the blue and green Light Emitting Diodes (LED) and later LDs. The production of LDs emitting between 532-632 nm has been severely lagging behind the rest of the visible spectrum. Yellow and orange LDs are still not accessible due to the lack of successfully grown material with high optical efficiency. AlGaInP is the quaternary compound semiconductor used to grow green to red LEDs and red LDs. At a material composition that is supposed to lase below 630 nm, the optical efficiency becomes low due to the oxygen-related defects associated with high Al content. The quantum well intermixing (QWI) is a post-growth process that is applied to laser structure to tune the wavelength of laser. Until now, there are limited reports on successful intermixing of InGaP/InAlGaP laser structures while maintaining the crystal quality. In this work, we introduced a novel intermixing process that utilizes the high strain induced by the dielectric film during
annealing to initiate the intermixing. We deposited SiO$_2$ capping by plasma-enhanced chemical vapor deposition (PECVD) onto the InGaP/InAlGaP laser structure emitting at 635 nm, and then annealed the structure up to 950 °C for different periods of time, resulting in an astonishing 100 nm blueshift. This blueshift allowed us to produce an unprecedented shorter wavelength orange lasers emitting at 608 nm. For low degree of intermixing, we have noticed an increase in the intensity of the photoluminescence (PL) signal. The improvement in the PL signal was translated to a reduction in threshold current. We implemented the technique on an LED structure with Al-rich QWs emitting at 590 nm. Significant increase in the PL intensity (20 folds) was observed. By analyzing the improved structure, we observed reduction in oxygen contamination. This may represent a solution to the oxygen-related defect. The thesis opens the door for major steps forward in GaInP/AlGaInP structures for manufacturing efficient optoelectronic devices in the green, yellow and orange visible range.
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Chapter 1

Introduction and Motivation

This chapter introduces the research problem after briefly presenting the related principles of laser diodes and needed concept. Then we discuss about the importance of the problem. Finally, We presented the research direction with a summary of the thesis.

1.1 Introduction to Laser Diodes

1.1.1 What is a Laser?

Laser diodes are light sources that are heavily utilized in plenty of applications in today’s modern life. Laser stands for (Light Amplification by Stimulated Emission of Radiation). Lasers in general, are composed of: (i) a gain medium consisting of an appropriate collection of atoms, molecules, ions or semiconductor crystal; (ii) a pumping source to excite the atom (molecules, etc.) into higher quantum mechanical energy levels; and (iii) an optical feedback element that allows a beam of radiation to get reflected to the gain medium and escape from one side to have the output beam as shown in figure 1.1. Various techniques were invented to come up with devices that employ these components and generate laser beams.
1.1.2 Types of lasers

Lasers are categorized according to the state of the gain medium. For example, the dye lasers are specified as liquid lasers. Krypton and Argon lasers are specified as gas or ion lasers. The third type of laser is the solid state laser. Ruby laser, was the first solid state laser and while the most common solid state laser is the Nd:YAG (neodymium-doped yttrium aluminum garnet; Nd:Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}. Light emitted from a laser is in coherence, making it differ from other sources of light. Coherence allows focusing light in a small area and traveling for long distances without diffraction. The laser diode has a solid state gain medium. It is not specified as a solid-state laser. The semiconductor laser diode is different in the sense that the light source, the gain medium, and the mirrors are all combined in the same medium. Because of this integration, semiconductor laser diodes are the most efficient lasers of all kind. Semiconductor lasers combine many branches of science at once. Knowledge of semiconductor lasers requires knowledge of electronics, material science, electromagnetics, and finally quantum mechanics.
1.1.3 Semiconductor Diode Laser

Semiconductor diode lasers or laser Diodes(LDs) are made of p-i-n junction as shown in figure 1.2. The intrinsic region has a band gap that is approximately equivalent to the emission wavelength. For semiconductor material, the band gap can be tuned by choosing the appropriate material composition. For example, the \((\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}\) gives an emission of 1.5 eV (816 nm) for \(x = 0.2\) and gives an emission of 1.3 eV (941 nm) for \(x = 0.1\). The active layer for a laser can be quantum wells, quantum

![Diagram of a single LD device with the p-i-n structure of a broad-area an edge-emitting laser (EEL) diode]

Figure 1.2: A schematic of a single LD device with the \(p-i-n\) structure of a broad-area an edge-emitting laser (EEL) diode

dashes or quantum dots structure. In this work we are interested in high power lasers, therefore the laser structure chosen is the QW laser structure. The carriers are confined within the active layer. As the laser is electrically pumped, the electrons and holes recombined, thus emitting photons with energy equivalent to the band gap. In lasers, the emitted photons are also confined in the active region due to the refractive index contrast.
1.1.4 Band Gap Engineering

bandgap engineering is the art of designing the band gap (emission wavelength) of a laser diode. The band gap of a quantum well laser structure can be engineered in three ways, namely, material composition, QW size and QW strain. There are many factors that determine the emitted wavelength and will be discussed later in chapter 3. However, the main factor which is of most interest in this thesis is the composition of the material in the QW. The band gap of a semiconductor can be changed by choosing the ratio of elements in the semiconductor alloy. For example, for III-V material, the band gap diagram shown in figure 1.3 provides a good guide in selecting the composition that gives certain wavelengths. One rule need to be followed, the lattice constant of the barriers, QW and the substrate should be equal.

Figure 1.3: Band gap energy and lattice constant of various III – V semiconductors [2]. The y-axis represents the band gap (emission wavelength) while the x-axis represents the lattice constants. Moving on the lines, say GaP-InP, represent changing in composition
1.2 Research Problem

In optoelectronic devices, the material system used determines the output power and the wavelength of the device. Very efficient material has relatively high radiative recombination efficiency, which means a high proportion of the injected electrons and holes get recombined and generated photons. There are many semiconductor binaries, such as GaAs and InP, have high efficiency. The ternaries and quaternaries made of two or three binaries, such as AlP, InP and GaP, showed good efficiency over a good range of composition. This makes them suitable for controlling the wavelength of fabricated devices while still having very good efficiency. Up to now, LDs emitting in the orange and yellow range are not available on the market. Figure 1.4 shows images of currently available LDs in the market. The difficulties in growing orange lasers emitting below 630 nm are still not resolved. The optical range that is still inaccessible by LDs is in the range from 532-632 nm. This range is in the middle of the visible range covering green, yellow and orange. The LDs emitting in this range will find important applications in communications, medicine and displays.

The shortest emission wavelength from commercial red LDs is 632 nm which are based on InGaP/InAlGaP layer structure. If an Aluminum-free active layer In$_x$Ga$_{1-x}$P is used during growth, then there is a limited window for the variation of mole fraction $x$ while keeping the layer lattice-matched to the GaAs substrate [4]. On
the hand, Aluminum-rich In$_x$(Al$_y$Ga$_{1-y}$)$_{1-x}$P active layers can be used to for active regions. Increasing the Aluminum (Al) content is the ideal solution as the lattice constant will hardly change. However, increasing the Al content $x$ more than 0.1 fraction severely reduces the optical efficiency of the material due the oxygen-related defects \[5, 6\]. Because of this reduction in material recombination efficiency, the LDs with wavelengths shorter than 632 nm are still not accessible. The approach of increasing the Al composition in the quantum well by the typical growth method such as the Molecular-Beam Epitaxy (MBE) or Metal-Organic Vapor-Phase Epitaxy (MOVPE) in order to increase the band gap led to the incorporation of oxygen residuals, that increases the nonradiative recombination centers in the active layer, and hence rendering the light emitters inefficient.

The reason behind the low efficiency is that Al is a highly reactive element that even at the high vacuum and high temperature of any growth. Because of this, increasing the Al content during growth does not results in efficient devices, thus constituting the main obstacle in producing efficient LEDs and LDs having Al-rich active layer. Moreover, it is the main reason that limits the production of laser diodes emitting below 630 nm \[7\]. According the road map report of Optoelectronics Industry Development Association (OIDA)\[8\], the requirement for having efficient

![Figure 1.5: Wavelengths and colors of the visible spectrum and the range inaccessible to LDs](image)

Figure 1.5: Wavelengths and colors of the visible spectrum and the range inaccessible to LDs
and economically worthy solid state lighting systems based on LEDs, the external quantum efficiency or wall-plug efficiency has to be more than 50%. The least efficient devices are the LEDs emitting in the yellow range as shown in figure 1.6. The present thesis address the bottle neck of the producing efficient Al-rich InAlGaP active layers by growth, thus rendering LDs in the yellow and orange range unachievable. The approach we are using in this PhD study is twofold:

- **to develop an intermixing technique on InGaP/InAlGaP laser structure that can be implemented to tune the wavelength with minimum damage to the laser structure which can be evident from the intermixed and fabricated devices**

- **to investigate intermixing as an alternate method for increasing the Al content in the active layer of red laser diodes and study the effect on fabricated devices**
1.3 Significance of Research

To the best of our knowledge, the studies on InGaP/InAlGaP intermixing is lacking, and there are no available studies on the effect of increasing Al content by quantum well intermixing on the efficiency of the InAlGaP active layer. The research in this thesis was conducted on edge-emitting laser structure. However, the research has a broader impact on the improvement of the InAlGaP material system as a whole. The results and understandings related to the material shall be applicable to other structures such as, InAlGaP LEDs and InAlGaP Vertical Cavity Surface-Emitting Lasers (VCSELs). The success in increasing the Al content while keeping the quantum efficiency of the material will help in achieving edge-emitting LDs emitting at wavelengths shorter than 630 nm, and VCSELs emitting at wavelengths shorter than 650 nm. Also, the technique will give rise to high efficiency LEDs in the green, yellow and orange range. These efficient LEDs and LDs with an Al-rich active layer will brought about impact on solid state lighting and communications. Devices produced using the technique can replace other types of lasers (Gas or Diode Pumped Solid-state (DPSS)) used in the visible range of 532-632nm, simply by tuning the GaInP/AlGaInP laser and LEDs. For example:

1. **Solid state lighting:** is the future of lighting industry as it will save a good amount of energy. One of the major issues is related to the efficiency, as listed by Sandias Report [9]. As shown in figure 1.7, the industry is in need for efficient devices to replace existing technologies such as fluorescent tube. Replacing fluorescent tubes with LDs can be done by using a combination of blue and yellow laser beams to have efficient white light, which can be used for lighting applications [9].

2. **Visible Light Communications and Li-Fi:** The ability to modulate the
light beam from LDs has extreme advantages in the field of visible light communications. With yellow LDs, new unlicensed communications bands can be covered by visible light communication system. Also, the Li-Fi technology which uses white light, can be easily implemented by modulating one or both lasers used in the solid state lighting as described above.

1.4 Thesis Organization

After introducing the topic in chapter 1, chapter 2 discusses the fundamental aspects of LDs, including semiconductor crystal structure, band structure, and confinements of carriers and photons in LD structure. Chapter 3 discusses the properties of the InGaP/InAlGaP material system, including growth, band gap, and the development of the history of the fabricated devices emitting from 680 nm to 630 nm. Also, we discuss the problem limiting the production of shorter wavelength LDs, and present the calculations needed to estimate the band gap of different compositions, taking into considerations their effect on strain and wavelength. In Chapter 4, which
is the core of the thesis, we will discuss the Quantum Well Intermixing (QWI) in general, and describe the process we have developed and optimized. In *Chapter 5*, the thesis describes the process of laser fabrication and characterization. In *chapter 6*, various fabricated devices after intermixing will be discussed. In *chapter 7*, we describe the oxygen-related defects and explain how this can be addressed using QWI. We compared the increase of Al content in InAlGaP by QWI and by growth for SQW and MQW LD structures. Then we used annealing to reduce oxygen-related defects in Al-rich AlGaInP/AlGaInP commercial LED. Processed LED has higher efficiency. Finally, in *Chapter 8*, we conclude the thesis and propose the future work.
Chapter 2

Fundamental Aspects of a Laser Diode

The purpose of this chapter is to serve as the relevant foundation for the topics covered later in the thesis. It reviews some of the principles of laser diodes, needed to understand the scope of this thesis. Numerous textbooks provide a more detailed explanation of these topics and details of these can be found in the reference section.

2.1 What is a Semiconductor Laser Diode (LD)?

2.1.1 Definition of Semiconductors

A semiconductor is a material with conductivity between metals and insulators and whose conductivity can be changed by order of magnitudes by doping, temperature and illumination [10]. The ability to control conductivity gives the importance of semiconductor material as they can be used to control the flow of electrons. That is why, electronic components are built from semiconductor material. Table 2.1 lists the typical conductivity, and band gap of insulators, semiconductors and metals (conduc-
Starting with atoms, an atom is formed from a nucleus and electrons. These electrons orbit the nucleus according to their energy level. Electrons in the outer-shell of atoms are called "valence electrons". In semiconductor material, atoms are linked together to form crystals in "covalent bonds". In covalent bonds, atoms adjacent to each other share the same valence electrons as shown in figure 2.1.

![Figure 2.1: The arrangement of Silicon(Si) atoms to form a crystal. Si atoms share electrons to make covalent bonds. Each atom is surrounded by eight electrons. Electrons that are bound to the atoms are called valence electrons](image)

Atoms in semiconductors tend to have the covalent bond surrounded by 8 electrons in their outer-shell to fill up all the orbits around them. The Silicon (Si) atom is always surrounded by four atoms to form a crystal.
2.1.2 Band Gap in Semiconductors

Metals differ from semiconductor in the chemical bonds. In metals, atoms are linked together in crystals through metallic bonds which are the strongest chemical bond between atoms. In these bonds all atoms lose an electron in the outer shell to become positive ions. All atoms in the metal share these free electrons. Atoms are surrounded by a "sea of electrons". These electrons are free to move from one atom to another and they can be affected by an external electric field to form an electric current. These electrons are in an energy level called a "conduction band". Metals have very low resistance compared to semiconductors. In semiconductors, because electrons are bound to the atoms they cannot move around, as in metals. For an electron to move freely in the semiconductor, energy need to be provided to the electron so it can move. The energy level of an electron in a semiconductor, where it is bound to the shell is called a "valence band". When a semiconductor is heated up, a number of electrons receive the required energy to move from the valence band to the conduction band, and as a result, the resistance of the semiconductors becomes smaller at higher temperature. Figure 2.2 shows the difference between metals and semiconductors. In metals there is no difference between energy levels of conduction bands and valence bands. While in the semiconductor, there is an energy difference between the valence band where electrons are bound to atoms and the conduction band where electrons can move freely around the semiconductors. The energy difference required to shift an electron from the valence band to the conduction band is called the "band gap" [12].

Again, starting from a single atom, there are two distinctive energy levels for electrons in the outershell, one for a valence electron and one for conduction electron. When, another atom is attached, the energy levels will split into four. As the number
Figure 2.2: The band gap of (a) metals, (b) semiconductors, and (c) insulators. In metals there is no difference in energy between the valence band and the conduction band while in the semiconductors, the difference is in the range 1.5 eV to 3.5 eV. Insulators have a band gaps of more than 4 eV.

of atoms(n) attached increases, the energy levels split into n-levels forming a valence band and a conduction band as shown in figure 2.3. The minimum energy level in the conduction band is $E_c$ and the maximum level in valence band is $E_v$. The difference between these two energy levels is called energy "band gap" of the semiconductor $E_g$ [13].

$$E_g = E_c - E_v$$  \hspace{1cm} (2.1)

At 0 $K$, all electrons of a semiconductor are in the valence band while the conduction band is empty. As the temperature increases, the kinetic energy of the electrons increases according to the equation

$$E = kT$$  \hspace{1cm} (2.2)

where $k$ is the Boltzmann’s constant, $1.38 \times 10^{-23} J/K$. To understand this equation, let us take Si as an example. At room temperature ($T = 300 K$), the intrinsic (Si) material has a carrier concentration "conduction electrons" in the range of $10^{10} cm^{-3}$.
Figure 2.3: Splitted energy levels of electrons in a semiconductor material as number of atoms \( n \) increases. Difference between lowest energy level in the conduction bands and highest energy level in the conduction bands is the band gap due to temperature. As one electron is excited, by heating for example, it moves from the valence band to the conduction band creating a hole. We can say a hole is excited from conduction band to valence band [14].

Figure 2.4: An electron in the valence band is excited by heat and moves to the conduction band. As electrons become excited, holes are created.
2.1.3 Crystal Structure

In a crystalline semiconductor, atoms will arrange themselves according to the electrostatic forces between the atoms. As the atoms arrange themselves in crystals, most of the properties are highly linked to this arrangement. The first property of the semiconductor is the lattice constant $a$. The size of one molecule from the semiconductor alloy is called the lattice constant and it’s measured in angstroms Å. It was found that the lattice constant is related to the band gap [3]. The crystal structure is also defined from the applied magnetic forces between the atoms. Figure 2.5 shows two important crystal structures for semiconductor material [15]

![Diamond Lattice and Zinc Blende Lattice](image)

Figure 2.5: 3-D arrangements of the semiconductor atoms due to the magnetic forces (a) diamond lattice, and (b) zinc blende lattice.

### 2.2 Electron Propagation in Semiconductors

The propagation of electrons in a semiconductor material is governed by electric and magnetic fields and the laws of quantum mechanics. An electron propagating inside a semiconductor, experience difference in potentials. We have mentioned earlier, heat as a form of energy that we can use to increase an electron energy from the valence band to the conduction band. Elevating the energy of an electron is called excitation.
Beside heat, an electron can be excited using light. The photo-electric effect is a well-known phenomenon observed for certain materials when irradiated with light, electrons are emitted from this material. When the intensity of the irradiated light is maintained to a constant level, the energy of emitted electrons is given by

\[ E - \phi = h \nu \omega \]  

where \( \phi \) is the required energy for an electron to leave the material. Planck postulated that the energy is related to frequency throughtout what is known today as Planck’s constant, such that \( h = 6.625 \times 10^{-14} \text{J.s} \)

\[ E = h \omega \]

Einstein suggested that there are discrete units of light called photons. This explains why the energy of emitted electrons are dictated by the frequency of irradiated light. The photoelectric effect can explain the interaction of light and photons. [16]

### 2.2.1 The Schrödinger Equation

Schroedinger is an Austrian physicist who try to solve the problem of electron and photon duality and derived this equation

\[ H \psi = E \psi \]

where \( \psi \) is the electron wave function, \( H \) is the Hamiltonian represents the total energy operator which corresponds to the kinetic and \( E \) the potential energy. By analogy with classical mechanics, the Hamiltonian is commonly expressed as the sum of operators corresponding to the kinetic and potential energies of a system in the
form

\[ H = KE + PE \] (2.6)

where \( PE \) is the potential energy, which is given by the potential energy operator

\[ PE = V(r, t) \] (2.7)

and \( KE \) is the kinetic energy given by the kinetic energy operator:

\[ KE = \frac{p^2}{2m} \] (2.8)

in which \( m \) is the mass of the particle and \( p \) being the momentum operator in quantum mechanics

\[ p = -i\hbar \nabla \] (2.9)

wherein \( \nabla \) is the del operator. The dot product of \( \nabla \) with itself is the Laplacian \((\nabla^2)\). In three dimensions using Cartesian coordinates the Laplace operator is

\[ \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \] (2.10)

Therefore,

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + V(r, t) \] (2.11)

Combining these together yields the familiar form used in the Schrödinger’s equation:

\[ (-\frac{\hbar^2}{2m} \nabla^2 + V(r, t))\psi = E\psi \] (2.12)

where \( \psi \) is the eigenfunction and \( E \) is the energy eigenvalues. The equation can be
rewritten as
\[
\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V)\psi = 0
\]
(2.13)

according to the equation, for every given potential variation \( V \) there is an energy eigenvalue value for a particle under consideration \([16]\).

Having discussed the propagation of electrons and quantum mechanics, now we can take a closer look at the electron propagation in a semiconductor. The semiconductor material can be modeled as a periodic potential as shown in 2.6. An electron propagating in a crystalline semiconductor experience periodic potentials (energy levels) \([13]\).

![Figure 2.6: periodic potential 1-D crystal](image)

An electron propagating in a periodic medium can be governed by the Bloch wave. A Bloch wave (also called Bloch state or Bloch function or Bloch wave function), named after Swiss physicist Felix Bloch, is a type of wavefunction that describe the propagation for a particle in a periodically-repeating environment, most commonly an electron in a crystal. A wavefunction \( \psi \) is a Bloch wave if it has the form:

\[
\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r})
\]
(2.14)

where \( \mathbf{r} \) is position, \( \psi \) is the Bloch wave, \( u \) is a periodic function with the same periodicity as the crystal, \( \mathbf{k} \) is a vector of real numbers called the crystal wave vector or crystal momentum, \( e \) is Euler’s number, and \( i \) is the imaginary unit. Substituting
the wavefunction in Schrödinger’s equation will give energy eigenvalues $E$ that are periodic in $k$ as shown in figure 2.7. For every allowed discrete energy level, there is a periodic function on the $k$ axis. Alternatively, for every given value of $k$ which is the reciprocal of the lattice constant, there are allowed discrete energy levels. The first boundary at $\pi/a$ to $-\pi/a$ is called the Brillouin zone and the point where $k = 0$ is called the $\Gamma$ point which is related to direct-band gap [3].

![Figure 2.7: Energy bands created by a 1-D crystal. The two energy bands are the solution of two bands, resulting from two discrete states](image)

### 2.2.2 Direct-Indirect Band Gap

A direct band gap material has the lowest energy level in the conduction band (CB) with highest energy level in the valence band (VB) at the same momentum $k = 0$. As a result, when an electron loses energy, it emits photons with energy equal to the band gap. In contrast, indirect band gap material, like Si, has the lowest energy level in the CB but not coincide with highest energy level in VB. This means, an electron has to release the excess energy as another form of energy usually heat or atomic vibration (phonons). Because of the indirect-direct band gap, direct band gap
materials are preferred in optoelectronics.

Figure 2.8: Energy levels versus momentum in different semiconductor materials: (a) direct band gap material where the lowest energy level in the conduction band coincides with highest energy level of the valence band resulting in radiative recombination, and (b) indirect band gap material
2.3 Laser Diode Structure

Figure 2.9 shows a cross-section of a broad area EEL. The structure is made from a lower contact electrode (n-contact), a substrate, epitaxial layers including the p-type, i-type and n-type material, and an upper contact electrode, the p-contact.

![Diagram of laser diode structure](image)

Figure 2.9: Structure of a typical laser diode growth

2.3.1 Material of Semiconductor Lasers

Elemental semiconductors

As previously mentioned, atoms in semiconductor material tend to share electrons to form an octet (8 electrons in the outer shell). The crystalline semiconductors are usually made of covalent bonds where atoms share electrons in the outer shell. Figure 2.10 lists the elements used to form different semiconductors. Elements in group-IV can surround themselves with the same atoms for example (Si) and form octets. Therefore, elements in group-IV are referred to as elemental semiconductors, for example: Si, Ge and Te. These elements have indirect band gap, which explains why, they are not used in active optoelectronic devices.
Compound semiconductors

By referring figure 2.10 combining elements from group-III and group-V like GaAs, InP and AlP or any combination of elements from these groups, may form a stable III-V semiconductor compound. Also, elements from group II and group VI can be combined to form stable binary compounds like ZnSe and HgSe. These are referred to as II-VI semiconductors. By looking at the electronic distribution, elements from group III have 3 electrons in their outer-shells. For example Al has an electronic distribution of $6s^2\ 6p^1$ at the outer-shell, a total of 3 electrons in the outer-shell. Therefore, an Al atom needs 5 extra electrons to form an octet. Since As has 5 electrons in its outer-shell, it is well suited to combine with Al. The atoms share their valence electrons to have 8 electrons in the outer-shell, which fills all energy levels around the atom, forming a stable compound.

Semiconductors from group II also, can be combined with group VI to form II-VI semiconductors. However, III-V are more stable and most of the optoelectronic devices in the visible range are made of III-V semiconductor material.

<table>
<thead>
<tr>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>B</td>
<td>6</td>
<td>C</td>
<td>7</td>
</tr>
<tr>
<td>10.81</td>
<td>13</td>
<td>12.01</td>
<td>14.01</td>
<td>16.00</td>
</tr>
<tr>
<td>26.98</td>
<td>Al</td>
<td>28.09</td>
<td>30.97</td>
<td>32.02</td>
</tr>
<tr>
<td>65.38</td>
<td>Zn</td>
<td>69.72</td>
<td>72.59</td>
<td>74.92</td>
</tr>
<tr>
<td>112.40</td>
<td>Cd</td>
<td>114.80</td>
<td>118.70</td>
<td>121.80</td>
</tr>
<tr>
<td>200.59</td>
<td>Hg</td>
<td>204.38</td>
<td>207.20</td>
<td>208.98</td>
</tr>
</tbody>
</table>

Figure 2.10: Elements of semiconductors and with last row showing the electronic distribution
Binaries have equal quantities of atoms to form a compound. Ternaries and quaternaries are made of more than two elements. The need for ternaries and quaternaries comes from the fact that, the band gap of ternaries and quaternaries can be tuned by controlling the mole fraction. For example, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is a III-V semiconductor compound with two elements from group-III and one element from group-V. Where $x$ is the mole fraction that can have a value between 0 and 1. By changing the composition ($x$), the band gap can be.

Doping

Pure semiconductor materials without impurities are called intrinsic semiconductors. When impurities are added to the semiconductor; the semiconductor can be either a positive (p-type) semiconductor or a negative (n-type semiconductor). Numerous applications of semiconductor material exist by fabricating devices of different layers. For example, the p-n junction diode is made from the p-type and the n-type semiconductors.

2.3.2 Growth of the Laser Diode Structure

Growth is the process of building the semiconductor layers. The process can be performed in bulk where growth is rapid, or it can be slow where it deposits only a single atomic layer. There are various methods to grow optoelectronics devices. A typical optoelectronic device consists of a substrate and epitaxial layers. substrates are usually grown by bulk growth methods.

Substrate Growth

In substrate growth there are two main techniques. The first technique is the Czochralski method shown in figure 2.11 where the substrate material is kept at melting point
and a seed crystal held just above the molten material. The seed crystal is oriented to the required direction and slowly dipped in the molten. Then, the seed crystal is slowly pulled up. As the seed crystal is pulled up, the material with it starts to crystallize as the temperature is reduced. According to the pulling speed, the size of the semiconductor rod produced is determined. The process is continued until the desired length of crystalline rod is reached. Length of the semiconductor rod may reach to 30 m. The semiconductor boule or ingot is then diced to provide substrate of the required thickness. [17, 18].

Figure 2.11: Czochralski growth method, a seed crystal is placed at the top of the molten semiconductor then pulled to form a rod of semiconductor material to be diced later to the desired thickness to make substrates [18]

The second technique which is typically used for limited thicknesses, is the Bridgman method, where the pulling mechanism in Bridgman method is horizontal instead. A single crystal seed is placed at the side of the crucible. As the crucible moves, the
seed temperature is reduced to lower temperature, crystalization occurs (figure 2.12). Figure 2.12: Bridgman growth method, where the seed crystal is placed at the side of the melting crucible moves, the crystallization occurs [18].

**Structure Growth (Epitaxial Growth)**

Growing laser structure includes QWs in the 2 to 8 nm range. Such grow requires a very slow growth rate that allows the change of material composition within this range. In epitaxial growth there are mainly three techniques used in growth; 1-liquid phase epitaxy (LPE), 2-vapor phase epitaxy (VPE) and 3-molecular beam epitaxy (MBE).

**Liquid Phase Epitaxy**

In LPE, as the name indicates, the starting material is liquid. As shown in figure 2.13 in a chamber, there is a graphite slider on which the substrate is placed. The melts are saturated solutions of the deposited film, for example, a saturated GaAs melt. Graphite slide is moved to make substrate below the melt. Then, the temperature is reduced slowly causing the GaAs to crystallize on the substrate. The thickness is determined by duration of lowering the temperature. LPE is very simple but the control of the thickness is not as precise as the other methods. Therefore, it is used for building bulk devices with thicknesses in the range of 1 $\mu$m [17, 18].
Vapor Phase Epitaxy

Vapor Phase Epitaxy (VPE) can be categorized into two growth methods: 1-Chloride and Hydride Growth and 2-Metal-Organic Vapor Phase Epitaxy (MOVPE), or Metal-Organic Chemical Vapor Deposition (MOCVD) Growth. The MOCVD growth method is the main method used to grow III-phoshide based material [18]. Figure 2.14 shows the process of growth. As shown, a flow of $H_2$ is applied to the reactive material that is in a liquid phase, in order to convert it into a vapor. The vapor of different material flows to the substrate in the chamber. With the substrate in the chamber, reaction occurs on the surface of the substrate and the layers of the structure get deposited. The name 'metal-organic' comes from the use of metallic ions combined with organic molecules, such as Trimethylgallium (TMG or TMGa). For example, in order to grow layers of GaAs the following reaction is used

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4$$ (2.15)
and to grow AlGaAs the following reaction is used

$$(CH_3)_3Ga + (CH_3)Al + AsH_3 \rightarrow AlGaAs + 6CH_4$$  \hspace{1cm} (2.16)

The process is very precise and can be controlled by controlling the flow rate of hydrogen for certain elements [17].

![Figure 2.14: Schematic of MOCVD growth method [18]](image)

**Molecular Beam Epitaxy**

In MBE growth, as shown in figure 2.15, there are different effusion cells through which atomic beams (for example, Ga, In, P etc) are emitted. Each effusion cell has its own shutter and in front of the effusion cells, the substrate holder can be found. Also, there is a Reflection High Energy Electron Diffraction (RHEED) gun and a fluorescent screen. Utilizing in-situ RHEED in MBE, surface morphology, growth rate and material composition can be analyzed during the growth. The fluxes of the atomic beams are controlled by changing the temperature of the effusion cell. As
atoms are deposited on the substrate, they arrange themselves in the lattice during growth. By changing the rates of deposition, the composition of deposited material can be controlled and the thicknesses can be controlled to mono layers [17].

![Figure 2.15: Schematic of MBE growth method [18]](image)

**2.4 Carriers and Photons Confinement in Laser Diodes**

Having discussed about growth of LD, we are ready to discuss the lasing in LD. In order for a LD to provide lasing, the process includes generation of photons in the active layer and then guiding these photons within the laser structure in a confined profile. photons propagate inside the LD structure and keep bouncing between the mirrors until they are allowed to leave.
Generation of Photons

Electrons pumped to a LD are in conduction band. The relationship between energy of and electron in (eV) and photon emission wavelength (nm) is given by

$$E_g = h\omega$$  \hspace{1cm} (2.17)

Interaction of an electron with energy \((E_g)\) interacts with a photon with wavelength \((\omega)\) in one of three methods.

- **Absorption**: When a photon with energy \(h\omega\) which is equal to or greater than the band gap \(E_g\) is irradiated on a semiconductor material, an electron in the valence band can make an upward transition to the conduction band. The energy of the photon is absorbed by the electron forcing the electron into the excited state and thus leaving behind a hole in the valence band. Therefore, a photon can generate a pair of an electron and a hole due to absorption.

- **Spontaneous emission**: An electron makes a downward transition on its own from the conduction band to a vacant state (hole) in the valence band. A photon is emitted as the electron makes the transition with an energy \(h\omega\) which corresponds to an energy level of \(E_g\).

- **Stimulated emission**: A photon is incident on a semiconductor material with an electron in the conduction band. The electron is stimulated to make a downward transmission and emit a photon in phase with the incident photon $[3]$. 
Figure 2.16: Photon-electron interactions: Absorption, spontaneous emission and stimulated emission

Propagation of Photons

The laser structure is a simple optical waveguide where the core, which is the active medium, has a higher refractive index, while the barriers have lower refractive indexes. As a result, all light generated within the active layer keeps propagating inside the active layer according to the total internal reflection principles. Figure 2.17 shows the profile of a propagating mode in the laser structure. Usually, the wavelength of the emitted wavelength is very large compared to the dimension of the dimension of the quantum well. For that purpose, separate waveguide structure above and below QWs is grown to form a proper waveguide and increase the optical confinement.

Figure 2.17: Confinement of photons generated in the active layers due to the refractive index change, forming the mode profile of photons propagation inside the LD structure
2.4.1 Electron Confinement

One of the advantages of laser diodes is the ability to pump them directly with carriers (electrons and holes). Electrons are injected into the n-type side of the laser structure. Electrons propagate all the way to the intrinsic region or the active region. From the p-type side, holes are pumped from the positive supply. Holes and electrons keep propagating inside the semiconductor material until they reach the intrinsic region (active region). Electrons and holes become confined in the semiconductor structure because of the energy barriers in the well. Electrons and holes get recombined in the active region and the amount of energy released create a photon. The photons are generated in the active region and become confined due to the refractive index, as shown in figure 2.18. Photons inside the laser come to be amplified through stimulated emission. The cleaved mirrors of the laser diode reflect the photons inside the laser structure. After a few trips, a small percentage of photons escape the mirrors imparting the laser beam that is coherent and confined [13].
Figure 2.18: Photons and carriers interaction in a LD structure. Carriers are confined because of the quantum well and photons are confined because of the difference in refractive index.

2.5 Conclusion

In this chapter we presented the necessary concepts required to understand the rest of the thesis. We started with the semiconductor materials and their bonds and how these bonds affect the conductivity and the band gap of the material. Then we discussed the various growth methods used to make LDs. Finally, we discussed the principles of photon and electron confinement and how LDs function.
Chapter 3

InGaP/InAlGaP Material System

In this chapter, we provide a brief history of the InAlGaP material system and discuss the effect of change in material composition and strain in the active layer on the emission wavelength of a LD.

3.1 Material Systems for Visible Laser Diodes

The first visible laser diode was demonstrated in 1962 by Nick Holonyak. It was a p-n junction diode and it was grown $Ga(As_{1-x}P_x)$. The peak emission wavelength was at 710 nm [19]. Later in 1971, the first p-i-n laser diode structure was used. The material system was AlGaAsP/AlGaAsP. The thickness of the active layer was 1.25 µm and the peak emission at 820 nm [20]. Later, in 1981, The GaAs/AlGaAs material system was employed to have shorter wavelengths. The double hetero-structure of GaAs/AlGaAs gave an emission of 710 nm [21].

Fabricating devices that emit in the visible range can be achieved by having semiconductor alloys with band gaps in the range of 3 eV to 1.6 eV corresponding respectively to emission wavelengths of 400 nm to 800 nm. Theoretically, material of group II-V like Zinc Selenide (ZnS), can be grown to emit in this range, however, the
low lifetime constraints makes it an unrealistic option for making commercial devices \cite{22}. The available high-efficiency visible LDs are primarily made of III-P and III-N material systems. These LDs are either InGaN/GaN-based, covering the violet to green wavelengths (405-530 nm), or InGaP/InAlGaP-based, covering the red (632-690 nm) wavelengths. High-efficiency LDs in the green-yellow-orange (GYO) (550-620 nm) wavelengths are still not available. Large strain and Indium (In) segregation in InGaN/GaN prevents the growth of high-quality LDs with emissions beyond 540 nm \cite{23}. For the InGaP/InAlGaP material system, incorporating more Aluminum (Al) in the active layer shortens the emission wavelength; however, oxygen-related defects severely reduce their efficiency \cite{24}. In addition, the small band offset between the quantum well (QW) and barriers leads to low carrier confinement and a large carrier leakage current \cite{25}.

### 3.2 Properties of InAlGaP Quaternary

InAlGaP is a very important quaternary that covers the optical range from green to red. First growth of InGaP/InAlGaP laser structure was done in 1978 \cite{26}. The ternary $In_xGa_{1-y}P$ system is a direct semiconductor alloy in most of the values ($x$) for In compositions. With In content ($x$) of 0.48, the material is latticed matched to the GaAs substrate (5.653 Å). Ga and Al atoms can be replaced easily without changing the lattice constant. Because of this, the Indium mole fraction is fixed around 0.48. Al mole fraction is changed to obtain a different band gap ($In_{0.48}(Al_yGa_{1-y})_{0.52}P$) to maintain a lattice constant matching the GaAs substrate.

The band gap energies of the ($In_{0.48}(Al_yGa_{1-y})_{0.52}P$) system have been determined through various methods \cite{27} and \cite{28}, yielding slightly different results. A commonly
accepted relation at room temperature is:

\[ Eg_\Gamma = (1.900 + 0.61x) \text{eV} \]  \hspace{1cm} (3.1)

\[ Eg_X = (2.204 + 0.085x) \text{eV} \]  \hspace{1cm} (3.2)

Figure 3.1: Band gap energy vs. mole fraction \( x \) at room temperature for the direct \( \Gamma \) and indirect \( X \) band gap of the \( \text{In}_{0.5}(\text{Al}_y\text{Ga}_{1-y})_{0.5}\text{P} \) system

for the direct and indirect bandgaps variation with composition, respectively \cite{29}. These values indicate that the \( \Gamma - X \) crossover takes place for \( x = 0.58 \), corresponding to an energy of 2.25 eV, or a wavelength of 550 nm, as illustrated in Figure 3.1.

### 3.3 Crystal Structure

The crystal structure of the AlGaNnP molecule is Zinc blende structure, as shown in figure 3.2. The quaternary, \( (\text{Al}_x\text{Ga}_y\text{In}_z\text{P}) \) is made of equal proportions of atoms from group-III and group-V. Nearly any combination of the alloy can be grown provided
Figure 3.2: Cubic unit cell of the Zinc blend structure. (a) The open spheres represent group III atoms (In, Al, Ga) and the full spheres group V atoms (P). The lines represent the tetrahedral bonds between atoms of the unit cell. (b) The Miller indices for various directions in the cubic lattice

that $x + y + z = 1$
3.4 Engineering the Band Gap of InAlGaP LDs

Here we are calculating the composition that gives emission shorter than 630 nm. The band gap, or emission wavelength, of a LD can be controlled by: 1-material composition of active layer, 2-strain applied on the active layer and 3- quantum confinement in the active layer. The following sections explain the effect these parameters on the wavelength through calculations. Then we will use these calculations to theoretically estimate the emission wavelength of the as-grown LD structure and determine the required Al composition to obtain yellow and orange wavelengths. The as-grown laser structure we are starting with is given in figure 3.3. For the calculations, we need only to know the compositions of the barriers and the QW. The barrier composition is In_{0.5}(Al_{0.6}Ga_{0.4})_{0.5}P and the QW has the composition In_{0.47}Ga_{0.53}P.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 nm</td>
<td>In_{0.5}Al_{0.3}Ga_{0.2}P</td>
</tr>
<tr>
<td>6 nm</td>
<td>In_{0.47}Ga_{0.53}P</td>
</tr>
<tr>
<td>80 nm</td>
<td>In_{0.5}Al_{0.3}Ga_{0.2}P</td>
</tr>
</tbody>
</table>

Figure 3.3: QW and barriers composition of a single QW LD structure

3.4.1 Material Composition

The experiments in this thesis utilize single and multi QW LD structures grown on GaAs substrate. Therefore, all calculations are based on QW structures. The QW structures are either (InGaP) Al-free QWs or (InAlGaP) Al-rich QWs. To calculate the band gap and lattice constant of InGaP QW, or InAlGaP QW, we need to know the lattice constant and the band gap of the binaries GaP, InP, and AlP, from which we can estimate the band gap of any composition. Table 3.1 presents the lattice constant and the band gap of the binaries.
Table 3.1: Band gap and lattice constants of GaP, InP and AlP

<table>
<thead>
<tr>
<th>Binary</th>
<th>GaP</th>
<th>InP</th>
<th>AlP</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice constant (Å)</td>
<td>5.4512</td>
<td>5.8688</td>
<td>5.4635</td>
</tr>
<tr>
<td>Band gap $E_g$ (meV)</td>
<td>2.26</td>
<td>1.35</td>
<td>2.52</td>
</tr>
</tbody>
</table>

Lattice Constant and Band Gap of Bulk InGaP

Parameters for the InGaP ternary can be calculated by interpolating the parameters of InP and GaP. For example, the lattice constant of $In_{0.47}Ga_{0.53}P$ can be linearly interpolated from the lattice constant of GaP (5.4512 Å) and InP (5.8688 Å) according to Eq 3.3:

$$a(In_xGa_{1-x}P) = x \cdot a(InP) + (1 - x) \cdot a(GaP)$$  \hspace{1cm} (3.3)

which gives a lattice constant of 5.647472 Å which is slightly less than the lattice constant of GaAs (5.65325 Å). Therefore the QW of $In_{0.47}Ga_{0.53}P$ is grown while it is slightly strained. All other parameters such as the effective masses, mechanical constants and deformation potentials are treated in the same manner. Except for the band gap, a special formula is given to account for the bowing which was determined experimentally, is given by [26]:

$$E_g(In_xGa_{1-x}P) = 1.35 + 0.643(1 - x) + 0.786(1 - x)^2$$  \hspace{1cm} (3.4)

Figure 3.4 shows the change in lattice constant and band gap as the composition of In in $In_xGa_{1-x}P$ changes. As can be seen, when the composition is approximately 0.5, the lattice constant is matched to the GaAs lattice constant, which is very important from a growth point of view. However, the emission is around 700 nm which is in the red region. In order to reduce the wavelength, smaller amount of (In) should be incorporated, but the lattice will not be matched anymore and cannot be grown on the GaAs substrate. The formula gives us the band gap of the ternary InGaP for any
composition of In. For that purpose, a simple MATLAB code was created. The code is listed in the appendices.

![Graph showing lattice constant and bandgap vs In mole fraction]

Figure 3.4: The lattice constant, bandgap and peak emission wavelength of \( \text{In}_x\text{Ga}_{1-x}P \) ternary as In mole fraction is increased. The lattice is matched to GaAs only when \( x \approx 0.5 \)

**Lattice constant and Band Gap of Bulk InAlGaP**

The other way to have shorter wavelength is by increasing Al content in the QW. To account for the incremental amount of (Al) in the material, another interpolation step need to be performed. The lattice constant of InAlP, \( a(\text{InAlP}) \), need to be calculated first by interpolating the binaries. The parameters of the ternaries of InGaP and InAlP are calculated as in shown below.

\[
a(\text{In}_x\text{Al}_{1-x}P) = x \cdot a(\text{InP}) + (1 - x) \cdot a(\text{AlP})
\]  

(3.5)

Then we interpolate the lattice constants of the ternaries to get the lattice constant of the quaternary

\[
a(\text{In}_x\text{Al}_y\text{Ga}_{1-y}P) = y \cdot a(\text{InAlP}) + (1 - y) \cdot (\text{InGaP})
\]

(3.6)
All other parameters can be calculated in this way except for the band gap. To calculate the band gap two extra steps need to be performed. The band gap of InAlP is given by

\[ E_g(In_{x}Al_{1-x}P) = 1.35 + 1.83 \cdot (1 - x) + 0.38 \cdot ((1 - x)^2) \]  \hspace{1cm} (3.7)

and the band gap of the quaternary is given by

\[ E_g(In_{x}(Al_{y}Ga_{1-y})_{1-x}P) = (y \cdot E_g(InAlP) + ((1 - y) \cdot E_g(InGaP) \]  \hspace{1cm} (3.8)

Figure 3.5 shows the effect of increasing the (Al) content on the band gap and lattice constant. Increasing the Al content has negligible effect on the lattice constant but has great effect on the band gap or emission wavelength. This is a very important feature as we can increase the Al content to increase the band gap without worrying about the lattice constant. As shown in Figure 3.5, Any composition within the active layer will remain matched to GaAs.

![Figure 3.5: The effect of varying Al content on lattice constant and emission wavelength of InAlGaP for fixed In composition (0.5). Reducing Al leads to the increases in wavelength, and the resultant alloys still maintain the lattice matching condition.](image-url)
Other than the lattice constant and matching to the GaAs substrate, it is very important the material of the active layer remain in the direct-band gap. Fortunately, the InAlGaP alloy has a direct-band gap in a wide range. Figure 3.6 shows a wide range of material compositions that give direct-band gap with the lattice constant and emission wavelengths that covers the visible range from green to red [30]. Only the shaded area of the compositions leads to indirect material.

Figure 3.6: The band gap and lattice constant of InGaP and InAlGaP as the composition changes [29]
3.4.2 Quantum Confinement

We have shown by calculation the effect of composition on the band gap of AlGaInP bulk material. Going from the bulk structure to the QW structure requires solving Schrödinger’s equation again for an electron in a QW potential. The allowable energy levels for electrons to satisfy Schrödinger’s equation will be higher than the band gap of the bulk material (Figure 3.7).

![Figure 3.7: Effect of quantum well thickness on the band gap.](image)

For the quantum confined transition energy, $E_{g(Q)}$, with the effective masses of electrons, $m_e^*$, and holes, $m_h^*$, are governed by Eq. 3.9 with $n$, $d$, and $n$ as the thickness of QW in nm and $n$ is integer number (1,2,...).

$$E_{g(Q)} = \frac{\hbar^2}{2m_e^*} \left( \frac{n\pi^2}{d^2} \right) + \frac{\hbar^2}{2m_h^*} \left( \frac{n\pi^2}{d^2} \right)$$  \hspace{1cm} (3.9)$$

and the band gap of the QW is given by

$$E_{g(QW)} = E_{g(bulk)} + E_{g(Q)}$$  \hspace{1cm} (3.10)$$

Effective masses of electrons and holes can be interpolated from the three binaries of GaP, InP, AlP as described in [13]. We have prepared a MATLAB function that
calculate the quantum in the appendix. For our case the calculated quantum confinement is approximately 80 meV. Figure 3.8 shows the reduction in wavelength as we change composition from 0.5 to 0.47. Then we calculate the emission as we change from bul to QW. Only 0.3 of Al in the QW can make the emission yellow.

![Figure 3.8: Effect of QW thickness (6 nm) on the emission wavelength](image)

### 3.4.3 Strain

The effect of strain can be easily understood if we look at the band gap diagram as a function of lattice constant, as shown in Figure 3.9. The distance between atoms is equal to the lattice constant. When a strain is applied it causes the lattice constant of molecules to change. As the lattice constant changes, the band gap of the material also changes. If tensile strain is applied the lattice constant becomes larger and the band gap becomes smaller.

The band gap of a QW grown on tensile strain can now be calculated as follows:

$$E_{g(QW)} = E_{g(bulk)} + E_{g(Q)} + E_{g(S)}$$  (3.11)
To account for strains, first we need to calculate the lattice constants for the barrier $a_{\text{Barrier}}$ and QW $a_{\text{QW}}$. From the calculated lattice constants, one can then calculate the strain values $\epsilon$. With $a$, $b$, the lattice deformation potentials, $C_{11}$ and $C_{12}$ the elastic stiffness coefficients given in the appendix A, the band gap change due to strain is calculated as follows:

$$\epsilon = \frac{a_{\text{QW}} - a_{\text{Barrier}}}{a_{\text{QW}}}$$  \hspace{1cm} (3.12)

Hydrostatic strain:

$$H(eV) = -2a \frac{C_{11} - C_{12}}{C_{11}} \epsilon$$  \hspace{1cm} (3.13)

Shear strain:

$$S(eV) = -b \frac{C_{11} + C_{12}}{C_{11}} \epsilon$$  \hspace{1cm} (3.14)

$$E_{g-S}(eV) = H + S$$  \hspace{1cm} (3.15)

The calculated band gap of the bulk material In$_{0.47}$Ga$_{0.53}$P is approximately
1.9116eV (650 nm). Going from the bulk bandgap to the QW band gap, the increase is approximately 60 meV making it 1.967eV (630 nm). Quantum confinement is approximately 80 meV and strain is approximately −25 meV, as per our calculation.

Now we determined that, the theoretical emission wavelength of the as-grown structure which is close to measured value, so we can estimate the emission wavelength as (Al) content is increased in the QW. Similar procedure was repeated and Figure 3.10 shows the change in $E_{g_{bulk}}, E_{g_{Q}}, E_{g_{S}}$, as a function of (Al) mole fraction, $x$. We found that, when we increase the (Al) composition, $x$, into the QW forming InAlGaP, there is negligible effect on the lattice constant. Hence, the effect of strain change due to Al change is small. Resulting in no change in wavelength due to strain. Figure 3.11 shows the resulting $E_{g_{QW}}$ with Al mole fraction. For example, a blueshift of approximately 30 nm (100 meV) is related to an increase in Al mole fraction of approximately 0.2.

![Graph of Eg_bulk, Eg_Q, Eg_S, and as a function of the (Al) mole fraction, x](image-url)
Figure 3.11: Graph of the resulting energy, $E_g(QW)$ and $\lambda_{QW}$ (QW emission wavelength), as a function of Al mole fraction, $x$.

3.5 Growth of GaInP/AlGaInP Material System

Normal Growth

The Growth of InAlGaP is mainly performed by MOVPE. In MOVPE, metalorganic (MO) precursors, usually the trimethyl compounds of (Al), (Ga), and (In) like $\text{Ga(CH}_3)_3$ (TMGa, also named TMG) react with sources of As and P, usually the hydrides $\text{AsH}_3$ and $\text{PH}_3$, on the heated substrate to form the epitaxial layer [31]. The first growth of an InAlGaP LD structure was in 1983 with emission wavelength of 683 nm [32]. Then 1985, 671 nm wavelength was reported by Masao, et al. They have grown a double hetero-structure [33]. Later in 1988, 640 nm wavelength emission was reached by the Holonyak’s group through increasing the (Al) content in a p-n junction laser diode with (Al) content of 0.2 [34]. To our knowledge, nobody has ever reported, the growth of a functioning AlGaInP LD with the (Al) content in active layer more than 0.2.
3.5.1 Shortening the Wavelength of InAlGaP LD

Increasing the band gap, (shortening the emission wavelength) of LD while keeping good efficiency was a major challenge in InAlGaP material system. There are four important approaches used, namely, growth on misoriented substrate, applying strain, increase quantum confinement, finally increasing the (Al) content.

Growth on Misoriented Substrate

In the material system of InAlGaP there is a problem that occurs during growth, called ‘ordering’. During growth, it is found that there is a tendency for an arrangement deviating from the expected random distribution on the group-III atoms. Figure 3.12 shows a TEM image of InGaP layers grown at different temperatures. The layer grown at 650°C is ordered while the layer grown at 720°C was disordered.

As shown in figure 3.13, ordering or arrangement of atoms in the ‘CuPtB’ ordering. This ordering leads to alternating preferential occupation. When the atoms are not random, then the band gap of alloy depends on the arrangement of these atoms rather than the composition [2].
In 1991, H. Hamad, et al., grew a laser structure on misoriented (off-cut) GaAs substrate and they have noticed the band gap of the grown material for both InGaP and InAlGaP is increasing as a function of increased off-cut angle. Using this technology, they were able to demonstrate a LD emitting at 631 nm [35].
**Growth of Strained QWs**

InGaP QWs can be tuned to give different wavelengths from red to green. However, to grow on the GaAs substrate the only composition is $In_{0.48}Ga_{0.52}P$. Therefore, composition of Al-free active layers cannot be changed much. Another approach is to grow on different substrate to have another composition of $In_xGa_{1-x}P$ with emission in the yellow for example. Because there are no substrate with such lattice constant, they have started the growth on InGaP substrate and gradually change the composition of the substrate to reach a lattice constant equal to the lattice constant of $In_{0.35}Ga_{0.65}P$. The idea is brilliant however, the fabricated devices emitted very low optical power of 0.18 $\mu$W per facet [4, 36]

![Figure 3.14: Schematic representation of the changes in band structure caused by introduction of tensile and compressive strains [2]](image)

**Improving quantum confinement**

By reducing the thickness of the QW, the wavelength can be shorten. However, thinner QWs have lower gain which makes it invalid approach. Instead, Adding
multiquantum barriers (MQB) in the barrier improves the quantum confinement and reduce the leakage current. Reduction in leakage current leads to lower operating temperature and the result is a reduction in wavelength by 5 nm only and the lasing was at 625 nm [37].

**Al-Rich Active Layer (InAlGaP)**

Finally, the last technique is increase Al content. The ideal alternative is to grow Al-rich QWs ($In_x(Al_yGa_{1-y})_{1-x}P$). Fixing Indium composition ($x$) approximately at 0.48, the quaternary remain lattice matched to GaAs with any (Al) content ($y$). However, increasing the (Al) content in the active layer reduces the quantum efficiency of the material exponentially [38, 51]. Shortest reported red LD is emitting at 615 nm with (Al) content of 0.1 [39]. The reason behind the drop of Al-rich QWs is oxygen-related defects. Al is very reactive and tends to form bonds with oxygen atoms and other species of contamination. These bonds in the active layer when Al content is increased form non-radiative recombination centers (deep-level traps) rendering the device to have very low quantum efficiency.

### 3.6 Conclusion

In this chapter we discussed the properties of AlGaInP semiconductor material. We presented simple calculation codes based on reported experimental data to calculate the the band gap of AlGaInP QW. The barrier and QW can take any composition of (In) and (Al). The calculations take into consideration the composition, the strain, and the quantum confinement to estimate the emission wavelength. We also, discussed the techniques used before to shorten the emission wavelength of AlGaInP LDs below 650 nm.
Chapter 4

Quantum Well Intermixing on InAlGaP

In this chapter we introduce the quantum well intermixing technique in general. We discuss about the different techniques of QWI including the impurity induced disordering (IID) QWI and the impurity-free vacancy disordering (IFVD). Then we discuss the intermixing on the InGaP/InAlGaP material system and the technique we invented.

4.1 Quantum Well Intermixing (QWI)

QWI is a post-growth process applied to laser structures to tune the band gap of the active layer by introducing impurities, interstitials or dislocations to disorder the QWs. It increases the band gap and blueshifts the emission peak. The disordering of semiconductor superlattice (SL) or QW structure is known to occur at temperatures above the growth temperature. In 1980 Nick Holonyak and his student were trying to dope AlAs/GaAs SL structure by Zn diffusion. The structure was grown by MOCVD
at 750°C. They annealed the structure at a temperatures between 500-600 °C which is, unlike the IFVD, below the growth temperature. The SL structure was not stable against the diffusion of Zn and disordering of Al and Ga atoms started to occur. Luminescence of the SL changed from red to yellow. The process was called Impurity-Induced Disordering (IID). Since Zn can be easily masked, the method was used to selectivity intermix certain areas [40]. During intermixing, new alloy is formed with a different composition from the as-grown. The new alloy has a higher band gap than the as grown and the peak emission is blueshifted as shown in Figure 4.2

Figure 4.1: Intermixing Process: the elements form group III interdiffuse between barrier and QW which causes a blueshift to the peak wavelength

4.2 Impurity-induced Disordering (IID)

Two approaches were considered which resulted in bandgap blueshift, namely impurity-induced disordering (IID) and Impurity-Free Vacancy Disordering (IFVD). In the IID intermixing process, a thin impurity film, for example Zn, is deposited, followed by annealing below the growth temperature to allow the impurity to diffuse to the structure. Because the impurities subsequently degrade the quality of the laser structure,
The peak wavelength of the intermixed sample is blueshifted due to the interdiffusion of group III elements between the QW and the barrier, in the laser structure. No active devices can be fabricated using this method [41, 42].

4.3 Impurity-free Vacancy Disordering (IFVD)

The IFVD technique is a very well-known technique that was implemented extensively on III-As based material system. The technique is low-cost and compatible with the fabrication process of LD. The IFVD involves the deposition of a dielectric (impurity free), such as Silicon Dioxide (SiO$_2$), followed by subsequent rapid thermal annealing steps [43].

4.3.1 IFVD Mechanism

The annealing of the laser structure causes group-III atoms to out-diffuse to the dielectric film creating point defects in the structure. Defects then propagate from the dielectric-laser interface to the QW. When defects reach the QWs, they enhance the intermixing process [44]. Figure 4.3 shows the IFVD mechanism.
Figure 4.3: A schematic of the IFVD process mechanism. The Ga atoms are absorbed by the SiO$_2$ dielectric film creating point defects that enhance the intermixing.

Defect density created in this technique are low and hence, the sample after IFVD maintain high crystal quality and low propagation losses compared to IID [45]. Figure 4.4 illustrate the difference between IID and IFVD process. Because of the low defect density after IFVD process, it is more popular than the IID and used for the fabrication of active devices. On the other hand, for passive section, such as fabrication of non-absorbing window (NAW) to take care off the catastrophic optical damage (COD), IID can be implemented [42].

Figure 4.4: a) Impurity Induced Disordering (IID) process, Zn atoms diffuse into the laser structure making point defects that help in the intermixing (b) Impurity-Free Vacancy Disordering (IFVD) process where defects are created due to the outdiffusion of Ga atoms to the capping layer. Defects created in IFVD are less than the density of defects created by IID.
4.3.2 Effect of Capping on IFVD

The capping material used during the IFVD process can have effect on the creation of the point defects, and 2- propagation of these point defects. The creation of defects is highly related to the quality of the film and metallurgical reaction between dielectric and laser, and the as-grown defects of the laser structure [46, 47]. The propagation of defects from dielectric/laser interface to QWs is highly dependent on the applied strain during annealing due to the difference expansion coefficient [48]. It has been reported that, compressive strain such as the strain applied by SiO2 enhances the outdiffusion of vacancies while tensile strain, produced by TiO2 for example, enhances the outdiffusion of interstitial defects [49]. The concept was applied to InGaAs/GaAs QD structure. The IFVD process gave different degree of intermixing due to the change in strain [50]. Figure 4.5 shows the applied stain on laser samples using different capping.

![Figure 4.5: Applied strain on laser samples during annealing when capped with different dielectric films (a) SiO2 capping applies compressive strain on the laser sample while (b) TiO2 capping applies tensile strain [50]](image)

Figure 4.6 shows the PL signals of samples were capped by SiO2 and TiO2. Due the difference in expansion coefficient, different degree of intermixing is achieved.

Furthermore, the lateral diffusion length is within 3 µm which is important for monolithic integration [51] in the In addition, this technique was used to selectively intermix different areas of QW lasers to achieve band gap-tuned devices in the mono-
Figure 4.6: Photoluminescence (PL) spectra for the InGaAs/GaAs quantum-dot structure capped with SiO$_2$ and TiO$_2$. The annealing condition is °C for 30 s[50].

lithic integration of photonic elements [52, 53, 54].

4.4 Intermixing on GaInP AlGaInP

In literature, intermixing on AlGaInP mainly is done using Zn or Si. Annealing at temperatures below growth temperature allows impurities to diffuse in the QW. Because the impurities degrade the quality of the QW, it has been used as passive section only like the nonabsorbent window [42, 41].

On the other side, IFVD reports on InGaP/InAlGaP material system is limited. Beernink et al. were first to apply this technique on the InGaP/InAlGaP material system using plasma-enhanced chemical vapor deposition (PECVD) to deposit a SiO$_2$ capping layer and reported a negligible bandgap blueshift [54]. Another group annealed bare (uncapped) and SiO$_2$-capped samples of InGaP/InAlGaP QWs at 900 °C for four hours and showed only a slight bandgap blueshift of 10 nm [43]. Kowalski et al. reported a differential shift of 100 meV using 200-nm sputter-deposited SiO$_2$, whereas no wavelength shift was observed for devices capped with PECVD-deposited
SiO$_2$ [55]. Hamilton et al, from the same group, reported an intermixed InGaP/InAlGaP laser emitting at approximately 670 nm. The device intermixed with this method was blueshifted (29 nm, 91 meV) and demonstrated lasing at 640 nm [56]. Recently, Hafnium Oxide (HfO$_2$) was also used to induce IFVD, and a bandgap shift of 18 nm was reported for the InGaP/InAlGaP material system emitting at 670 nm [57]. There are no reports of IFVD at the short wavelength of 640 nm, or with a large degree of intermixing in this material system.

**Laser Structure**

The single quantum well (SQW) GaInP/AlGaInP laser structure was grown on 10° off-cut GaAs substrate using metal-organic chemical vapor deposition (MOCVD) as shown in figure 4.7(a). The structure consist of a 200 nm Si-doped GaAs buffer layer with carrier concentration of $1 - 2 \times 10^{18}$ cm$^{-3}$, 1µm thick n-In$_{0.5}$Al$_{0.5}$P with carrier concentration of $1 \times 10^{18}$ cm$^{-3}$ lattice-matched lower cladding layer, a single GaInP-QW sandwiched between two 80 nm undoped In$_{0.5}$Al$_{0.3}$Ga$_{0.2}$P waveguide layers, 1µm thick Zn-doped In$_{0.5}$Al$_{0.5}$P with carrier concentration of $1 \times 10^{18}cm^{-3}$ lattice-matched upper cladding, 75nm lattice matched p-In$_{0.5}$Ga$_{0.5}$P with carrier concentration of $3 \times 10^{18}cm^{-3}$ barrier reduction layer, and 200 nm highly doped p-GaAs with carrier concentration of $2 - 3 \times 10^{19}cm^{-3}$ contact layer. The emission of the laser was designed to be at 635±3 nm as shown in figure 4.7(b).

**4.4.1 Effect of Strain on Intermixing**

In the begining of this work, we tried to deposit different types of films and annealed at various temperatures and we obtained negligible blushifts only. Later we decided to go closer to the QW by etching the cladding layer. We have noticed, an increase in the degree of intermixing as the etching depth is increases.
Figure 4.7: (a) Dark field (002) cross-section TEM image of the AlGaInP laser structure with a single GaInP QW, and (b) room-temperature PL emission around 638nm.
Effect of Etching

We have conducted two experiments. The first includes the process of etching the top cladding of the laser structure. There are two possible reasons for intermixing to occur. First, the distance between dielectric—laser interface and QWs is smaller than as grown, hence more point defect diffusion is expected. Second, as the distance is smaller, then more strain is imposed on the QWs as illustrated in figure 4.8.

Figure 4.8: Etching steps performed on the laser sample in order to apply more strain on the QW during intermixing.

Figure 4.9(a) shows the normalized spectra of the etched samples from 340 nm to 915 nm etch depth as measured by the surface profiler after the intermixing process at 600 °C for 60 s. As seen, as the etch depth increases, the blueshift increases. The annealing temperature (600 °C) was lower than the growth temperature (680-720 °C), but there was a blueshift of approximately 18 nm for samples etched to approximately 800 nm (presumably due to the strain relaxation in the active region). No significant band gap shifts have been observed from the annealed-unetched regions. Those were not etched exhibited no blueshift. Figure 4.9(b) shows the amount of blueshift as a function of etch depth. The blueshift is etch-depth dependent. As the etch depth approaches the barrier, the blueshift becomes saturated. From the above experiment,
we postulate, that the close distance between dielectric—laser interface and QWs created more point defects and caused more Ga vacancies to outdiffuse. Also, more strain was the cause of the intermixing.

**Thickness Dependent Intermixing**

In this experiment, without any etching, we increased the thickness of the dielectric film which have two effects that are beneficial for the process of intermixing. First, the thicker the dielectric film the more outdiffusion of Ga vacancies will occur. Second, more strain will be applied on laser structure. This is performed in separate runs, in which batch-to-batch process variation is expected. Figure 4.10(a) shows the normalized spectra of samples annealed at a temperature of 925 °C for 120 s. The capping film thicknesses are 200 nm, 500 nm, 800 nm, 1000 nm, and 2000 nm. As the thickness of the capping film increases, the amount of blueshift increases as expected. At a thickness of 2000nm, the dielectric film started cracking, and some areas of the top surface were damaged. Figure 4.10(b) shows the increase in band gap blueshift as a function of dielectric film thickness up to 37 nm. This validated the effect of strain in enabling the intermixing process. The saturation of the intermixing degree can be explained by reaching the maximum amount of point defects created due to strain. Hence, a thicker film will rather get fractured instead of imposing more strain on the laser structure.

**Intermixing Mechanism**

As shown in Figure 4.11, we believe the intermixing process in our work is due to the high strain applied and the elevated temperature. The deposited SiO$_2$ film has a thermal expansion coefficient ($\alpha = 0.510^{-6} \, C^{-1}$) that is lower than that of the p-GaAs cladding layer ($\alpha = 5.73 \times 10^{-6} \, C^{-1}$) [58]. During annealing, the mismatch
Figure 4.9: Measurement of (a) RT PL of InGaP/InAlGaP laser structures with different etching depths capped with SiO₂ film annealed at 600 °C for 60 s and (b) the relationship between the etching depth and the amount of blueshift on the InGaP/InAlGaP laser structure.
Figure 4.10: Plot of: (a) RT PL of InGaP/InAlGaP laser structures annealed at 925 °C for 120, with SiO₂ capping film thicknesses of 200 nm, 500 nm, 800 nm, 1000 nm and 2000 nm, and (b) the relationship between the capping film thickness and the amount of blueshift in the InGaP/InAlGaP laser structure.
in expansion at the interface of the dielectric and semiconductor induces high compressive strain, whereas the QW is under tensile strain. The opposite strains applied on the barriers create point defects at (1) the interface of the dielectric and the laser structure and at (2) the interface of the barrier and the QW, as shown in Figure 4.11. These point defects, with energy given to the atoms by heat, facilitate the interdiffusion of (group III) atoms between the QW and the barrier.

Figure 4.11: Intermixing mechanism of the strain-induced QWI on the InGaP/InAlGaP material system. Opposite strains applied on the barriers cause point defects to be generated at the QW-barrier interface. As the point defects are created, and with sufficient energy given to the atoms, they started to interdiffuse between the QW and barrier. [The built-in strain is illustrated.]

4.4.2 Process Optimization

In this study, a relatively thick film of SiO$_2$ and a higher annealing temperature was utilized to induce high strain and enhance QWI. The optimum process conditions are obtained from the QWI process that provides a high degree of intermixing while maintaining strong PL intensity, narrow Full-Width at Half Maximum (FWHM) and good surface morphology in the laser sample. Maintaining these parameters ensures high quality of the laser structure after the intermixing process for further laser fabrication. These parameters are analyzed in the following sections.
Figure 4.12: Graph of the setpoint and the measured temperature by the thermocouple inside the RTP during an annealing step.

**Optimizing Annealing Temperature**

A 1000 nm of Silicon Dioxide (SiO$_2$) cap was deposited using PECVD on the sample surface. The deposition was carried out at a chuck temperature of 300 °C, process pressure of 1000 mT and RF power of 20 W, using SiH$_4$, N$_2$O and N$_2$ as reactive gases. The samples were then cleaved to approximately 2×2 mm and annealed using a Rapid Thermal Processing (RTP) equipment at temperatures between 700-1000 °C for annealing duration between 30 s and 240 s, along with bare (uncapped) as-grown samples. The temperature in the RTP in an annealing step is plotted as a function of time in Figure 4.12.

During annealing as shown in Figure 4.13, the top surface samples were facing downward, and sandwiched between two fresh pieces of GaAs proximity caps in order to provide the required Arsenic over-pressure environment as described in [57, 59]. The bandgap shifts induced by the above procedure were measured at room-
Figure 4.13: Intermixing steps: 1-dielectric film is deposited by PECVD, 2-sample is placed in the RTP, 2-sample is flipped backward to protect the top surface during annealing and placed between fresh GaAs pieces to keep over-arsenic pressure during annealing, 4-sample is annealed. The process can be repeated to achieve the required blueshift temperature using Photo-Luminescence (PL) spectroscopy, equipped with a 473 nm cobalt laser as the excitation source.

We studied the effect of the annealing temperature on group-III elemental intermixing to find the threshold temperature at which the intermixing process initiates. The annealing duration was set to 120 s, and the samples were annealed at different temperatures from 700 °C to 1000 °C. Figure 4.14(a) shows the PL spectra for the InGaP/InAlGaP samples as a function of RTP temperature. The SiO2-capped samples exhibit negligible blueshifts for temperatures in the range of 700°C to 900°C. Above 900°C, the wavelength blueshift increased rapidly with increasing annealing temperature. Figure 4.14(a) presents the blueshift and FWHM obtained for SiO2-capped samples as a function of temperature. The blueshift started at temperatures of 900 and 925°C. Above these temperatures, the blueshift rapidly increased to over 60 nm (200 meV) at 1000°C. Up to 975°C, all the samples retained high PL inten-
sity with a negligible increase in FWHM while maintaining good surface morphology. The uncapped samples were also annealed, and a negligible blueshift was obtained, as shown in 4.14(b). To further investigate the effect of annealing below the activation temperature, we annealed the SiO2-capped samples for several cycles and obtained a negligible blueshift (not shown). Therefore, the threshold temperature for initiating interdiffusion is 900°C.

To determine the optimum annealing temperature, we studied the blueshift as a function of annealing temperature above the threshold temperature of 900 °C, as indicated in Figure 4.15. For simplicity of analysis, we selected regions that showed a linear intermixing process. The slope of the linear fit provides the rate of intermixing, which is 1 meV/°C and 3 meV/°C for annealing temperatures of 900-950 °C and 950-1000 °C, respectively. This quantitative analysis confirms our earlier observation that the degree of intermixing rapidly increases above 925 °C, in this case, by more than a factor of 3 for 950-1000 °C. Based on the above analysis, 950 °C is the critical temperature, at which slope changes, for enhanced intermixing in this material system.

**Optimizing Annealing Duration**

We further investigate the effect of annealing duration on the GaInP/InGaAlP intermixing. We selected the 950 °C and varied the annealing duration from 30 s to 240 s. The PL spectra of all annealed samples are shown in Figure 4.16(a). A progressive blueshift is observed as annealing time increases. The increase of blueshift against annealing time was almost linear compared to the exponential increase of blueshift against temperature. Hence, varying the annealing duration while keeping the temperature constant provides better control on wavelength blueshift. In Figure 4.16(b), the peaks emission and the FWHM is extracted and plotted against annealing time.
Figure 4.14: PL analysis of: (a) the peak shift as a function of annealing temperature for InGaP/InAlGaP with a 1-µm thick PECVD-deposited SiO₂ capping layer annealed for 120 s and (b) the extracted peak wavelength and FWHM from (a) and the reference uncapped sample after annealing.
High crystal quality of the active layer after annealing below 180 s is indicated by the FWHM curve. As annealing time was increased to 240 s, the PL intensity decreases with subsequent broadening in FWHM. A maximum blueshift in peak wavelength up to 595 nm was obtained after 240s annealing, with an equivalent blue-shift of 45 nm (140meV). A noticeable blueshift only occur after an annealing duration of 90s, and therefore it is safely concluded that the activation time for 950 °C is around 90 s. Below these conditions, no significant blueshift can be achieved.

Figure 4.17 plots the linear fitting of the PL peak shift as a function of annealing duration for 950 °C. As shown before, the slope of linear fit line provides the rate of intermixing, which is 0.67 meV/s for the annealing duration of 30-240 s. Furthermore, a duration of 45s is extrapolated from the linear fit, which is minimum annealing duration for the initiation of intermixing process related to the diffusivity and diffusion length of the inter-diffusion mechanism for the capped samples.
Figure 4.16: (a) Room temperature PL spectra of as grown (shown only 120 s annealed sample) and of SiO$_2$-capped sample annealed at 950 °C. Curves are shown after 30, 60, 90, 120, 180 and 240 s anneal time. (b) Extracted peak wavelength and FWHM from (a) plotted against the anneal time.
Figure 4.17: Linear fitting of the PL peak shift as a function of annealing duration

Optimization of Cyclic Annealing

We achieved a large degree of blueshifting at 240 s, but the associated decrease in PL intensity and broadening of FWHM suggests the material quality deteriorated. As mentioned above, cyclic annealing was reported to enhance the material quality of the intermixed structure \[59\]. In this section, the objective was to determine the optimum duration for cyclic annealing at 950 °C. For each sample, we fixed the annealing duration and repeated the process for up to three cycles. The annealing durations were 30 s, 60 s, 90 s, 120 s, 180 s and 240 s. Figure 4.18 shows the blueshift versus the number of cycles. Cycle 0 represents the peak wavelength before intermixing. As can be seen, the same wavelength, yellow (580 nm) for example, can be achieved by several schemes, e.g., 2 cycles of 240 s or 3 cycles of 120 s. However, note that the PL intensity and the surface quality of the shorter durations are better. From the above study, we determined 950 °C and 30 s as the optimum annealing temperature and duration, respectively. With this process, we were able to blueshift
the peak emission from red (640 nm) to yellow (565 nm) (250 meV) with number of cycles of annealing, which is largest blueshift reported for this material system.

### 4.4.3 Modeling Diffusion

The atoms from group-III when they interdiffuse between the QW and the barrier they follow Fick’s law of diffusion. Atoms diffuse from higher to lower concentration according to the formula:

\[
\frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c)
\]  

(4.1)

Where C is the material concentration and D is the material diffusivity. The formula can be solved by an error function to give the QW profile as a function of diffusion time \( t \) or diffusion length \( L_D \) [43].
\[ C(t) = C_B + \frac{(C_W - C_B)}{2} \left\{ e^{rf} \frac{b - z}{L_D} + e^{rf} \frac{b + z}{L_D} \right\} \tag{4.2} \]

Where \( C(t) \) is the concentration profile in the z-direction, \( C_B \) and \( C_W \) are concentrations in the barrier and QW respectively, \( b \) is the QW thickness and \( z \) is the position.

We applied the formula using the code in the appendix to calculate the profile for different diffusion length. Figure 4.19 shows the profile of the Al concentration inside and outside the 6 nm QW of AlGaInP.

![Figure 4.19: The Profiles of the Al concentration in the QW before and after intermixing and the effective concentration](image)

An accurate calculation of band gap requires solving the Schrödinger equation for the new QW profile after intermixing. An approximate approach is assume an effective QW that gives emission in the measured peak.
4.5 Conclusion

In this chapter we discussed QWI on InGaP/InAlGaP material system. From the above experiment we learned that intermixing on InGaP/In AlGaP laser structure can be initiated using PECVD SiO$_2$ film. By increasing the capping film thickness, we implemented more strain on the laser structure. We presented a novel strain-induced QWI technique on an InGaP/InAlGaP red laser structure that induces a large degree of band gap blueshift. By optimizing the annealing temperature, the annealing duration, and the number annealing cycles, we made the first observation of a band gap blueshift as large as 250 meV (75 nm) in this material system at the short wavelength of 640 nm. The QWI samples were characterized by PL measurements, the results of which indicated the high quality of the material and operational devices. The novel technique presented in this paper may represent the solution for producing high-efficiency AlGaInP devices at the shorter wavelengths of yellow and orange color and has potential application for producing passive sections, e.g., the non-absorbing window, in the InGaP/InAlGaP material system
Chapter 5

Laser Diodes Fabrication

In this chapter, we describe the fabrication steps we followed. Fabrication of lasers in our cleanroom was a challenge as we needed to optimize the process from scratch. Laser fabrication is a set of processes used to make proper contacts and facets for laser devices with a desired length. The process requires a clean environment, therefore, all fabrication steps have to be performed in the clean room. Many machines in the cleanroom were used. The working principles of each machine need to be understood by the fabricator to ensure proper operation. The fabrication begins by having a laser wafer with the laser structure already grown, either by MBE or MOCVD. The laser structure can be a quantum well, quantum dash or quantum dots. The material of the wafer affect the process as different recipes are needed. The wafers used in this thesis are grown on a GaAs substrate and the structure is a quantum well. Details of recipe are given in appendix C. Figure 5.1 shows a summary of fabrication steps performed on laser samples.
Figure 5.1: Fabrication process from laser wafer to thin laser devices with top and back contacts.

5.1 Sample preparation

Laser wafers are expensive and very fragile. They come in sizes of 4 and 2 inches. The size of a single LD is around 1 mm long and 200 µm wide. Therefore, a laser sample which is a small piece of the laser wafer is used to start the fabrication steps, usually in the range of 1.5 × 1.5 cm

5.1.1 Cleaving a Laser Sample

Wafer cleaving is an important skill for semiconductor process researchers. The perfect cleaving process is one with minimum particles on the sample. For cleaving, a scratch is made at the front surface of the wafer. Then, the wafer is flipped and a gentle rolling force is applied. The scratch should extend as a crack along the crystal plane causing the whole wafer to be cleaved. The process is repeated to have the required sample size. Figure 5.2 shows the steps of manual cleaving in order to have a laser sample.
Figure 5.2: Steps for manual cleaving a laser wafer to have laser samples. (a) A scratch on the top surface is made. (b) The wafer is flipped and rolling force is applied. (c) Process is repeated the have desire sample size.

5.1.2 Cleaning

After cleaving, the sample needs to be cleaned from all particles on the surface of the sample coming from cleaving and any sort of dirt. Chemical solvents and the ultrasonic bath is used. The sample is rinsed by acetone and immersed in a beaker filled with acetone. The beaker is placed in the ultrasonic bath for five minutes. After that, the same process is repeated with isopropanol alcohol (IPA). After cleaning, the sample is kept in a small holder and never touched by hand. Figure 5.3 shows the image of a laser sample being cleaned by a solvent and then placed in an ultrasonic bath.

Figure 5.3: Cleaning the laser sample includes (a) rinsing the sample in a solvent and then (b) immersing in an ultrasonic bath to remove debris and particles from the top surface.
5.2 Front Side Fabrication

Now the sample is ready for fabrication steps. The fabrication starts from the top side for one reason. The sample is still thick and can tolerate the fabrication steps. Front side fabrication comprises of three steps: 1- insulator deposition, 2- first lithograph and 3-second lithography.

Insulator Deposition

After cleaning the sample a layer of SiO$_2$ is deposited on the sample. The thickness of the SiO$_2$ film used is 200 nm using the PECVD deposition. The recipe used has a deposition rate of 62 nm per minute. After the deposition is done, the thickness of the SiO$_2$ is measured using the ellipsometer as shown in figure 5.4.

![Figure 5.4: Deposition of 200 nm of SiO$_2$ film as a dielectric insulator using the PECVD and measurement of the thickness using the ellipsometer](image)

First Lithography

After depositing the insulator, The first lithography is to make openings in the SiO$_2$ film. These openings will allow the metal to be deposited later to make the p-contact.
as shown in Figure 5.5

Figure 5.5: Front side fabrication steps including insulator deposition, insulator etching, fabrication process from laser wafer to thin laser devices with top and back contacts

A photoresist is spin coated on the sample, then baked to the required temperature and given time to harden and become activated for the UV exposure as shown in Figure 5.6.
Figure 5.6: Images of laser sample with (a) photoresist to be spin coated and (b) to be baked

After baking, the sample need to be exposed to UV. To insure perfect cleaving, the directions of the bar need to be either parallel to the GaAs wafer major flat which is the (110) plane or perpendicular to the major flat which is (110) plane. The mask and the sample need to be aligned to an edge of the sample to produce laser bars as displayed in figures 5.7(a).

Figure 5.7: (a) Alignment of mask to the crystal plane of the sample. (b) Photoresist after development

After alignment is performed, the sample under the mask is exposed to UV then the developer will remove the exposed areas as in figure 5.7(b). After development of the photo-resist, using inductively coupled plasma (ICP), SiO$_2$ is etched away.
Etching recipe we used has an etching rate of 200 nm/min making the etching time 30 s. Usually, after etching, some residuals of photoresist remain on the sample. The residuals of photoresists can be removed by applying plasma stripping as shown in figures 5.8(a) and 5.8(b).

![Figure 5.8: Images of photoresist residuals after first lithography (a), which can be removed by plasma as in (b)](image)

**Second Lithography**

The second lithography process is the step where the p-contacts are deposited. The process can be summarized by depositing the contact then performing the lift-off as shown in figure 5.9. In our fabrications, the lasers are broad-areas with ridges of 75 µm and separations of 150 µm. This process is completed by sputtering a thin film of metal under high vacuum conditions using magnetron sputtering shown in figure 5.10(a). To form the Ohmic contact to p-type GaAs Ti/Pt/Au (10/20/250 nm) is used where the Ti layer acts as an adhesive layer. Prior to loading, the samples are placed in a 1:1 HCl:H₂O solution for 20 sec, in order to remove native surface oxides. After deposition of the metals the sample is placed in warm acetone for a process known as lift-off as shown in figure 5.10(b). During this process the photo-resist underneath the metal dissolves in acetone thereby lifting-off the metal and leaving well defined metal contacts as in
Figure 5.9: Second lithography steps. The PR is developed and top contact is deposited and then finally lift-off is performed.

Figure 5.10: Deposition of the p-contact by sputtering. (a) Sputtering system, (b) Sample after deposition. (c) Sample after lift-off process.

The sample is then cleaned using IPA. After that, sample is annealed at 380 °C for 1 min using the rapid thermal annealing process (Jipelec JetFirst 200). We annealed under N₂ atmosphere, to drive the Ti/Pt/Au in the upper semiconductor layer in order to reduce the metal/semiconductor barrier height, thus reducing the voltage drop across the contacts.
5.3 Back Side Fabrication

Before back contact metallization, the samples are thinned so that they can be cleaved properly to get the mirror facets, and to aid in heat sinking. The process is done by mounting the sample on a metal block with wax as shown in figure 5.11(a). The thickness of the sample is measured in every corner to account for uniformity and wax thickness. The sample is thinned by mechanically rubbing down to 100 \( \mu \text{m} \) 150 \( \mu \text{m} \) using diamond polisher with a coarse grain size of 9 \( \mu \text{m} \). Figure 5.11(b) shows the laser sample being mounted on the thinning chunk by wax and then being thinned. After this process the sample is cleaned and de-mounted on a hot plate.

![Image of backside thinning process](image)

Figure 5.11: Backside thinning process. (a) A laser sample is mounted on the thinning chunk by wax. (b) The laser sample is being thinned.

The sample is then cleaned with acetone and IPA. Finally, if required, the sample is again mounted on a carrier wafer and the n-contact metal is deposited on the polished back side by e-beam evaporator. The n-metal consists of Au/Ge/Au/Ni/Au (14/14/14/11/250 nm). The sample is again annealed at 380 °C for 1 min to allow
the metal to partially diffuse into the doped semiconductor, thereby facilitating a low resistance ohmic contact. Figure 5.12 shows the front view of LD sample after depositing back and front contacts.

Figure 5.12: The front view of laser sample after depositing back and front contacts.
5.4 Cleaving

The last step is to cleave laser bars to the required lengths, usually it is in the 1 mm range. The sample is cleaved into laser bars of various cavity lengths and the as-cleaved mirror facets is obtained via notch and break technique of the motorized scribe tool (Loomis LSD-100). After cleaving the laser bars, the laser devices are ready for testing. Figure 5.13 cleaved laser bars under test.

![Cleaved Laser Bars](image)

(a) Sample after being cleaved. (b) Cleaved lasers are under test.

5.5 Laser Testing

In this thesis, we are interested in two measurements. We have fabricated broad area lasers with 75 µm ridges and cavity length of 1 mm as shown in Figure 5.14. Testing the laser is performed by The LDs were electrically pumped in pulsed mode with duty cycle of 5%. Figure 5.15 shows the lasing spectrum of as-grown device. The emission wavelength is around 640 nm with very sharp peak with FWHM approximately in 2 nm range. The second measurement we are interested in is the Light-Current (LI) curve from which most of LD characteristics can be calculated.
Figure 5.14: Schematic of cleaved laser bar with a number of broad area LDs. The length of LDs is 1 mm and the stripe is 75 µm

5.6 Conclusion

In this chapter, we presented the fabrication technique we followed at KAUST to fabricate LDs. The processes and recipes used are standard to any fabrication process. Some of the recipes were modified to suit the conditions at the clean-room and used machines.
Figure 5.15: Plot of (a) as-grown lasing spectrum of a fabricated laser and (b) The L-I curve
Chapter 6

Intermixed Devices (SQW)

In this chapter, we have intermixed lase structure samples and then fabricate them as devices. We have used two sets of wafers grown by different growers but with the same design. The first sets of wafers were easier to intermix. All the analysis and the measurements performed in chapter 3 were based on that set of wafers. The second set of wafer was harder to intermix. It required more annealing time and higher temperatures.

6.1 Emitters

In this section, we intermixed samples using the optimum parameters of 950 °C and 30 s, as described previously. For each cycles a blueshift of 5 to 8 nm is obtained. The samples were annealed for 2, 5 and 9 cycles to obtain the desired wavelengths of red (620 nm), orange (595 nm) and yellow (575 nm), respectively. Emitters were prepared by removing the capping dielectric and applying front and back contacts to the samples. Broad area pumping of current was applied to the samples. Figure 6.1 shows the images of the as-grown laser and the intermixed emitters. Efficient emission was obtained, even for the yellow emitter, where the band offset is less than
150 meV.

Figure 6.1: Images of (a) as-grown laser and intermixed devices emitting (b) 620 nm, (c) 595 nm and (d) 575 nm. The value of peak PL of each device is mentioned.

Figure 6.2(a) shows the EL spectra of the spontaneous emission of the emitters with the as-grown red laser. The EL peak was approximately 5-10 nm redshifted from the PL peak due to heating induced by the broad-area pumping. The peak PL emissions of (a) the as-grown LD structure, (b) intermixed to 620 nm, (c) intermixed to 595 nm and (d) intermixed to 575 nm. Figure 6.2(b) shows the turn-on voltages of the intermixed emitter. The yellow emitter has a turn-on voltage of 2.1 V, which is approximately the band gap of the device emitting at the operating wavelength of 585 nm. The emitter also has a low series resistance (≤ 5 Ω). These are good electrical characteristics for the yellow emitter with the highest degree of intermixing. That shows process is good. In addition, the result confirms that the dopant concentration in the top contact and the cladding layers remained at a similar level and did not diffuse into the active region of the laser structure, even after the successive annealing at elevated temperatures.
Figure 6.2: Graph of the EL of: (a) as-grown intermixed devices emitting at 628 nm, 602 nm and 585 nm, and (b) the turn-on voltages of the intermixed laser structures compared to those of the as grown structures.
6.2 Slightly Tuned LDs

Studies of the annealing effect on device performance has been characterized, in particular on the InGaP/InAlGaP laser structure. The main concern when annealing InGaP/InAlGaP laser structure is the top surface. Annealing at high temperatures causes the top surface to become rough. A layer of dielectric film is needed to protect the surface. P. Floyd, et al, performed annealing after capping the top surface by SiO$_2$ film deposited from PECVD. The annealing temperature was limited to 400 °C. Improvement in threshold current $I_{th}$ from 20 mA to 18 mA was achieved [60]. A similar procedure was performed; the annealing temperature was set to 450 °C for a duration of 30 minutes. Improvement in the threshold current was observed for ridge lasers from 33 to 25 mA [61]. J. Dekker, et al, increased the temperature to 875 °C for a duration of 1 s [62]. No devices were shown. Improvements are illustrated by the improved carrier lifetimes from the time-resolved PL measurements and the reduction of deep-level traps by deep-level trap spectroscopy. In this work, we annealed at relatively elevated temperature, 950°C, for relatively longer time, 2 minutes, and applied a relatively thick film of SiO$_2$, 1.5 m. We then studied effect of annealing on PL peak, PL intensity, threshold current $(I_{th})$, internal efficiency $\eta_i$ and optical losses $<\alpha_i>$. 

Figure 6.3 shows the PL of the sample before and after intermixing. The intensity of the PL signal was enhanced approximately ten-fold, from 70 to 735 counts and the FWHM was reduced from approximately 30 nm to 20 nm. The strong PL signal, the narrow FWHM, and the good surface morphology after the intermixing process suggests that the fabricated devices were comparable to as-grown lasers. The as-grown QW emitted at 641 (displayed 641 nm signal in Figure 6.5) nm. The blueshift of approximately 6 nm (15 meV) is due to the interdiffusion of Al and Ga atoms.
between the QW and the barriers. Calculations of the change in QW composition shows an increase of Al content to 0.03 as shown in Figure 6.4. Here we are using similar design but different growth batch. Therefore, the blueshift is lower than previously reported.

Figure 6.3: The PL signal of the annealed laser structure compared to the as-grown PL signal. Annealed sample emissions are blueshifted by approximately 6 nm with an increase in the PL intensity ($\times 10$) and a reduction in the FWHM by approximately 10 nm.

Next, we cleaved the as-grown and intermixed laser samples to lengths of 0.4 mm, 0.6 mm, and 0.8 mm and measured the thresholds of multiple devices at each length. Measurements were performed on pulsed mode with 5% duty cycle. Figure 6.6 shows the threshold current of the annealed devices compared to the as-grown devices. The threshold current $I_{th}$ of the annealed laser with a length of 1 mm is 1.5 A, while the as-grown laser has a threshold current of 2 A, which is approximately 25% lower. As the length of the devices is reduced, the threshold current difference between the annealed and as-grown devices becomes smaller. The slope efficiency of the annealed devices is lower than that of the as-grown devices.
Figure 6.4: Calculation of bandgap and wavelength of a 6 nm QW of In0.47(AlxGa1-x)0.53P as the mole fraction x is increased. With 15 meV (5 nm) blueshift after taking care of the confinement and applied strain on the wavelength.

Figure 6.5: The electroluminescence of as-grown and intermixed devices cleaved to 1 mm long devices. The as-grown and intermixed devices have lasing peak at 642 nm and 638 nm respectively.
Figure 6.6: Threshold currents of as-grown devices compared to annealed devices of different device lengths. Annealed devices have lower threshold currents and lower differential efficiencies. For longer devices, the differences are clearer.
Figure 6.7 shows LI and IV curves at high pumping for 0.4 mm and 1 mm devices. The rolling over for annealed devices is faster, and the turn-on voltage is higher. We believe that the increase in the series resistance is due to annealing at elevated temperature, which causes As to diffuse out of the contact layer. Similar behavior has been reported on InGaAs/AlGaAs material system as discussed in [63]. Other factors such as the diffusion of the dopants and the increase in the surface roughness due to annealing play an role in increasing the resistance.

![LI and IV curves](image)

Figure 6.7: LI and IV curves of the annealed and as-grown laser devices with 0.4 mm and 1 mm lengths. The rolling over of the annealed devices is faster, and the series resistance is higher.

In order to determine the internal optical loss and the quantum efficiency we followed the standard procedure in [64] and plotted the inverse differential quantum efficiency against device length L in Figure 6.8. Quantum efficiency for intermixed devices is 68 percent which is better than the as grown. The internal optical losses are increased from 14.3 $cm^{-1}$ to 18.6 $cm^{-1}$. 
Figure 6.8: A plot of the inverse differential quantum efficiency versus the laser cavity length.

Figure 6.9 shows a plot of the threshold current density of intermixed and as-grown laser devices versus the inverse length. The transparency current ($J_{th0}$) for as-grown devices is 1850 A/cm$^2$ while intermixed is 1100 A/cm$^2$.

For limited degree of intermixing on InGaP/InAlGaP material system, annealing has improved the performance of the laser devices. The results can be explained if we split the process into three sub-processes. The first sub-process is the creation of defects. These defects are created at the interface of the capping dielectric-laser interface and propagate throughout the laser structure. The point defects are created due to the difference in expansion coefficients [58]. Defects, created during annealing, increase the non-radiative recombination centers and the optical losses for light propagation inside the structure. We believe the defects created during the annealing process are responsible for the increase in $< \alpha_i >$ in the intermixed devices. The amount of defects can be controlled by reducing the annealing time or reducing the applied strain from the dielectric film. The second sub-process is the interdiffusion
Figure 6.9: Threshold current density, $J_{th}$, versus the inverse cavity length, $1/L$

of group-III atoms between the QW and the barriers. As a result, the band gap of the QW is blueshifted as more Al atoms diffuse into the QW. As the temperature and time are increased, the amount of diffusion increases. The third sub-process is the reduction of deep-level traps. The considerable improvement in PL intensity and reduction in FWHM with the enhancement in the threshold current $I_{th}$ can be related to the reduction in deep-level traps and oxygen-related defects due to the elevated temperature as explained in [60].
6.3 LDs Tuned to Orange

6.3.1 The Need for Orange Laser Diodes

The orange wavelength spans from 595 nm to 615 nm. There are plenty of applications that require the orange wavelength. One of the very important applications of orange lasers is flow cytometry. Flow cytometry is a technology that is used to analyze the physical and chemical characteristics of particles in a fluid as it passes through at least one laser. Cell components are fluorescently labeled and then excited by the laser to emit light at varying wavelengths. This technology is extensively used in medicine to quickly count the number of cells of different kinds [65]. The lasers used in current technological applications have wavelengths in the yellow and orange range. Therefore, Dye lasers which can cover the whole yellow orange spectral region is utilized [66]. Helium Neon (HeNe) lasers can utilize an orange laser from 612 nm to 595 nm [67]. Also, solid state lasers like the DPSS laser are utilized [68]. There is a need for laser diodes in orange range [69]. By looking at these other types of lasers used in the current technology, LDs in the orange range have the potential of utilization due to their low power consumption and small size.

The only reported room-temperature LD in the orange range is emitting at 615 nm which uses the misoriented substrate, tensile strained QW with (Al) content of 0.1 [39]. Beyond 615 nm, no one has ever reported lasing until the 530 nm by InGaN/GaN material system. It has been noticed that, any technique to reduce the wavelength fails, due to the increase in the threshold current ($I_{th}$) [70]. In our work, we used QWI as a technique to reduce the wavelength.
6.3.2 Fabrication of Orange LDs

We implemented our technique to intermix the laser sample. We applied 5 cycles of 950 °C for 30 s annealing. The peak wavelength of the sample was blueshifted from approximately 640 nm to 601 nm. Figure 6.10 shows the PL signals of as-grown and intermixed laser samples. The PL signal of the intermixed sample was strong and the surface was clear. We removed the dielectric film and cleaned the sample for fabrication.

![Figure 6.10: Room-temperature PL signals of as-grown laser sample and annealed sample for 5 cycles of 30 s at 950 °C](image)

We fabricated broad area lasers of 1 mm cavity length and 75 µm stripe width. Figure 6.11 shows the lasing spectra of the as grown and orange laser at a current injection of 1.2×Jth. The embedded mini-graph displays the power-current characteristics with a threshold current density (Jth) of 3.4 kAcm² and total output power of 46 mW (two facets). For comparison, the as-grown sample of similar device fabrication exhibited approximately three times lesser current density and approximately six times higher output power at the lasing wavelength of 640nm. The increased current
density and decreased output power is attributed to the increased optical losses due to the defects created by the intermixing process. To the best of our knowledge, this is the first demonstration of room-temperature orange LD.
Figure 6.11: (a) Room-temperature lasing spectra obtained at a current injection of 1.2Jth for novel QWI intermixed and as grown sample. Inset shows the power-current characteristics as a function of current density from the 1mm-long broad area laser. (b) The orange LD under electrical testing at room temperature.
6.4 LDs Tuned to Yellow

6.4.1 The Need for Yellow Laser Diodes

The yellow wavelength is between 570 nm to 595 nm. In this wavelength, there are no laser diodes in the form of either edge-emitting or surface-emitting lasers. The only optoelectronic device is in the LED form. The low efficiency of the quaternary AlGaInP material emanates from incorporating a relatively high ratio of Al. A wavelength of 585 nm is equivalent to a band gap of 2.11 meV. For bulk AlGaInP, the Al mole fraction is approximately 0.4, which is relatively high and no growth method can provide an optically efficient material with such a high Al content. For QWs, the Al content can be reduced to, say 0.3, to achieve the yellow due to quantum confinement. However, available LEDs are inefficient and in order to surmount the efficiency problem, fabricators usually grow LEDs with several QWs ranging from 30 to 70 MQW [71]. Furthermore, there are plenty of fabrication techniques that optimize the LED structure to insure high extraction from yellow LEDs [72, 73, 74].

6.4.2 Applications of Yellow Laser Diodes

There are numerous potential applications for yellow lasers. However, there are more important applications that need LDs that do not exist. Two examples of the applications of yellow LDs include optical communication and solid-state lighting. In optical communication, the Plastic Optical Fibers (POF) are the cheapest type of fibers used in this communication. These fibers have low losses at the wavelength of 570 nm and since there are no yellow LDs in this range, this band is not used. Currently, white LEDs are made of blue InGaN/GaN LEDs covered with a layer of yellow phosphors. The phosphor is used to convert blue light to yellow light. Yellow
light and blue light when added together gives white emission. With yellow LDs, we can combine the emissions as shown in Figure 6.12 to generate a white laser beam. This laser beam can then be projected through a diffuser to give white light that replaces the white LED. The advantage of such a system is the ability to modulate the blue laser and the yellow laser to carry signals. This can improve the performance of Li-Fi technology.

Figure 6.12: A white light source created from blue and yellow LDs.

6.4.3 Fabrication

We implemented our technique to intermix the laser sample. We applied nine cycles of 950 °C for 30 s annealing. The peak wavelength of the sample was blueshifted from approximately 640 nm to 575 nm. The PL signal of the intermixed sample has a strong PL signal and good surface. We removed the dielectric film and cleaned the sample for fabrication.

Next, the samples were fabricated into devices with 75 µm ridges. The devices were then cleaved to 800 µm long. Good emission is obtained and the devices had a good turn on voltage of 2 V. the devices were then tested. The output power was around 5 mW per two facets and the electroluminescence peak was around 582 nm as shown in figure 6.14 Such an output at this wavelength is considered very high compared to LED structures. If we compare our structure which is SQW to an LED structure with 30 MQW then we are having an efficient device in the yellow range.
Figure 6.13: Room-temperature PL signal of as-grown sample with annealed sample for nine cycles at 950 °C for 30 s.

6.4.4 Factors Limiting LDs’ Power

The possible reasons for the low output power and not having stimulated emission are as follows:

Defects: amount of defects created during the intermixing process is relatively high. These point defects create nonradiative recombinations and thus reduce the output power. The point defects also will create scattering points in the path of photons which increases the losses. We postulate, the density of defects created is related to expansion and contraction during in each cycle. Hence the more the number of cycles is applied the more defects density is generated. Possibly, annealing for longer time may give better results as we expect the number of defects created to be less if the annealing cycles are reduced.

Band-offset The difference between the conduction band of the barrier and the conduction band of the QW is referred to as the band offset. It is a measure of how the depth of the QW. A low-band offset or shallow QW reduces the number of confined
Figure 6.14: (a) Power-current characteristics as a function of current density from 1.5mm long and 75μm wide broad area laser fabricated from InGaP/InAlGaP inter-diffused sample. Inset: yellow amplified spontaneous emission spot at 583nm, (b) amplified spontaneous emission spectra at 583nm
carriers. More electrons can escape the QW resulting in a higher leakage current. In our case, the As-grown laser has a band offset of 187 meV, which is already small \[75\]. By intermixing, the band gap of the QW increases causing the band offset to decrease. For an Al content of 0.3, the band offset will reduce to approximately 100 meV. This is relatively shallow and will cause high leakage current.

**GaAs Absorption:**

The absorption of GaAs increases as the wavelength is reduced towards the yellow range \[67, 68\]. Because of the importance of this issue, DBR layers, for example, are implemented in the design of yellow emitters to reduce the absorption from the GaAs substrate \[76\]. Therefore, we obtain reduced output power. Having this low output power of only 5 mW is actually encouraging as the output is much greater than previous attempt to grow laser structures of the same material system but grown on modified substrate to account for lattice matching\[36\]. Also, this power is relatively high, keeping in mind we have only SQW while LEDs in industry use 30 to 70 MQWs to provide an output in the range of 32 mW \[29\].

### 6.5 Green Emission

We were able to blueshift the emission from red to green using our intermixing technique. The number of annealing cycles reached 18-20. It was difficult to maintain a good surface of the laser structure after this number of cycles. Despite this limitation, we managed to produce such devices. The output power was relatively low. Beside the difficulties faced by yellow devices, green devices have a relatively high Al content. Referring to Figure 3.8, the Al content is approximately 0.5. With such an Al content, the quaternary is very close to the $\Gamma - X$ crossover. Figures 6.15(a) and 6.15(b) show images of the green devices under electrical pumping. The emission is
very dim.

Figure 6.15: Images of intermixed laser structures from 635 nm to (a) 555nm (real green) and (b) 565 nm (yellowish green)
6.6 Conclusion

In this work, we used the QWI technique to blueshift the emission of the red laser devices. We have noticed improvements in the devices performance in terms of PL strength and threshold current when the intermixing degree is low. With higher intermixing, the degree the performance of the devices deteriorates. We were able to demonstrate the first laser diode emitting at 608 nm. We were able to create a relatively efficient edge-emitting yellow LED from the laser structure. Finally, we have green electro-luminescence from the AlGaInP material system. We killed two birds with one stone, we achieved the ability to reduce the wavelength and provide better performance. We improved and intermixed the operational devices. The technique may represent the solution for achieving high efficiency AlGaInP devices at the shorter wavelength of yellow and orange and has potential application for making passive sections like the non-absorbing window in the InGaP/InAlGaP material system.
Chapter 7

Reduction of Oxygen-Related Defects In AlGaInP Structure

In this chapter we investigate the effect of annealing on oxygen related defects. increasing the Al content in the active layer by intermixing and the effect on the efficiency. The study was applied to edge-emitting lasers, however, the results are related to the quaternary, AlGaInP and hence other structures, such as the LEDs and VCSELs which will have similar results.

7.1 Increasing Al In AlGaInP QWs

7.1.1 Increasing Al by Growth

To understand the problem why Al-rich active layer have low efficiency, We need to discuss the concept of deep level-traps and why do they increase when Al content is increased. What is the origin of this problem. Why it can’t be solved by both growth methods.
What are Deep-Level Traps?

Deep-level centers are one of the nonradiative recombination centers in semiconductors. A nonradiative recombination process is one that does not involve emission of a photon. There are three types of nonradiative recombination processes due to the defects. As shown in Figure 7.1(a), the defects that are created during growth are crystal imperfections or point defects. Such defects may give rise to a continuum of states in the band gap joining the conduction band to the valence band. Electrons and holes may recombine in a nonradiative manner. Figure 7.1(b) shows a discrete deep level in the band gap. Recombination through a deep-level trap may be nonradiative and may be accompanied by photon emission with lower energy than that of the band gap. Figure 7.1(c) shows the surface state nonradiative recombination. On the surface of a semiconductor there is usually dangling bonds and impurities from the ambient forming energy levels in the mid-band gap [3 77].

The presence of oxygen atoms in the semiconductor as contamination create deep-level traps. Because the deep-level traps form non-radiative recombination centers. They block some of the carrier from getting recombined and hence reduce the PL intensity of the EL. The recombination through a single deep-level trap in the band gap consists of four steps: 1-electron capture, 2-electron emission, 3-hole capture, and
4-hole emission, as shown in Figure 7.2 [3]. It was also found, the density of these traps increases exponentially when density oxygen atoms increase. Therefore, the more Al content in active layer of the quaternary AlGaInP the less efficient it is. The presence of oxygen atoms during growth creates such deep-levels in the quaternary, AlGaInP [24,78].

![Figure 7.2: Recombination steps that occurs during electrical pumping of an active layer with deep-level traps [3]](image)

**Oxygen-Related Defects Problem**

All AlGaInP-based optoelectronic devices emitting in the green, yellow and orange visible range suffer from low internal quantum efficiency [8], constituting the green-gap. Hence, commercial LDs in the wavelength range of 530 nm to 630 nm are largely inefficient or unavailable, although low-efficiency LEDs are currently produced in this visible spectral region. The InAlGaP QWs containing low Al content, or Al-free, are the dominant III-V quaternary/ternary alloys used for the growth of efficient optoelectronic devices in the visible spectrum towards the red wavelength regime. Currently, the available commercial LDs have the shortest emission wavelength at 630 nm, while the shortest reported wavelength by growth is at 615 nm, with Al content $y=0.1$ [39]. The band gap of the $\text{In}_y(\text{Al}_x\text{Ga}_{1-x})_{1-y}\text{P}$ QW can be tuned by
controlling the Al content (x). However, introducing Al into the active region by the usual growth methods, such as metal-organic chemical vapor deposition (MOCVD), or molecular beam epitaxy (MBE), is accompanied by a reduction in efficiency. As a result, LEDs emitting in the yellow range utilizing Al-rich QWs typically have 30 to 50 QW stacks, and special fabrication techniques are utilized to improve light extraction [71]. The low efficiency problem in Al-rich active layer comes from the chemical property of Al atoms. Al atoms are very reactive. During growth process, Al atoms react with oxygen atoms in the background of the growth process. The contamination of oxygen leads to oxygen-related DX-centers, forming deep level traps in the QW, and thus increasing the non-radiative recombination centers and compromising radiative efficiency, which can be aggravated with increasing incorporation of Al [5]. Although growth at elevated temperatures may lead to reduced oxygen-related defects, the elevated growth temperature beyond 780 °C does not favor In incorporation due to significant In evaporation [2], degrading the surface morphology [79]. These inevitable effects are the main obstacles in realizing the orange and yellow LDs using the InAlGaP alloy [29]. The problem exist for MBE and MOCVD growth. Figure Increasing the Al content by MBE or MOVPE has the problem of incorporating more oxygen atoms. As Al content is increased, as shown in Figure [7.3], the PL intensity decreases [5, 38].
In that work, they increased the Al content by growth and measured the PL intensity. The results show clearly how the PL intensity decreases exponentially as the Al content is increased.

### 7.1.2 Increasing Al by QWI

Now we know the problem of increasing Al by growth. We have already shown orange lasing and efficient yellow LED from our process, as in Figure 7.4.

In our approach, instead of increasing Al during epitaxy growth, we employ QWI to achieve more Al driven into the InGaP QWs, thus inter-diffusing elements among the barriers and QWs, while achieving a blueshift in the emission wavelength, as shown in Figure 7.5.

Eventhough, the diffusion can be used to accurately calculate the change in wavelength. We preffered to use a simple calculation approach that assumes an effective concentration of Al and Ga after intermixing of a QW with same dimension of as-grown QW. Figure 7.6 shows the calculated wavelength of a 6 nm thick SQW laser structure. We took into account the strain, quantum confinement and composition.

We can use this curve to estimate the Al composition in SQW after the QWI
Figure 7.4: Efficient Devices from QWI at orange and yellow visible range

Figure 7.5: Illustration of QWI as a method to increase the Al content in the QW
Figure 7.6: Estimated diffusion as the peak emission changes due to the intermixing process. For example, a peak emission at 600 nm means the Al content in the QW is 0.2. Similarly, an emission of 580 nm means the Al content in the active layer reached 0.3. Figure 7.7(a) shows the PL signals of intermixed samples with estimated Al content. Figure 7.7(b) shows images of the fabricated devices with estimated Al content.
Figure 7.7: (a) Room temperature PL signal of laser sample after increasing Al mole fraction in SQW. (b) Images of fabricated LDs with Al content increased by intermixing. The indicated Al content was estimated by calculations and PL peak emission was measured.
7.2 Annealing Al-free QWs

7.2.1 Design of Al-free Structures Intermixed

For this study, we used the results from the SQW laser structure and we applied the QWI on a MQW laser structure (Figure 7.8). We believe that increasing the number of QWs will improve the gain of the intermixed device so that it can overcome the losses and defects created and hence, yellow lasing is achieved. Unfortunately, the MOCVD grown wafers were not working properly as devices and because of the lack of time, we could not use them to fabricate intermixed LDs. Anyhow, we have used the structure as a PL structure to see the effect on intermixing on the MQW laser structure. We had doubts that MQW intermixing process will be more difficult than SQW as the barriers are different in this design.

Figure 7.8: (a) SQW Laser structure and (b) MQW laser structure used in the intermixing process
7.2.2 Results

Figures 7.9(a) and 7.9(b) show the PL signals of SQW and MQW laser samples intermixed to have blueshifts of 10nm, 15nm and 30 nm. From these blueshifts, the composition of Al can be estimated by calculation. The PL intensity of the intermixed samples are much stronger than the As-grown samples. The increase in PL signal means there is an improvement in the quantum efficiency of the QW.

Figure 7.9: The PL signals of intermixed LD structures. (a) SQW LD structures, (b) MQW LD structures. A huge increase is gained when Al is increased by diffusion for SQW an MQW
Figure 7.10 shows the effect of increasing the Al content by diffusion. We normalized the intensities with As-grown devices. For a small increase in Al, there is a huge increase in the PL intensity. As we increase the Al by diffusion more than 0.1, the intensity starts to drop. The drop in intensity can be explained by the increase in defects introduced by QWI. The same procedure was performed for the SQW laser structure and similar behavior is noticed. However, when we compare it to growth, Increasing the amount of Al by growth causes the PL intensity to drop significantly due to the increase of deep-level traps [5].

![Graph showing PL intensity vs. Al content](image)

Figure 7.10: The PL intensity AlGaInP laser structure versus increment of Al content. As the Al is increased by growth PL intensity drops rapidly while a huge increase is gained when Al is increased by diffusion for SQW an MQW.
7.3 Annealing Al-rich QWs

The main problem that have prevented orange and yellow Al-rich active layer from lasing is the oxygen-related defects. We have noticed that, Annealing have two effects on the PL signal. It can increase the PL intensity significantly as we have seen in section 6.3. The PL s was increased by 10 folds. Annealing can also, cause the PL signal to be blueshifted due to intermixing. Now, if we are interested in having orange and yellow lasers, why don’t we start with Al-rich structure !.

During intermixing process, point defects are created causing a reduction in PL intensity. That was clear when we blueshifted the emission from red to orange, yellow and green. The idea here is to start with an as-grown structure that is Al-rich. Annealing this structure without intermixing should increase the PL intensity significantly and hence, it is the way to have lasing structures in the orange and yellow range. To test this hypothesis, and due to the lack of time, we purchased a commercial yellow LED wafers that are grown to emit at 590 nm.

7.3.1 Al-rich AlGaInP Structure

We started this time with a yellow LED structure consisting of MQW of AlGaInP/AlGaInP with p-gap layer to enhance light extraction from top and DBR mirrors to enhance reflection and reduce GaAs absorption from bottom. Samples of the yellow LED were annealed at 850 °C.

7.3.2 Experiment and Results

Similar procedure was used as before. An SiO₂ dielectric film was of 1 μm thick was deposited by PECVD on the LED structure. Three samples were prepared for annealing for different number of cycles. Annealing temperature was 950 °C and
Figure 7.11: (a) Schematic of the Al-rich AlGaInP/AlGaInP structure grown in GaAs to emit at 590 nm. (b) A plot of the PL signal of the yellow LED structure.

Annealing duration is 30 s. The dielectric film was removed by wet etching and the PL was measured. Figure 7.12 shows the PL signals of four samples. One of the sample is as-grown used as a reference and the other samples are annealed for 1, 2 and 3 cycles. The PL intensity of the annealed samples increased to 20 folds for the sample annealed for three cycles.

To investigate the reason behind this improvement in PL signal, we measured the concentration of elements in the z-direction (growth direction) using the Secondary Ion Mass Spectroscopy (SIMS). Figure 7.13 shows the reduction in GaO level and oxygen contamination levels in the structure. Which is a clear evident the annealing process reduced the oxygen-related defects in the structure.

Figure 7.14 shows microscopic images of the LED surface before and after annealing. The annealing process increases the surface roughness. To make sure the LED samples are still in having good electrical characteristics after the annealing process. We have deposited contacts on the LED structure to measure its electrical
Figure 7.12: PL signal of LED samples annealed for 1, 2 and 3 cycles at 950 °C for 30 s. The as-grown PL signal is plotted as a reference. PL intensity of increased as the number of annealing cycles increases.

characteristics.

Figure 7.15 shows a plot of the IV curve of both LED samples. Both LEDs have turn-on voltage around 2 V and the series resistance of the as-grown is approximately 2 Ω while for the annealed LED the series resistance increased to 4 Ω. Increase in the series resistance is due the increase in the roughness and outdiffusion of Ga from the contact layer as previously discussed.

Finally we compared the electroluminescence from as-grown and annealed LED sample. We connected the LED samples in parallel and pumped them together by same current source at 0.05 A DC. By connecting them together in parallel and pumping them at the same time. The difference in electroluminescence will be very clear to human eyes. Having in mind that, the resistance of the annealed sample (R2) is higher than the resistance of the as-grown which means the current that pumps the annealed sample is less than the current pumps the as-grown. Electroluminescence
Figure 7.13: SIMS measurement of P, GaO and O levels in the LED structure for as-grown and annealed LED sample. The is a reduction in GaO level which is a major contributor of oxygen-related defects and oxygen contamination while the P level is same.

Figure 7.14: Microscopic images of the LED surface before and after annealing.
Figure 7.15: IV curves of as-grown and annealed LED samples after applying front and back contacts. Turn-on voltages are the same and series resistance increased from approximately 2 Ω to 4 Ω after annealing from the annealed sample is stronger.
Figure 7.16: (a) and image of as-grown LED (D1) and annealed LED(D2) connected in parallel to the same current source of 0.05 A DC. (b) schematic diagram of the circuit with R2 greater than R1. The emission from the annealed structure is stronger due to the reduction of oxygen-related defects by annealing.

7.4 Conclusion

QWI intermixing process is well known to introduce defects to the laser structure. As a result, the intermixed devices are expected to have lower performance characteristics than As-grown. However, in the InGaP/InAlGaP material system, annealing has improved the performance of laser devices. Therefore, results can be explained if we look at the QWI as three sub-processes. The first is the creation of defects. These defects are created at the interface of the capping dielectric and the laser top surface and propagate throughout the laser structure. The point defects are created due to the difference in expansion coefficients [50]. Defects created during QWI increase the non-radiative recombination centers and also increase the optical losses for light propagation inside the structure. We believe the defects created during QWI are responsible for the increase in intermixed devices. The amount of defects can be controlled by reducing the annealing time, or reducing the applied strain. The second process is the inter-diffusion of group-III atoms between the QW and the barriers. As a result, the band gap of the QW will be blueshifted as more Al atoms diffuse into the
QW. As the temperature and time is increased, the amount of diffusion increases. The third process is the reduction of deep-level defect i.e. oxygen-related defects. Thus, the huge improvement in PL intensity with reduced FWHM, and reduced threshold current $I_{th}$ was successfully demonstrated.
Chapter 8

Conclusions

8.1 Summary

In the thesis, we introduced a repeatable quantum well intermixing on the InGaP/InAlGaP laser structure, which resulted in wavelength blueshift. This was regarded as impossible in the past. The key for our success in achieving this process was the use of a considerably thick dielectric film, at higher annealing temperature and over a longer annealing duration than previously reported. The use of cyclic annealing process allows us to maintain the surface and crystal quality throughout. We were able to intermix the constituent compositions across the well-barrier interface, to a very high degree, resulting in a large blueshift, while the fabricated devices were still functioning. With this process, we were able to demonstrate the first laser diode emitting at 608 nm (orange), which is impossible to achieve simply by exitaxy growth due to high lattice mismatch. Furthermore, we have demonstration yellow LED emitting at 583 nm, which is relatively higher performance than that reported for as-grown LEDs. As we increase the number of annealing cycles, we were able to demonstrate the first green emission ever, from the laser InGaP/InAlGaP laser structure.
By PL characterization of the intermixed samples, we observed a huge improvement in the intermixed samples. The increase in PL signal was by a factor of ten for some cases. This can only be explained by the quenching of the non-radiative recombination centers. In this material system, Al-rich active layers are inefficient and any increase in the mole fraction by more than 0.1 will stop the devices from lasing. The problem is linked to oxygen-related defects that cannot be avoided by typical growth. In our case, we have increased the Al content by more than 0.1 and yet the device was still lasing. From these results, we arrive at an alternate approach in driving Al into the quantum well while eradicates the oxygen-related deep-level defect centers.

8.2 Contribution of the Thesis

The thesis has the following significant contributions

- The first report on intermixing of the InGaP/InAlGaP laser structure.
- The large degree of intermixing enables the wavelength tuning of the QW from red to green emission.
- Intermixing process was achieved for both the MQW and SQW.
- Intermixing was achievable in QWs grown either regardless of strain conditions.
- Increasing the Al content in the QW by interdiffusion gave rise to better optical efficiency than by increasing the Al content by growth.
- Annealing laser samples to elevated temperatures without or with minimum intermixing reduces the oxygen-related defects in the structure.
8.3 Future Research Work

The research on this thesis can be extended in two directions: 1- research on the intermixing technique and 2- reduction of oxygen-related defects.

8.3.1 Research on Intermixing Process

The process of intermixing can be further enhanced and optimized. Ways to investigate are:

1. Intermixing on other quantum structures

   Research was done on QW structures only. However, the work can be extended on AlGaInP based quantum dots and quantum dash structures.

2. Different Capping

   In this thesis we have shown results for SiO$_2$ capping deposited by PECVD only. Other types of capping can be applied such as SiN$_4$, TiO$_2$ and SoG. Different thickness and different strain applied may give different results as explored on other material systems.

3. Selective Intermixing

   All the work was done on entire surface of lasers and LEDs. Selective intermixing is an important technique used before of GaAs/AlGaAs material system to have different emission from same chip. This technique can be implemented on InGaP/AlGaInP material system. For example, The non-absorbing windows is fabricated at the moment using the IID technique. The technique presented in this thesis may gave higher catastrophic optical damage current.
8.3.2 Reduction of Oxygen-related defects

1. **Yellow and Orange laser diodes**
   
   A direct extension to the thesis will be to redesign the SQW and MQW laser structures used with more Al content in the QWs. For example, 0.2 and 0.3 will emit in the orange and yellow respectively. The efficiency of the structures is low after growth. However, annealing them to reduce the oxygen-related defects will enhance the efficiency and structures may lase. Low band-offset is expected resulting in high leakage current.

   Low Band-offset between QWs and barriers at the yellow range is expected. This problem may be solved by either including multiquantum barrier concept or replacing the material in the barrier with a III-V alloy of wider band gap.

2. **Efficient LEDs in Orange, Yellow and Green.**

   The efficiency of AlGaInP optoelectronics in OIDA’s report is low. Removal of oxygen-related defects of LED structure will increase the efficiency. Specially, for the green emission which is preferred by III-N material system.

3. **VCSELs**

   The research in this thesis was done on EEL. However, similar results are expected on VCSEL structure. Having in mind, the shortest lasing from AlGaInP VCSELs is at 650 nm.

4. **Other AlGaInP-based optoelectronics**

   reduction in oxygen-related defects from AlGaInP material help in improving the performance of any optoelectronic device such as solar cells and detectors based on AlGaInP material.
APPENDICES

Appendix A:

Constants of AlGaInP Material System

The parameters of the binaries constituting the quaternary AlGaInP from [13]

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice Constant (Å)</th>
<th>Deformation Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>5.4512</td>
<td>-9.76 -1.5 -4.6</td>
</tr>
<tr>
<td>InP</td>
<td>5.8688</td>
<td>-6.16 -2.0 -5.0</td>
</tr>
<tr>
<td>AlP</td>
<td>5.4635</td>
<td>-8.38 -1.75 -4.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic Moduli (10^11 dyn/cm^2)</th>
<th>(10^-6 eV/bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>14.12 6.235 7.047</td>
<td>11.0</td>
</tr>
<tr>
<td>InP</td>
<td>10.22 5.76 4.60</td>
<td>8.5</td>
</tr>
<tr>
<td>AlP</td>
<td>13.2 6.3 6.15</td>
<td>9.75</td>
</tr>
</tbody>
</table>
Appendix B:

MATLAB Codes

1. Program (MATPAR)

This is a matlab code that loads all the parameters required for the functions in the thesis. It stores the parameters in the memory in a matrix form.

```matlab
% All Material Constants Required in the codes
% lattice constants of InP,GaP, AlP
a_GaP=5.4505; a_InP=5.8697; a_AlP=5.4572;
% a_GaP=5.4512; %a_InP=5.8688; %a_AlP=5.4635;

% Bandgap
Eg_GaP=2.26; Eg_InP=1.35; Eg_AlP=2.52;
Eo_GaP=2.78; Eo_InP=1.35; Eo_AlP=3.63;

% Refractive Index
n_GaP=3.02; n_InP=3.1; n_AlP=2.8;

% Mechanical Constants
C11_GaP=14.05e11; C12_GaP=6.20e11; C44_GaP=7.03e11;
C11_InP=10.11e11; C12_InP=5.61e11; C44_InP=4.56e11;
C11_AlP=13.30e11; C12_AlP=6.3e11; C44_AlP=6.15e11;
```
Effective masses
me_{GaP}=0.13; \quad m_{hh}\{GaP=0.79; \quad m_{lh}\{GaP=0.14;
me_{InP}=0.08; \quad m_{hh}\{InP=0.85; \quad m_{lh}\{InP=0.089;
me_{AlP}=0.22; \quad m_{hh}\{AlP=0.8; \quad m_{lh}\{AlP=0.155;

deformation potentials
dp_{a}\{GaP=-3.0; \quad dp_{b}\{GaP=-1.5;
dp_{a}\{InP=-2.9; \quad dp_{b}\{InP=-2.0;
dp_{a}\{AlP=-3.0; \quad dp_{b}\{AlP=-1.5;

% Saving parameters into a matrix to be recalled
Par=zeros(3,12);
Par(:,1)=[a\{GaP;a\{InP;a\{AlP];
Par(:,2)=[E_{GaP};E_{InP};E_{AlP}];
Par(:,3)=[E_{o}\{GaP;E_{o}\{InP;E_{o}\{AlP];
Par(:,4)=[n\{GaP;n\{InP;n\{AlP];
Par(:,5)=[C_{11}\{GaP;C_{11}\{InP;C_{11}\{AlP];
Par(:,6)=[C_{12}\{GaP;C_{12}\{InP;C_{12}\{AlP];
Par(:,7)=[C_{44}\{GaP;C_{44}\{InP;C_{44}\{AlP];
Par(:,8)=[me\{GaP;me\{InP;me\{AlP];
Par(:,9)=[m_{hh}\{GaP;m_{hh}\{InP;m_{hh}\{AlP]; \quad % effective mass of heavy hole
Par(:,10)=[m_{lh}\{GaP;m_{lh}\{InP;m_{lh}\{AlP]; \quad % effective mass of light hole
Par(:,11)=[dp_{a}\{GaP;dp_{a}\{InP;dp_{a}\{AlP]; \quad % deformation potentials a
Par(:,12)=[dp_{b}\{GaP;dp_{b}\{InP;dp_{b}\{AlP]; \quad % deformation potentials a

2. Function (IntPar(xIn,yAl,Int))

This is a function that interpolates the parameters for any given Indium composition x or Aluminum composition y. The integer represents the parameter
function IntPar=InterPar(xIn,yAl,Int)

% interpolates the parameters of GaP.P(1), InP.P(2) AlP.P(3)
MaterialConst;
%GaP.P(1), InP.P(2) AlP.P(3)
    P_InAlP=xIn*Par(2,Int)+(1-xIn)*Par(3,Int);
    P_InGaP=xIn*Par(2,Int)+(1-xIn)*Par(1,Int);
    P_InAlGaP=yAl*P_InAlP+(1-yAl)*P_InGaP;
    IntPar=P_InAlGaP;

---

3. Function(Eg_Bulk(xIn,yAl))

This is a function that calculate the band gap of bulk quaternary certain composition.

function E=Eg_Bulk(xIn,yAl)

Eg_InAlP=1.35+1.83*(1-xIn)+0.38*((1-xIn)^2);
Eg_InGaP=1.35+0.643*(1-xIn)+0.786*((1-xIn)^2);
E=(yAl+Eg_InAlP)+((1-yAl)*Eg_InGaP);

---

4. Function (QWEnergy2 (xIn,yAl,l))

This is a function that calculate the band gap of a QW given the composition and QW size

function Eg=QWEnergy2(xIn_QW,yAl_QW,l)
materialConst
% effective mass in QW given Al and In concentration
me_QW=InterPar(xIn_QW,yAl_QW,8);
mhh_QW=InterPar(xIn_QW,yAl_QW,9);
mlh_QW=InterPar(xIn_QW,yAl_QW,10);

%potential barrier
QWEg_InAlP=1.35+1.83*(1-xIn_QW)+0.38*((1-xIn_QW)^2);
QWEg_InGaP=1.35+0.643*(1-xIn_QW)+0.786*((1-xIn_QW)^2);
BulkQWEg=(yAl_QW*QWEg_InAlP)+((1-yAl_QW)*QWEg_InGaP);
Ve=BulkQWEg*0.67;
Vh=BulkQWEg*0.33;

%ground state infint well
Ee=(3.76/me_QW)*((100/l)^2)/1000;
%distance from E=0 at the bottom of the well
Ehh=(3.76/mhh_QW)*((100/l)^2)/1000;
Elh=(3.76/mlh_QW)*((100/l)^2)/1000;

% Calculate max number
nme=sqrt(Ve/Ee);
nmhh=sqrt(Vh/Ehh);
nmlh=sqrt(Vh/Elh);

%calculate adjusted energy levels ussing
Eqwe=Ee*(effectiveQW(nme))^2;
Eqwhh=Ehh*(effectiveQW(nmhh))^2;
Eqwlh=Elh*(effectiveQW(nmlh))^2;
if (Eqwhh < Eqwlh)
    Eqwh=Eqwhh;
else
    Eqwh=Eqwlh;
end

%calculate adjusted QW bandgap
Eg=BulkQWEg+Eqwe+Eqwh;
5. **Function (QWstrain)**

This function calculates the change in band gap due to strain

```matlab
function Es=QWStrain(xIn_BR,yAl_BR,xIn_QW,yAl_QW)
materialConst;

%calculate lattice constant in Barrier
a_BR=InterPar(xIn_BR,yAl_BR,1) % lattice constant
a_QW=InterPar(xIn_QW,yAl_QW,1) % lattice constant
fin=(a_QW-a_BR)/a_QW;

%Calcualte QW mechanical parameters
C11_QW=InterPar(xIn_QW,yAl_QW,5) ; % 5 C11 lattice constant
C12_QW=InterPar(xIn_QW,yAl_QW,6) ; % 6 C12 lattice constant
C44_QW=InterPar(xIn_QW,yAl_QW,7) ; % 7 C44 lattice constant

dpa_QW=InterPar(xIn_QW,yAl_QW,11) ; % 11 dpa
dpb_QW=InterPar(xIn_QW,yAl_QW,12) ; % 12 dpb

H=(((-dpa_QW)*2*(C11_QW-C12_QW))/C11_QW)*fin;

S=(((-dpb_QW)*2*(C11_QW+2*C12_QW))/C11_QW)*fin;
Es=H+S;
```

6. **Program (Diffuse)**

This program calculating QW profile after diffusion using either diffusion length or diffusion time

```matlab
clear
```
SimThick=20; \% nano meters simulation area
QW\_Thick=6; \% nano meter
dz=0.1; \% nm discretization
C\_b = 0.6 ; \% Al concentration in the barrier
C\_w = 0.0 ; \% Al concentration in the QW
z=[-SimThick/2:dz:SimThick/2];
e1=zeros(1,length(z));
e2=zeros(1,length(z));
z0=find(z==0);
zQW1=z0-(QW\_Thick/2)/dz;
zQW2=z0+(QW\_Thick/2)/dz;

C0z=C\_b*ones(1,length(z));
C=ones(1,length(z));
C0z(zQW1:zQW2)=C\_w;

\% t=[0:30:150]; \% time steps
t=1500; \% seconds

D=6e-5 ; \% D is the diffusivity
L\_D=2*sqrt(D*t); \% diffusion length
\% L\_D=1:3;
L\_D=0.2;

\textbf{for} i=1:length(z);
\hspace{1em} e1(i)= erf((QW\_Thick-2*dz*(i-z0))/(4*L\_D)); \%(4*L\_D);
\hspace{1em} e2(i)= erf((QW\_Thick+2*dz*(i-z0))/(4*L\_D)); \%(4*L\_D);
\hspace{1em} C(i)=C\_b-0.5*(C\_b-C\_w)*(e1(i)+e2(i));
\textbf{end}
hold on
plot(z,C,z,C0z);
axis([min(z) max(z) -0.1 0.7]);
grid
# Appendix C:

## Fabrication Recipes

1-This recipe is used to fix the laser sample on the carrier wafer.

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>DESCRIPTION</th>
<th>MATERIAL</th>
<th>EQUIPMENT</th>
<th>TAG</th>
<th>RECIPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cleaving</td>
<td>cleave the wafer to have the desired sample size</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 2 cleaning               | rinse in acetone/IPA
Dry by N2                                                      | 3 small beakers        | Solvent Bench             | LIT-016  | 30 s each                                  |
| 3 Insulator deposition   | deposited 200 nm of SiO2                                                       | PECVD - Oxide and Nitride | DEP-009                    | SiH4 06 sccm
N2O 850 sccm
N2 162.5 sccm
RF power 20W
Pressure 1000 mT
Table Temp 300 C
Dep Rate 63nm/minute |
| 4 spin coating carrier wafer | carrier wafer is coated by a thick photoresist to fix the sample            | Az9260                 | JST Resist Spin/Bake      | LIT-001  | recipe 3
step1
speed 300 rpm
ramp 150 rmp/s
time 3 s,
step2
speed 1500 rpm
ramp 1000 rmp/s
time 3 ,
step3
speed 2400 rpm
ramp 1500 rpm/s
time 60 s.
thickness 10 um |
| 5 align sample on carrier wafer | the sample is align on the carrier wafer parallel to the wafer line        | JST Resist Spin/Bake   | LIT-001                    |          |                                             |
| 6 carrier wafer baking   | baking to stick the sample                                                    | JST Resist Spin/Bake   | LIT-001                    | 110 C, 180 Sec |                                            |
## 2-Recipe for first lithography

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>DESCRIPTION</th>
<th>MATERIAL</th>
<th>EQUIPMENT</th>
<th>TAG</th>
<th>RECIPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>spin coating</td>
<td>Az5142</td>
<td>JST Resist Spin/Bake</td>
<td>LIT-001</td>
<td>recipe 3 step1 speed 800 rpm Ramp 1000 rmp/s time 3 s, step2 speed 1500 rpm speed 1500 rmp/s time 3, step3 speed 3000 rpm ramp 3000 rmp/s time 30 s. thickness 1.6 um</td>
</tr>
<tr>
<td>8</td>
<td>pre baking</td>
<td>JST Resist Spin/Bake</td>
<td>LIT-001</td>
<td>120” 105 C</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>UV exposure</td>
<td>Mask 1 DEV6 broadarea laser</td>
<td>EVG 6200 UV contact aligner</td>
<td>LIT-022</td>
<td>100 Watt</td>
</tr>
<tr>
<td>10</td>
<td>baking</td>
<td>JST Resist Spin/Bake</td>
<td>LIT-001</td>
<td>120” 110 C</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Flood UV exposure</td>
<td>Glass Mask or no Mask</td>
<td>EVG 6200 UV contact aligner</td>
<td>LIT-022</td>
<td>100 watt</td>
</tr>
<tr>
<td>12</td>
<td>development</td>
<td>Dev 7261 MIF</td>
<td>Base Develop Hood</td>
<td>LIT-017</td>
<td>30” only</td>
</tr>
<tr>
<td>13</td>
<td>dry etching</td>
<td>Sio2 etching</td>
<td>ICP plasma etcher</td>
<td>PE-001</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Removing PR residual</td>
<td>Sio2 etching</td>
<td>NanoPlas DBS-6000 Plasma Strip</td>
<td>LIT-013</td>
<td>Module 3, Oxygen only 1 Minute</td>
</tr>
<tr>
<td>15</td>
<td>cleaning</td>
<td>Solvent Bench</td>
<td>LIT-016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Notes
- Spin coating: Spin coat the sample for negative lithography.
- Pre baking: This step is critical for negative lithography.
- UV exposure: Unwanted areas are covered.
- Flood UV exposure: Use clear glass mask to expose all areas of the photoresist to UV light.
- Development: Remove unwanted photoresist.
- Dry etching: Remove exposed SiO2 by ICP plasma etching.
- Cleaning: Clean by acetone and IPA and dry by N2.
### 3-Recipe for second lithography

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>DESCRIPTION</th>
<th>MATERIAL</th>
<th>EQUIPMENT</th>
<th>TAG</th>
<th>RECIPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>spin coating</td>
<td>spin coat the sample Az5142 JST Resist Spin/Bake</td>
<td>LIT-001</td>
<td>1 800 1000 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 1500 1500 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3 3000 3000 30</td>
</tr>
<tr>
<td>thickness 1.6 um</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Mask alignment</td>
<td>align samples to mask2 MASK 2 DEV6 EVG 6200 UV contact aligner</td>
<td>LIT-022</td>
<td>100 mW</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>UV exposure</td>
<td>removing unwanted photoresist</td>
<td>Dev 7261 MIF Base Develop Hood</td>
<td>LIT-017</td>
<td>60 °</td>
</tr>
<tr>
<td>19</td>
<td>development</td>
<td>deposited top contact</td>
<td>Reactive sputter</td>
<td>DEP-002</td>
<td>Ti 10, Pt20 Au 250</td>
</tr>
<tr>
<td>20</td>
<td>sputtering</td>
<td>thining</td>
<td>thining paper</td>
<td>Multipe prep polisher</td>
<td>remove 150-200 um</td>
</tr>
<tr>
<td>21</td>
<td>Lift-off</td>
<td>immerse the sample in acetone until left off starts</td>
<td>Solvent Parts Clean hood</td>
<td>LIT-018</td>
<td>it may take 1 day</td>
</tr>
<tr>
<td>22</td>
<td>annealing</td>
<td>anneal to have better contact</td>
<td>Rapid Thermal Process</td>
<td>THE-005A</td>
<td>60 ° at 340 C</td>
</tr>
</tbody>
</table>

### 4-Recipe for back side preparation

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>DESCRIPTION</th>
<th>MATERIAL</th>
<th>EQUIPMENT</th>
<th>TAG</th>
<th>RECIPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>fix to thinner plate</td>
<td>using hot plate at 150 C put wax on the thinner plate then put the sample</td>
<td>Hotplate</td>
<td>Heat until wax becomes liquid</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>thinning</td>
<td>thin the back side of the sample 9 um thining paper</td>
<td>Multiprep polisher</td>
<td>remove 150-200 um</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>back contact evaporation</td>
<td>deposit back contact using evaporation</td>
<td>Ebeam evaporator</td>
<td>In 10nm Ge 10nm Au200nm</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>annealing</td>
<td>anneal to have better contact</td>
<td>Rapid Thermal Process</td>
<td>THE-005A</td>
<td>60 ° at 380 C</td>
</tr>
<tr>
<td>27</td>
<td>Laser bar cleaving</td>
<td>Cut laser bars into desired length</td>
<td>Loomis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix D:

Publications During PhD

Patents

1. B. S. Ooi, M. A. Majid, Rami Afandy and A. A. Al-Jabr, "Controlling the emission wavelength in III-V semiconductor laser diodes"

2. B. S. Ooi and A. A. Al-Jabr "Method for making Al-rich oxygen-related-defects-free active layer for optoelectronic devices" Under revision

Journal Paper

1. A. A. Al-Jabr, T. K. Ng and B. S. Ooi "Efficient Al-rich active layer for InAlGaP/InAlGaP optoelectronics" under preparation

2. A. A. Al-Jabr, M. A. Majid, T. K. Ng and B. S. Ooi "Effect of annealing InGaP/InAlGaP laser structure at 950 °C on laser characteristics" -under review Journal of Nanophotonics

3. A. A. Al-Jabr, M. A. Majid, T. K. Ng and B. S. Ooi "ed to green emitters from InGaP/InAlGaP laser structure by strain-induced quantum-well intermixing" -SPIE Proceeding


**Conferences**


2. M.A. Majid, **A. A. AL-Jabr**, Tien Khee NG, Boon S, First demonstration of orange-yellow light-emitter devices in InGaP/InAlGaP laser structure using strain-induced quantum well intermixing technique Photonics West 2016, San Francisco, USA

3. M.A. Majid, **A. A. AL-Jabr**, Tien Khee NG, Boon S First demonstration of InGaP/InAlGaP based 608nm orange laser and 583nm yellow superluminescent diode IPC2015, Virginia, USA (Presenter)


REFERENCES


[44] Y. Jang and J. Lee, “Microstructural and compositional modification of in0.53ga0.47as/in0.52al0.48as multiquantum wells using rapid thermal annealing process,” *Materials Science and Technology*, 2013.


