Chapter

Diffusion and Quantum Well Intermixing

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Abstract

Diffusion or intermixing is the movement of particles through space. It primarily occurs in every form of matter because of thermal motion. Atom diffusion and intermixing can also happen in crystalline semiconductors whereby the atoms that are diffusing and intermixing move from one side of the lattice to the adjacent one in the crystal semiconductor. Atom diffusion, which may also involve defects (including native and dopant), is at the core of processing of semiconductors. The stages involved in semiconductor processing are growth, followed by post-growth, and then the construction stage comes last. The control of every aspect of diffusion is necessary to accomplish the required goals, therefore creating a need for knowing what diffuses at any point in time. This chapter will briefly summarize the techniques that are in existence and are used to create diffused quantum wells (QWs). Also, it will outline the examples of QW semiconductor lasers and light-emitting diode (LED) by the utilization of inter-diffusion techniques and give recent examples.

Keywords: intermixing, semiconductors, diffusion, QWI, lasers, LED, intermixing techniques, inter-diffusion, fabrication

1. Introduction

The demands of device technology have yielded the primary motivation for looking over atomic diffusion, as depicted by a semiconductor lattice. Since there has been a shrinking of the devices’ physical dimensions, more problems have emerged concerning comprehending features of diffusion in more complex structures [1]. There is a link between some common problems with the deterioration of a doped structure, for instance, a superlattice or p-n junction, diffusion barrier, or a metal contact’s endurance [1–4].

Knez pointed out four diffusion situations that are separate from each other, which can crop up in the post-processing of the substrate’s surface layer. The layer can be thin like mercury telluride (HgTe) or cadmium telluride (CdTe) [4–6]. There are four different diffusion situations for the post-processing, which are the following:

Firstly, there is components’ lateral diffusion in the surface layer.
Secondly, there is surface component diffusion into the substrate (surface into substrate).
Thirdly, there is substrates’ component diffusion into the surface layer (substrate to surface).
Fourthly is the diffusion barrier stationed between the substrate and surface layer. The type of diffusion within the crystal lattice is called lattice diffusion, and it takes place by either substitutional or interstitial mechanisms. Interstitial lattice diffusion involves a diffusant like carbon in an iron combination diffusing in the middle of the lattice structure of one or more crystalline elements. On the other hand, substitutional lattice diffusion involves self-diffusion or inter-diffusion (where self-diffusion takes place in pure metals because atoms exchange location for the same type and there is no net mass transport, while inter-diffusion occurred in alloys which have net mass transport and atoms diffuse into different metals) whereby the movement of an atom is made possible by its substitution with another atom to replace it [6–10]. This diffusion is usually made possible by point vacancies’ availability all over the crystal lattice. Diffusing particles relocate fast from one vacancy point to another, basically by random jumping termed as jump diffusion, as shown in Figure 1. Considering that the regularity of point vacancies multiplies in line with the Arrhenius equation, the frequency of diffusion crystal solid state improves with temperature [11–15].

The use of inter-diffusion of quantum wells (QWs) is an emerging technology that is significant for fabricating semiconductor lasers since it improves devices’ optical and electrical properties [16]. Selective inter-diffusion is achievable by obscuring into the QW wafer’s desired regions. Since the 1980s, there have been extensive investigations regarding inter-diffusion [16, 17]. It comprises disordering or intermixing of heterostructures that are quantum-confined like QWs and quantum dots (QDs). The thorough investigations are due to its potential to achieve monolithic integration of optoelectronic/photonic devices. Among the inter-diffusion techniques, there has been a consideration of impurity-free vacancy disordering (IFVD) as the technique that is most promising for device applications because of its simplicity and causes lesser residual damage to the sample [17–19].

During inter-diffusion, there will be a resultant modification of refractive index and electrical conductivity between the regions that are as-grown together with disordered ones. The technology allows a homogenous process that leads to the enhancement of the sideways electrical and optical restraint of laser semiconductors in such a manner that the bottom threshold current, as well as single operation that is lateral mode, is obtainable. Moreover, the QW’s shape alters as a result of inter-diffusion between QWs and barriers that are next to it. In turn, there is a modification of the sub-band energy in valence and conduction bands. Eventually, the inter-band transition energy is modified. Therefore, the inter-diffusion technique could be utilize the fabrication of QW lasers and LED for multiple wavelengths without using complicated epitaxial regrowth or etching processes. Other merits of utilizing inter-diffusion techniques include one, its simplicity. And there is also compatibility with existing semiconductor lasers’ fabrication technologies [20–25].

![Figure 1](image.png)

**Figure 1.** Atomic movement that results in atomic diffusion. (a) Interstitial diffusion, (b) self-diffusion or inter-diffusion, (c) vacancy diffusion.
2. Diffusion mechanism and coefficient

For the vacancy diffusion mechanism, the probability for any atom in a solid to move is the product of the probability $P$ of finding a vacancy in an adjacent lattice site \[25, 26\]:

$$P = z \exp \left(- \frac{G_f}{K_B T} \right)$$ (1)

where $z$ is the coordination number (number of atoms adjacent to the vacancy), $G_f$ is the free energy necessary to form the defects, $T$ is the absolute temperature (K), $K_B$ is the Boltzmann constant, and the frequency of jumps (probability of thermal fluctuation needed to overcome the energy barrier for vacancy motion)

$$R_j = V_0 \exp \left(- \frac{\Delta G_m}{K_B T} \right)$$ (2)

where $R_j$ is the probability of such fluctuation or frequency of jumps, $V_0$ is an attempt frequency related to the frequency of atomic vibrations, and $G_m$ is the activation free energy for vacancy motion.

Therefore, the diffusion coefficient \[27\] is

$$D = z V_0 a^2 \exp \left(- \frac{\Delta G_m}{K_B T} \right) \exp \left(- \frac{G_f}{K_B T} \right)$$ (3)

where $a$ is the mean distance between atoms in a crystal lattice.

Eq. 3 can be rewritten as

$$D = D_0 \exp \left(- \frac{\Delta G_m - G_f}{K_B T} \right)$$ (4)

where $D_0$ is a parameter of material (both matrix and diffusing species).

Thus, the diffusion coefficient is the measure of the mobility of disusing species:

$$J = -D \left( \frac{dC}{dX} \right)$$ (5)

where $\frac{dC}{dX}$ is the concentration gradients (negative in the direction of diffusion), as shown in Figure 2.

Hence, from Eq. 5

$$D = D_0 \exp \left(- \frac{Q_d}{RT} \right)$$ (6)

where $D_0$ is the temperature-independent preexponential (m$^2$/s), $Q_d$ is the activation energy for diffusion (J/mol or eV/atom), and $R$ is the gas constant (8.31 J/mol K or 8.62 × 10$^{-5}$ eV/atom K).

By taking the logarithm for Eq. 6, we can get

$$\ln D = \ln D_0 - \frac{Q_d}{RT}$$ (7)

$$\log D = \log D_0 - \frac{Q_d}{2.3RT}$$ (8)

From Eq. 8, $Q_d$ the activation energy for diffusion and $D_0$ independent preexponential can be measured by estimating the $\log D_0$ versus $1/T$ or $\ln D_0$ versus $1/T$ as the Arrhenius plots (Figure 3). Figures 1 and 2 and Tables 1 and 2 were taken from Porter and Easterling textbook and Smithells Metals Reference Book \[1\].
Figure 2.
The slope of particular point on the concentration gradient.

Figure 3.
Arrhenius plots. $Q_d$ as the function of $D_0$, diffusion temperature dependence [1].

| Impurity   | $D_0$ (mm²/s⁻¹) | $Q_d$ (kJ/mol) |
|------------|-----------------|----------------|
| C in BCC Fe| 1.1             | 87             |
| C in FCC Fe| 23              | 138            |
| N in BCC Fe| 0.74            | 77             |
| N in FCC Fe| 0.34            | 145            |
| H in BCC Fe| 0.12            | 15             |
| H in FCC Fe| 0.63            | 43             |

Table 1.
Examples of the temperature-independent preexponential and the activation energy for diffusion of some atoms in the case of interstitial diffusion mechanism.
In Eq. 7, it seems that the vacancy diffusion mechanism is slower than interstitial diffusion, as shown in Figure 4 and Tables 1 and 2 (self-diffusion or diffusion of substitutional atoms) [28–31].

From Eq. 6, the big atoms cause more distortion and take more time to diffuse than the smaller atoms during the migration process as we can see from Tables 1 and 2. Also the diffusion is slower in a close direction and lattices.

3. Fabrication of quantum well intermixing (QWI)

The fabrication of photonic integrated circuits (PICs) by employing an integration of lasers and transparent waveguides on a single epitaxially grown substrate demands the actual understanding and definition of regions possessing different bandgap energy characters. The approach to work out a solution to this
problem can be categorized into intermixing and growth approaches. Among the growth approaches, the most popular ones are selective area growth approach and use of a plated substrate to etch-and-regrowth approach [29, 30, 32]. The former one allows for simultaneous epitaxy employing the use of different growth rates, which in turn allows for flexibility toward the growth of quantum wells with varying thicknesses [32–34]. In contrast to the former approach, the latter approach uses different quantum well thicknesses along with subsequent growth of material. Using impurities or vacancies toward the selective partial intermixing of quantum wells provides an alternative approach. The change in the shape of quantum well and thus the transition energies associated occur due to the intermixing of barrier material and quantum well material, which happens during a high-temperature annealing. The capability to identify and define regions that are not to be intermixed and which are to be intermixed acts as the key factor to the viability of the QWI approach. Intermixing method that does not demand epitaxial regrowth is identified to be more cost-effective and potentially simpler [35]. This is the main advantage of the intermixing method. In the following, the means of patterning non-intermixed and intermixed regions along with several QWI approaches are described.

4. Techniques utilized for QW intermixing

There are three techniques of inter-diffusion that are in existence and are widely used. These are the inter-diffusion that is impurity-induced disordering (IID), vacancy diffusion that is IFVD, and laser-assisted disordering (LAD) laser-induced QW intermixing. The first technique uses impurities to accomplish inter-diffusion for the considerable alteration in electrical conductivity and refractive index. Its common utilization is in achieving sideways optical and electrical confinement in semiconductor lasers. In contrast, IFVD does not involve impurities in obtaining inter-diffusion such that there is the conservation of the electrical properties of the diffused QWs. Its typical use is in fabricating tuning LAD technique that has been tested and developed in the last three decades. This method is based on the direct writing of the laser beam into the structure [36–38].

5. Intermixing types and history

Impurity-induced layer disordering (IILD) was the first quantum well intermixing technique to be ever demonstrated. In 1981, the affirmation of disordering of an AlAs-GaAs superlattice employing Zn (Zinc) as the active species was carried out by Laidig et al. [33, 34, 39]. In this affirmation, thermal annealing for several hours was conducted at a temperature of 600°C. As a result, it was identified that in a superlattice, different grades of intermixing can occur according to the anneal conditions used. The fabrication of lasers with emission wavelength (blue shifted) was conducted in 1983 employing this technique [33]. In 1984, it was made possible to laterally define the waveguide of a buried heterostructure employing stripe geometry QW laser devices using IILD [35, 40]. A year after, the first QW laser utilizing transparent facet windows was developed using IILD [33, 41, 42]. The refining of the intermixing method has been happening since then and has currently transformed into one of the best methods which are understood and employed in many commercial products; the most prominent of these includes high-power semiconductor lasers integrated with disordered facet windows. It should be noted that ion implantation can be utilized instead
of incorporating impurities (impurities include Si, Mg, or Zn) into the lattice utilizing the process of diffusion. Ion implantation possesses the primary benefit of not automatically incorporating heavy p-type or n-type doping while introducing the reactive species and of having a larger variety of species made available. On the flip side, high implant energies utilized have been identified to cause crystal damage which is not easily removable as in the case with other material systems (e.g., Si material systems). Both of the intermixing processes discussed above rely on the use of impurity atoms to intensify the Al-Ga self-diffusion process by employing different mechanisms. Although discussions and debates still exist around the exact nature relating to the process of intermixing, several experiments and authors have confirmed the unquestionable role of column-III vacancies and column-III interstitial types. A decade ago, methods such as VED, which are impurity-free intermixing methods, gained their popularity since they offered the possibility of intermixing without employing the doping process which prevent the absorption of the free carrier and without crystal damage created by implantation which would, on the other hand, be responsible for scattering loss. An As-rich ambient in a quartz ampoule was employed in the first experiments to prevent crystal surface damage by arsenic out-diffusion [36, 37]. In 1988, the use of an evaporated SiO$_2$ encapsulant in order to improve the intermixing process was first demonstrated [38]. Soon after, the process of generating vacancies and thus supporting the process of intermixing became possible by employing other dielectrics such as SiON or SiN. In 1993, fluorides (such as SrF or AlF) were identified to prevent QWI in a more effective manner [39]. Essential for the development of optoelectronic devices and instruments, these materials identified allowed for the definition of a certain pattern with dissimilar bandgap energies.

The IILD process makes use of an Ar-based laser beam that is very highly focused in nature. To develop the AlGaAs-GaAs DFQW, the beam of laser marking a wavelength measurement of 488 nanometers (nm) is used to scan the sample which is heterostructure in nature and is also enclosed using a layer of Si-Si$_3$N$_4$, which is approximately 90 nm in thickness. The speed of scan employing the laser beam could be marked up to the highest value of 85 pds. The area in which the laser beam interacts will develop an enhanced cylindrical segment identifiable to the range of microns. The process of annealing is then initiated in order to guide the silicon into the required crystal, which will result in the local intermixing of the layers of crystal. On the other hand, to selectively intermix GaInAs over GaInAsP quantum well structure, pulsed photo-absorption-induced disordering (PAID) technique is employed, which was deliberated employing the utilization of time-resolved photoluminescence of high spatial resolution. As a consequence of the above-said process of intermixing, a reduction of approximately two orders of measure in the time of non-radioactive recombination was achieved, which was confirmed from the measurements conducted.

Impurity-induced, impurity-free (dielectric cap), implantation-induced, and laser-induced techniques are some of the QWI techniques that have been advanced. Out of these techniques, the use of impurity-free techniques is strongly advised since optical absorption occurs as a result of the process that the semiconductor waveguide being instituted to dopants which are electrically active in nature. In order to develop vacancies on the group III lattice site, the impurity-free vacancy disordering (IFVD) technique employs the utilization of dielectric caps, which are placed on the semiconductor’s exterior surface [3, 7]. The vacancies happen to diffuse through the surface of the semiconductor resulting in solitary atoms bouncing among different lattice sites. Resultantly, it is found that the quantum well intermixes with the adjoining barrier material [34].
6. QW intermixing in industries

From the development of individually addressable laser arrays of higher density to laser-based products within extreme power ranges, monolithic integration platform which is highly innovative and known as quantum well intermixing (QWI) is reshaping methods in which laser diodes are used to solve the ever-increasing optoelectronic requirements. This is particularly important since laser systems which are QWI-enabled are found to deliver far better performance characteristics in factors of power output, luminosity, yield, and dependability.

The QWI is utilized to develop passive waveguides to the interior of the laser cavities adjoining to each facet. It is identified that excellent electro-optical performance is achieved owing to the incorporation of the passive waveguides, especially referring to high-power, single-mode function. An idiosyncratic attribute of this approach is that it allows for the mass production of huge numbers of lasers in parallel, on the very same chip, with very superior efficiency since the passive waveguides are adequately long enough to relax mechanical-related cleaving tolerances. The QWI technologies can be largely employed in many other applications, owing to their farthest versatility. Some of the areas in which the extremely versatile nature of the QWI technology could be utilized to its maximum potential include monolithic photonic integrated circuits (PICs) and in the comprehension of the broad area and stack lasers which provide atypical high-power characteristics and dependability. PICs mainly find their application in broadband optical systems, optoelectronic signal processing systems, microwave photonics, and biophotonics.

QWI gains its importance since it is an integration technique that permits the tampering of the properties of a semiconductor quantum well structure, after its growth. The quantum well intermixing technique combines active and passive components on the very same chip. To manufacture complex laser diodes, laser diode array systems, and photonic integrated circuits (PICs) in a manufacturing environment, intense proprietary QWI technology is utilized. The result of this process is the development of next-generation laser technology which can easily be utilized for a variety of applications [31, 41, 42].

The evolution of the next-generation systems is driven today by the latest innovations in laser diode technology. Intense is providing laser products with far better brightness, improved lifetimes, and increased dependability by employing modernized semiconductor design and patented QWI technology. The ways in which lasers are providing viable solutions to mission-critical problems are revolutionized by the quantum well intermixing method developed by the company, innovatively by producing integrated chips at efficient levels and yields which was unidentified in the industry before.

7. Real applications and fabrication using QWI

In this section, we will summarize some of the laser and light-emitting diode (LED) QWI applications that have been fabricated and tested by our group at the University of Central Florida (UCF) cleanroom facility [14, 43]. These experiments will show the important role of the intermixing and how it can be used for the integrated devices. We will start with the laser followed by the LED.

7.1 Laser diodes

When quickly heated at higher degrees and topped using SiNx and SiOxNy films of various constitutions, quantum well frameworks InGaAsP are interlinked to
different degrees. Laser diodes are fabricated with shifted samples of both blue and red, and their output is recorded.

Selective area mixing of semiconductor-based multiple quantum wells (MQWs) could be considered a crucial strategy toward the development of consolidated optoelectronic circuits and instruments. The bandgap energy of the substance can be controlled with stability over a wide spectral range by monitoring the intensity of the intermixing process. The lasers generated on a single monolithic substrate may, therefore, have wavelengths of output which differ widely. The correct combination of the encrusted films may vary the wavelength to either blue or red. The narrow-field semiconductor regrowth procedures have not been very successful in repeatedly producing high-yielding optoelectronic products. Others have documented many techniques for the after-growth combination of QW. In the analysis, we selected a method of induced disorder by impurity-free vacancy that works by rapid thermal annealing (RTA) of QW specimen coated by SiNₓ or SiOᵧNₓ. The range of intermingling could be precisely controlled by changing the dielectric layer capping constitution. Employing this method, we were able to manufacture multiple lasers using a single sample of the InGaAsP multiple quantum well framework, which has been covered by various SiOᵧNₓ configurations in different parts and annealed at 800°C for 30 s. Slope efficiencies, threshold currents, and laser diodes that are manufactured in the separate section are then carefully defined based on their lasing wavelengths. Such output properties are then juxtaposed with that of the laser diode made employing the primary as-grown multiple quantum well specimen as shown in Figure 5 [14, 17, 32, 40, 41].

7.1.1 Result

Increasing the ratio between NH₃ and SiH₄ to N₂O during the SiOᵧNₓ film growth has been found to result in a higher refractive index. It is noted that wavelengths (lasing) of the instruments manufactured on intermixed specimens are identified to be shifted to lower frequencies (red shift). At the same time, the capping film refractive index throughout RTA is higher than the value of 1.95 (refractive index). In comparison, the instruments covered with films having a refractive index lower than 1.95 in value show lasting wavelengths changed blue to higher frequencies. Accordingly, the absolute value of the laser spectrum is experiencing a red shift with a larger ratio in SiNₓ film and blue shift with a smaller ratio in SiOᵧNₓ film as shown in Figure 6.

Laser diode made from an as-grown multiple quantum well specimen acted as a base standard and is identified to have a lasing wavelength of 1556 nm. In Figure 7, all the fabricated laser diodes are shown with the accompanying spectra. The
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Figure 6. The absolute values of all lasers’ spectrum as a value of the refractive index of the film for different capping layer combinations. The blue shift is associated with SiO\textsubscript{x}N\textsubscript{y} films, while the red shift is associated with SiN\textsubscript{x}.

Figure 7. Laser spectrum of all fabricated devices. It shows the blue and red shifted from the as-grown ones. This figure is taken from [14].

The highest blue-shifted wavelength of laser noted is 1392 nm (164 nm change compared to as-grown laser), and 1687 nm (131 nm change as compared to as-grown laser) is the most excellent noted red-shifted wavelength of the laser. Throughout this review, it is discovered that the laser light is not emitted by a system manufactured utilizing a noncapped RTA manufactured multiple quantum well sample. Thus, uncapped regions of the MQW specimen were found to have sustained irreparable harm during thermal annealing [14].

Figure 8 shows the output power curve (L-I curve) for all intermixed laser devices. The laser that fabricated using the most intermixed MQWs had the lowest output power, while the as-grown laser diode has the highest output power. Therefore, as we intermixed more, we create more losses that affect the device efficiency.

7.2 LED and modulators on InGaAsP

Using a controllable technique for the red and blue shifting of bandgap energy of the quantum well, we were able to develop LED sources that reach a broad
frequency spectrum along with all-optical modulator intensity instruments. Through using an impurity-free vacancy diffusion method, they show bandgap adjustment of multiple quantum well structures of InGaAsP. By utilizing SiO$_2$, SiO$_x$N$_y$, and SiN$_x$ capping layers, and by regulating the related oxygen and nitrogen
content, a significant modification of the bandgap energy toward the red and blue portions of the spectrum is identified. The subsequent degree of tuning, with band-to-band wavelength emissions of up to 120 nm red shift and 140 nm blue shift, was analyzed using photoluminescence at room temperature, following the emission spectra acquired from LED semiconductor instruments manufactured on this framework. The intensity modulator instruments are made along with compatible LED sources for the chosen frequency, designed to achieve minimal material losses and modulation of residual amplitude as shown in Figure 9 [43].

The fabricated LED has been integrated with transparent intensity modulator as shown in Figure 10. The intensity modulator is based on a Mach-Zehnder
interferometer (MZI) where the phase control is achieved by injecting electrons into the core of the waveguide.

As the light source from the LED passes through the MM-MZI device, the outpower changes. The result has been recorded and evaluated as the function of the passing current as shown in Figure 11.

8. Conclusion

In this chapter, we have studied and compared the different methods for diffusion of atoms into both surface and internal layers. Also, we have shown the variety of QWIs that change and modify the refractive index and energy bandgap of QW’s structures. There are several QWI techniques accessible, and each technique has specific characteristics that are useful under various circumstances. Very likely, more than one process will be used to produce a semiconductor chip. Among the techniques used for this purpose, owing to their capacity to preserve the electrical properties of the QW structure and its strong selectivity throughout the spatial domain, triggered disordering of MQWs by using impurity-free vacancy diffusion process gained much interest. A selective area QWI procedure is used that includes vacancy diffusion via the fast-thermal strengthening of the sample which is capped by silicon dioxide or different silicon oxynitride coatings. Prior to the fast-thermal annealing of the specimen, it is identified that the bandgap energy of the intermixed QW system can be efficiently managed by varying the dielectric capping film composition. As an illustration, for laser, we displayed the implications of intermixing of laser diodes based on InGaAsP QWs. By adjusting the proportion of mixed films, it was possible to adjust the lasing wavelength to the red or blue shift regions. Using an impurity-free vacancy diffusion method, we illustrated bandgap adjustment of several quantum well structures of InGaAsP, which was then used for the LED applications. By utilizing SiO$_2$, SiO$_y$N$_x$, and SiN$_x$ capping films and by regulating the corresponding oxygen and nitrogen levels, a significant alteration of the bandgap energy toward the red and blue segments of the spectrum was achieved. The resultant level of adjustment was noted, red shift up to 120 nm and band-to-band blue shift of 140 nm.

Acknowledgements

I want to give special thanks to my professor and advisor Prof. Patrick Lickamwa for his help and advice through all my PhD. Also, I would like to thank UCF and CREOL for letting me use their cleanroom facility. Finally, many thanks go to King Abdulaziz City for Science and Technology for their supports.
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