

IMPURITY-FREE QUANTUM WELL INTERMIXING FOR HIGH-POWER LASER DIODES

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POWER LASER DIODES

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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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M.S. in Physics

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The demand for ever higher powers and efficiencies from semiconductor lasers, continues. State-of-the-art high power lasers require not only sophisticated designs but also complex fabrication technologies to push the boundaries. A major obstacle to ever higher powers is catastrophic optical mirror damage that occurs at the mirrors of the cavity. Among several approaches to increase the threshold for damage, local manipulation of the band gap near the mirrors stands out, as it eliminates reabsorption. The structure of modern lasers employing quantum wells surrounded by large band gap and low index claddings gives the opportunity to intermix the quantum well and increase the effective band gap close to cavity edges during fabrication. The research presented in this thesis reports the results of Impurity-Free Vacancy Disorder (IFVD) of GaAs quantum wells in high power laser diode structures that leads to blue shifting of the effective band gap. In contrast with previous work, this study concentrates on actual large optical cavity (LOC) high power laser diode structures where the waveguide and cladding layers are thick. Using selective area QWI can be extremely beneficial in terms of enhancing catastrophic optical mirror damage (COMD) threshold, spatial mode instability, propagation losses and overheating which are the main limitations to fabricate HPLDs. In the course of the fabrication of HPLDs, the last and most problematic step is to manage QWI. IFVD was realized by capping the crystal surface with a sputtered dielectric layer of SiO_2 to enhance intermixing and thermally evaporated SrF_2 to prevent intermixing for selected parts of the laser cavity. Disorder the layers takes place by diffusion of Ga atoms from GaAs QW into sputtered SiO_2 layer during rapid thermal annealing (RTA), leaving Ga vacancies in QW. It allows the Ga vacancy defects free to move $Al_xGa_{1-x}As$ layers providing interstitial Al atoms to move into QW. The results were monitored using low temperature photoluminescence spectroscopy to determine the shift in

the photoluminescence peak. Relative composition in the layers that make up the laser structure was measured with X-ray photoelectron spectroscopy in conjunction with depth profiling. A blue shift of 65 nm (154 meV) was achieved, in parallel with both Ga and Al diffusion in the laser structure.

Keywords: Quantum well, High-power laser diode, Quantum well intermixing, Impurity-free vacancy disordering, photoluminescence.

ÖZET

YÜKSEK GÜÇLÜ LAZER DİYOTLAR İÇİN SAFSIZLIK ATOMU OLMAĐAN KUANTUM KUYULARINI BİRBİRİNE KARIŐTIRMA

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Daha güçlü ve verimli yarıiletken lazerlere olan talep artarak sürmektedir. Modern yüksek güçlü lazerler, güç ve verim sınırlarını zorlamak için sadece sofistike tasarımlara değil aynı zamanda karmaşık üretim teknolojilerine ihtiyaç duymaktadır. Daha yüksek güçler için en büyük engel kavitenin aynalarında meydana gelen yıkıcı optik ayna hasarıdır (YOAĐ). Bu hasar eşiğini artırmak için çeşitli çözümler arasından, aynaların yanında bölgesel manipulasyon işlemi, yeniden optik soğurma olayını ortadan kaldırdığından dikkat çekmektedir. Etrafı geniş bant aralığı ve küçük kırılma indisli yeleklere sahip kuantum kuyuları kullanan modern lazer yapıları, üretim sırasında kavite kenarlarında kuantum kuyusunu birbirine karıştırmak (KKBK) ve etkin bant aralığını artırmak için uygun bir yapıya sahiptir. Bu tezdeki çalışma, GaAs kuantum kuyuları ile kuyu engellerinin safsızlık atomları olmadan boşluklarla düzensizleştirme (SAOBD) yaparak etkin bant aralığının maviye kaymasına sebep olması ile ilgilidir. Daha önceki işlerin aksine, bu çalışma dalga kılavuzu ve yelek tabakalarının kalın olduğu gerçek geniş optik kaviteli yüksek güçlü lazer diyotlara konsantre olmuştur. Bölgesel KKBK kullanımı YOAĐ eşiğini artırmak, uzaysal mod kararsızlığı, ilerleme kayıpları ve aşırı ısınma gibi yüksek güçlü lazer diyot (YGLD) üretimini sınırlayan ana sebepler açısından son derece faydalı olabilir. YGLD üretimi sırasında, en son ve en problemli basamak KKBK işlemini gerçekleştirmektir. SAOBD, birbirine karıştırmayı, artırmak için kristal yüzeyine sıçratılmış SiO_2 , lazer kavitesinin seçili bölgelerinde engellemek için termal buharlaştırma işlemiyle SrF_2 kaplayarak gerçekleştirilir. Tabakaları düzensizleştirme, hızlı ısı tavlama sırasında (HTT) kuantum kuyusunda Ga boşlukları bırakarak GaAs kuantum kuyusundan Ga atomlarının sıçratılmış SiO_2 tabakasına difüz etmesi ile gerçekleşir. Bu olay, ara yüzeydeki Al atomlarının kuantum kuyusuna girmesine

olarak sağlayarak, Ga boşluk kusurlarının serbestçe $Al_xGa_{1-x}As$ tabakalarına doğru hareket etmesini sağlar. Fotolüminesans pikindeki kaymayı saptamak için düşük sıcaklıklarda fotolüminesans spektroskopisi kullanıldı. Lazer yapısını oluşturan tabakalardaki göreceli bileşim derinlik profile, bu iş için uygun bir yöntem olan X-ışını fotoelektron spektroskopisi ile ölçüldü. Hem Ga hem Al difüzyonuna paralel olarak, 65 nm (154meV) maviye kayma elde edildi.

Anahtar sözcükler: Kuantum kuyusu, Yüksek güçlü laser diyot, safsızlık atomu olmadan boşluk düzensizleştirilmesi, fotolüminesans.

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Chapter 1

Introduction

In the quest to design and fabricate semiconductor lasers with ever higher optical powers many obstacles need to be overcome. These lasers are used in many applications where compact coherent light sources with high efficiencies are required. Semiconductor lasers in 800-1000 nm region of the electromagnetic spectrum are particularly suited for optical pumping of solid state and fiber lasers. Such lasers are usually offered as single emitters or an array of single emitters on the same semiconductor chip, called laser bars. Typical high power semiconductor employs a single quantum well (GaAs or InGaAs) embedded into an undoped waveguide layer (AlGaAs) which is sandwiched between doped cladding layers (AlGaAs). Typically the device is fabricated into a 100 μm wide ridge waveguide with appropriate electrical contacts and the cavity length varies between 2-4 mm. Such devices are electrically pumped and exhibit high external quantum efficiency. Current commercial values are at 55 percent EQE (External quantum efficiency) with optical powers obtained from single emitters reaching 15 W.

Many factors limit higher efficiencies and optical powers. Among them, is the quality (defect free) of the epitaxial layer growth to reduce nonradiative carrier recombination, removal of excess heat with appropriate packaging, and reabsorption of generated light, in particular at the output mirrors. At high powers, light absorbed or scattered at the mirrors leads to catastrophic optical mirror damage,

limiting the optical power output. To alleviate the problem, surface passivation techniques are used to minimize defects, impurities and in particular unwanted oxide complexes at the semiconductor/multilayer coated mirror interfaces. Alternatively, one could also seek to widen the semiconductor band gap close to mirror area and eliminate optical absorption at the mirror interface. This may be accomplished by changing the composition of the quantum well. However, once grown, it is not easy to change the composition of the quantum well, locally.

Defect induced interdiffusion of atoms modifying the composition of interfaces and adjacent layers can be used to intermix quantum wells. Increasing the local defect concentration, and providing the environment for their mobility is critical for control of compositional modification. Starting with as grown, ideally sharp interfaces defining the quantum well into a square compositional profile, diffusion of selected atoms in or out of the quantum well layer is needed. Among atoms that make up such structures, Ga is notable for its fast diffusion characteristics. Generating point defects on the surface, and allowing them to migrate into the depths of the epitaxial layers, will enhance the diffusion of Ga atoms. In the case of GaAs quantum wells, Ga migration from quantum well to the surface will result in the diffusion of Al atoms from the cladding layers into the GaAs quantum well thereby changing both composition and profile of the quantum well, which modifies the quantum well potential. Introduction of Al into GaAs quantum well leads to an AlGaAs quantum well upon quantum well intermixing (QWI), which increases the band gap leading to a blue shift. Thus application of local QWI at both ends of the laser cavity extending to the mirrors will widen the band gap at the mirrors eliminating reabsorption of light generated in the quantum well increasing the threshold for catastrophic optical damage at the mirrors.

Semiconductor lasers or laser diodes has become significant part of modern technology by virtue of advances in last four decades. They are the key technology that revolutionize the laser industry. They are used in wide range of applications, such as laser pointers, CD drivers and optical fiber communication systems. Today, however, they are mainly used to pump multi-kilowatt solid-state laser systems as well. Fiber-coupled diode laser systems can reach up to 15 kW in a 1.0 mm fiber [35]. There are great variety of laser diodes, such as

high-power laser diodes (HPLDs) in the 8xx and 9xx nm region, vertical-cavity surface emitting lasers (VCSELs), quantum cascade lasers (QCLs), etc. operating at variety of wavelengths extending from UV to mid- and far-infrared [15].

This thesis focuses on the problematic and important fabrication step of innovative HPLDs, which is the QWI technique for increasing the band gap energy at the laser cavity mirrors leading to non-absorbing mirror (NAM) regions. Accumulation of a large number of photons leads to non-radiative emission which results in facet degradation and is called catastrophic optical mirror damage (COMD). NAM technology is utilized for increasing the COMD threshold, e.g. COMD threshold from a ridge waveguide laser has been increased by a factor 2.6 in comparison using standard laser with NAMs obtained by QWI [16].

Interdiffusion leading to QWI can be induced in different ways. Impurity induced layer disordering (IILD) requires additive use of impurity atoms such as Zn or Si to facilitate disordering leading to interdiffusion [1]. Introduction of impurity atoms complicate the physical model with additional possibilities of effects that may lead to unwanted doping of layers as well as formation of new alloys. Alternatively impurity free vacancy disordering (IFVD) may be used [1]. In this work, IFVD was studied as the most practical QWI technique. IFVD is the most applicable method because it is not a impurity induced process, therefore material resistivity and trap concentrations changes and the residual damages which reduce device lifetimes are eliminated [1].

The most common IFVD method is based on diffusion of Ga vacancies (V_{Ga}) in, for example, (Al)GaAs quantum well laser structures. In general, SiO_2 is sputtered on the as-grown laser structure generating point defects. SiO_2 is also a good absorber of Ga atoms (from GaAs cap layer of laser structure) during rapid thermal annealing (RTA) at 800 – 1000°C. Out-diffusion of these Ga atoms from GaAs layers results in diffusion of V_{Ga} into GaAs quantum well stimulating the intermixing between AlGaAs-GaAs quantum barrier (cladding) and well via Al-Ga self-diffusion. Local intermixing concept also requires the assurance of no intermixing in adjacent areas of the intermixed regions. For preventing intermixing and protecting the non-mixing surfaces there are mainly three materials used

to cover the surface during annealing (Si_3N_4 , SrF_2 and SiO_2 : P capping methods). However, by far, the most successful technique is patterning SrF_2 on the non-intermixing region of the sample [2]. In this work, both the enhancement and the suppression of IFVD technique were studied. Enhancement of the intermixing was achieved using sputtered SiO_2 layer, while prevention of intermixing was managed by patterning SrF_2 on the structure. Theoretical background was investigated to get complete understanding of the disordering mechanism, although, in the literature, the theory of IFVD has not yet been understood entirely.

In Chapter 2, IFVD QWI technology used for NAM fabrication in semiconductor lasers, fundamental aspects of the physics of semiconductor laser is described. First, since disordering is directly related with energy band structure of the layers, semiconductor band structure is briefly explained. To understand the basics of quantum well optical physics, particle in a box model is explained followed by a discussion of realistic picture of optical absorption and emission. Finally, the essence of quantum well based laser diode is set out developing the basic principles of simple laser diode.

Chapter 3 begins with basic concepts of defect theory in semiconductors related to QWI. Main point of this part is directly related with point defects, hence the point defects in (Al)GaAs structures are explained. In order to convey the mechanism of IFVD which is one of the main techniques of QWI, theory and brief history of QWI and other QWI methods are introduced. QWI is used for several semiconductor devices successfully, however, since we used it for HPLDs, the role of QWI for HPLDs is explained.

In Chapter 4, experimental techniques used in this work is explained in detail, starting with sample preparation and followed with analysis techniques. IFVD mechanism is discussed in depth and all experimental studies and results are placed in this Chapter. Chapter 5 is a final part of the thesis and conclusions and possible future work related to this field are discussed.

Chapter 2

Physics of High Power Semiconductor Lasers

2.1 Introduction

Modern high power lasers are an exercise in innovation and technology with ensuing high efficiencies and optical powers. They invariably depend on solid state quantum well structures embedded in higher band gap and lower refractive index claddings. A solid state quantum well is a potential depression in the band structure of the crystal under study, leading to quantized energy states for the charged carriers, be they electrons or holes. Depending on the width of the quantum well and the magnitude of the potential depth, the carriers are found in discrete energy level, Fig. 2.1. The band offsets between the conduction bands of GaAs and AlGaAs, ΔE_c and the band offsets between the valence bands of GaAs and AlGaAs, ΔE_v lead to confinement of carriers generating bound states for electrons, such as e1, and h1. Thin film deposition technology allows us to observe the quantum well effects in thin semiconductor structures where quantum confinement takes place. Quantum confinement occurs when the well layers have nearly atomic layers thickness, i.e. that is of the same magnitude as the de

Broglie wavelength of the electron wave function. The elements in a semiconductor can be materials from group IV, III-V and II-VI semiconductors.

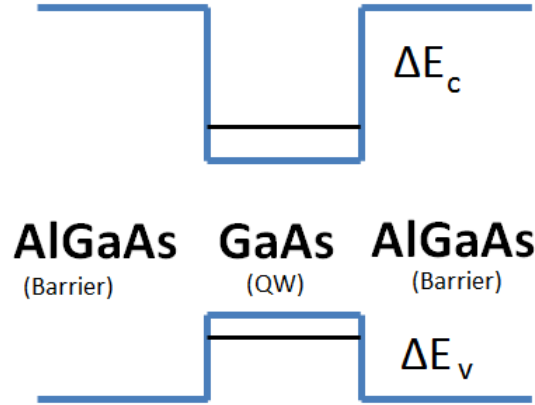


Figure 2.1: Schematic of band gap structure of GaAs-AlGaAs quantum well-barrier structure.

Quantum wells (e.g. GaAs) are formed in semiconductors sandwiching low band gap semiconductors (GaAs) with wide band gap semiconductors (AlGaAs) acting as “barrier” (e.g. $Al_xGa_{1-x}As$, where x gives the Al mole fraction). These structures can be epitaxially grown with of molecular beam epitaxy (MBE) and molecular chemical vapor deposition (MOVPE) technologies.

Since the (optical) physics of quantum wells are realized via semiconductor structures, this chapter begins with the basics of band theory of semiconductors to understand the essential properties of quantum wells, ‘particle in a box’ model followed by ‘principals of optical absorption and emission’ are explained.

2.2 Particle in-a-box model of a quantum well

The light emitted off the quantum well in a laser diode (LDs) is spread out from the quantum well (e.g., GaAs) which is sandwiched between barriers (e.g., Al-GaAs). Therefore it is important to understand the physical mechanisms behind the fundamental properties of quantum well.

For a one dimensional infinite quantum well for an electron (or hole), the Schrödinger equation is given by

$$-\frac{\hbar^2}{2m} \frac{d^2 \varphi_n}{dz^2} + V(z) \varphi_n = E_n \varphi_n \quad (2.1)$$

where $V(z) = 0$ for $0 < z < L$ and the the solution of the wave function inside the well can be given as

$$\varphi_n(z) = A \sin(kz) \quad (2.2)$$

from boundary conditions (the wave function vanishes at the walls)

$$k_n L = n\pi \implies E_n = \frac{\hbar^2}{2m} k_n^2 = \frac{\hbar^2 \pi^2}{2m L^2} n^2 \quad (2.3)$$

can be found effortlessly (where $n = 1, 2, 3, \dots$ is quantum number). The result of discrete energy spectrum shows that the particle are found in quantized levels, Fig. 2.2a. For 10 nm GaAs quantum well the lowest energy level for an electron is about 56 meV above the bottom of the well.

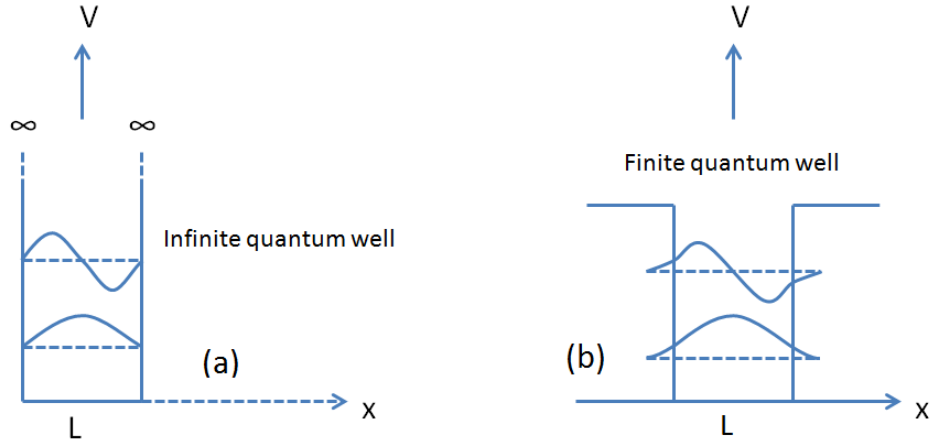


Figure 2.2: Schematic of infinite and finite quantum wells

For realistic cases such as a quantum well in a laser, the quantum well potential is finite leading to some important differences (Fig. 2.2b). The energy states of a real finite quantum well in a solid matrix is determined by the band offsets defining the magnitude of the potential which is determined by the composition of adjacent barrier and well materials at the interface as well as the associated strain. The conduction band offset and valence band offset in the GaAs (quantum well) and AlGaAs (barrier) system is a function of Al mole fraction, Fig. 2.3. It is clear that changes in the composition as well as interface strain will affect the energy band structure of such quantum wells. Finally, in a real quantum well it is possible to have the wave function of the particle to extend beyond the quantum well.

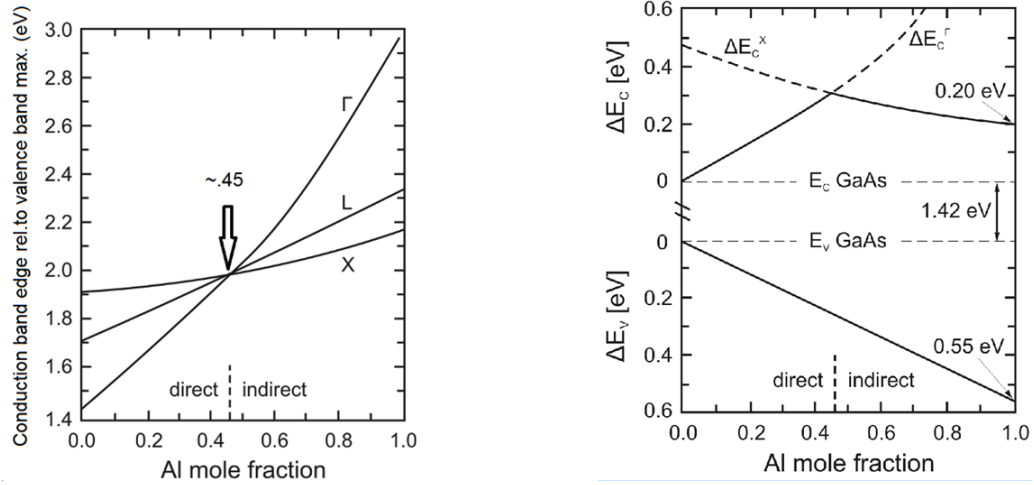


Figure 2.3: Conduction and valence band dependence on Al mole fraction.

As indicated, the realistic behaviour of quantum well problem employs finite well picture. Important parameters in the quantum well intermixing (disordering) problem are conduction band offset, valence band offset and quantum well width which are modified after intermixing and specify the degree of intermixing. According to the report of E.S. Koteles in Chapter-6 of [20], it is observed that energy shift dramatically falls for $5 \text{ nm} > \text{quantum well width}$. It is clearly demonstrated that magnitude of the band gap shift depends on the quantum well width profile and composition. Total band offset value in the intermixing phenomenon, on the other hand, changes approximately 30-200 meV.

2.3 Fundamentals of optical absorption and emission

To understand the working principles of a laser diode it is important to understand the radiative transitions between energy levels of an electron which can be extended to transitions between available states in a solid state system. The concept and relation between absorption and emission is put into perspective by Einstein, introducing ‘coefficients for emission and absorption’ which is crucial to understand the operating principles of the laser. Transition probabilities between energy levels are given by ‘Fermi’s golden rule’.

If we call the upper energy level as E_u and the lower one as E_l , the transition of an electron from E_u to E_l losing its energy by emitting a photon spontaneously is called **spontaneous emission**. The frequency of the photon emitted during this process is given by $(E_u - E_l)/h$ where h is the Planck’s constant. The transition of an electron from a lower to a higher energy level by absorbing a photon is called **absorption**. To find the relationship between absorption and emission, in 1917, Einstein defined **stimulated emission** because he recognized this transition phenomenon was incomplete. During stimulated emission, in contrast with the spontaneous case, the field of the stimulating photon induces the transition of the electron from a higher energy level to a lower energy level. The photon emitted during a stimulated emission is in phase with the stimulating photon leading to coherent light. In the presence of a photon field, the competition between absorption and emission is determined by the ratio of the number of electrons in the lower energy state to those in the upper energy states. When the number of electrons in the upper energy level is larger than those in the lower energy level, incident photon field induces stimulated emission. This is called **population inversion**.

The spontaneous emission rate is given as

$$\frac{dN_u(t)}{dt} = -A_{ul}N_u(0) \quad (2.4)$$

where N is the number of electron densities at specified level and A_{ul} is the

Einstein coefficient and this proportionality constant is the inverse of ‘Natural radiative lifetime’ of the excited state.

It is clear that the absorption rate and the stimulated emission rate are written requiring the energy density of the photon,

$$\frac{dN_l(t)}{dt} = -B_{lu}N_l(0)u(\nu) \quad (2.5)$$

$$\frac{dN_u(t)}{dt} = -B_{ul}N_u(0)u(\nu) \quad (2.6)$$

where B_{ul} and B_{lu} are the Einstein B coefficient for absorption and stimulated emission and $u(\nu)$ is the energy density of the photon.

In equilibrium at a given temperature, the energy density of the photon is given by Planck’s (blackbody radiation) law and applying the principle of detailed balance, *under equilibrium each elementary process should be equilibrated by its reverse process*,

$$0 = A_{ul}N_u + B_{lu}N_lu(\nu) + B_{ul}N_uu(\nu) \quad (2.7)$$

and according to the ratio of a Boltzmann distribution we get

$$\frac{N_u}{N_l} = \frac{g_u}{g_l} e^{-\frac{h\nu}{k_B T}} \quad (2.8)$$

where g_u and g_l are the degeneracies of the respective energy levels. The relationships between Einstein coefficients can be derived from the above two equations (Using Planck’s radiance formula as our photon density),

$$\frac{A_{ul}}{B_{ul}} = \frac{8\pi h\nu^3}{c^3} \quad (2.9)$$

$$\frac{B_{ul}}{B_{lu}} = \frac{g_l}{g_u} \quad (2.10)$$

so that measuring one coefficient gives us other two coefficients. This also tells us that high absorption probability results in high emission probability. In a semiconductor laser diode, population inversion condition is provided in the pn junction, under bias. The application of bias voltage and subsequent injection of carriers shifts the electron and hole densities accompanied by a shift of the respective Fermi levels. Under this non-equilibrium condition, the new shifted Fermi levels are called quasi Fermi levels. The difference between quasi Fermi levels in n- and p-type semiconductors of a p-n junction is a measure of the population inversion.

Transition rate is the transition probability per unit time and is given by **Fermi's golden rule** can be written as

$$w_{i \rightarrow f} = \frac{2\pi}{\hbar} |M_{if}|^2 \delta(E_f - E_i) \quad (2.11)$$

where $|M_{if}|$ is the matrix element which defines the transition between initial(i) and final(f) energy level and is written as follows

$$|M_{if}| = \langle f | H' | i \rangle = \int \varphi_f^*(\mathbf{r}) H' \varphi_i(\mathbf{r}) d^3(\mathbf{r}) \quad (2.12)$$

and $\delta(E_f - E)$ part can be written as $\rho(\hbar\omega)$ which is more common for solids, it describes the density of the continuum levels of final state. Initial and final wave functions of the electrons give us the absorption and emission rates as follows:

$$B_{if} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |\langle f | \mathbf{r} | i \rangle|^2 \quad (2.13)$$

$$A_{fi} = \frac{w_{fi}^3 e^2}{3\pi \epsilon_0 \hbar c^3} |\langle f | \mathbf{r} | i \rangle|^2 \quad (2.14)$$

Last but not least, using **selection rules** make the transition allowed or forbidden due to *parity*, *azimuthal quantum number*, *magnetic quantum number* and *spin quantum number* we can get more detailed and accurate picture.

2.4 Basics of high-power laser diodes

The simplest laser diode (semiconductor laser) comprises of a p^+n^+ junction working under forward bias on which the metal contacts are provided for electrical injection(**homojunction laser diode**). The *active region*, where lasing (population inversion) occurs, is the depletion region. In addition to population inversion and emission, for lasing, it is also essential to have an *optical cavity(resonator)* to generate to provide the photonic feedback necessary for stimulated radiation. This is achieved by cleaving the ends of the optical waveguide and coating a multilayer dielectric mirror with one side reflecting >90 percent whereas the output mirror is dielectric coated for anti-reflection by <10 percent. Such a cavity is a *Fabry-Perot resonator*.

The emission spectrum of the laser is determined by resonant **longitudinal modes** that must obey to standing wave condition between the cleaved surfaces (mirrors). If we call the length of the cavity as L, this condition is described as

$$L = m\left(\frac{\lambda}{2n}\right) \quad (2.15)$$

where m is the integer and n is the refractive index of the medium.

Due to population inversion there is *optical amplification* inside the medium and it is formulated as (Beer's law)

$$I(x) = I_0 e^{gx} \quad (2.16)$$

where I is the intensity of emitted light and **g** is the **gain coefficient**. On the one

hand the medium gains intensity due to stimulated radiation, on the other hand it loses intensity of light owing to reflections from the mirrors, scattering by defects, absorption by free carriers, impurities etc. the total of which can be described as **attenuation**, (α_s). Based on the gain and attenuation, the threshold condition for lasing, for net round-trip gain, can be written as

$$P = P_0 R_1 R_2 e^{g(2L)} e^{-\alpha_s(2L)} \quad (2.17)$$

where P_0 and P is the initial and final value of power of the light. For steady-state oscillations, gain must be balanced by losses $\frac{P}{P_0} = 1$, so that the *threshold gain* is (once the injection level at carrier density is between $10^{18} - 10^{19} \text{ cm}^{-3}$ the generated photons overcome the attenuation) given by

$$g_{th} = \alpha_s - \frac{1}{2L} \ln(R_1 R_2) \quad (2.18)$$

defines the threshold gain for laser oscillating and the relation between the output power (P_{out}), the injected current (I_{inj}) and threshold current (I_{th}) are,

$$P_{out} = \eta(I_{inj} - I_{th}) \frac{h\nu}{e} \quad (2.19)$$

where η is the **quantum efficiency** and defines the ratio of injected electron-hole pairs to created photons by recombination of them.

As illustrated in the Fig.2.4, the gain increases with the injected current and at threshold laser begins to oscillate with constant value of g_{th} . After threshold current is exceeded the output power, it can be increased with applied current by injecting extra electrons though they cannot increase the gain further.

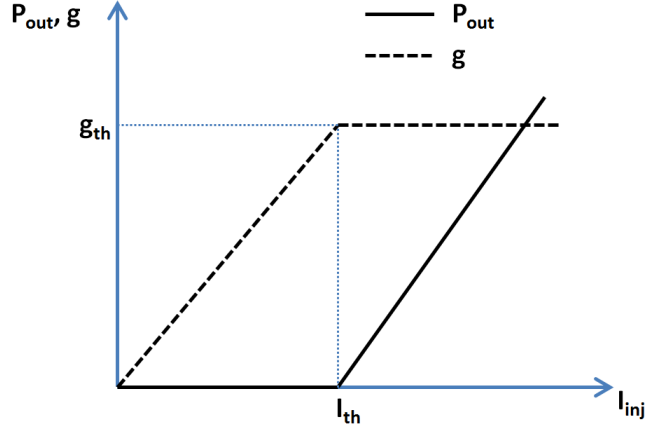


Figure 2.4: Schematics of optical threshold gain, output power and threshold current relation

The main limitation of the homojunction laser diode is that its threshold current value is too high, typically $400 A/mm^2$ or more [12]. For practical uses the threshold current must be decreased which can be achieved by a heterostructure laser diode, Fig. 2.5.

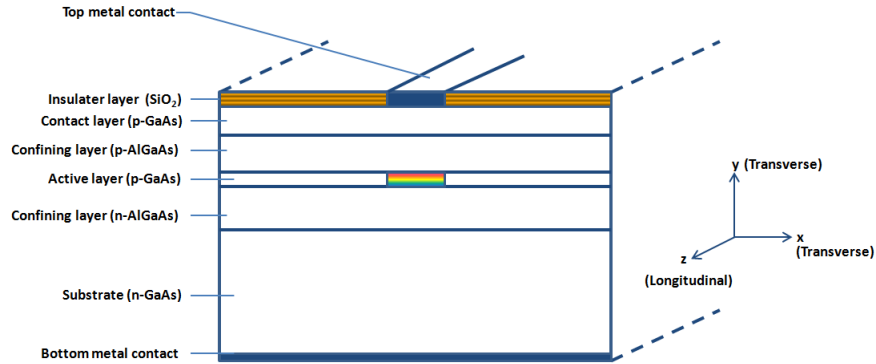


Figure 2.5: A schematic description of a heterostructure laser diode

In order to lower the lasing threshold, it is important to increase the current density at the active region. This can be achieved by injecting the current into a narrow region emission (electrical confinement). a laser operates under constant optical feedback by the photons in the cavity to induce stimulated emission.

Hence, photon confinement for feedback can be achieved by constructing a waveguide to increase photon density (optical confinement). This can, for example, be achieved by $Al_xGa_{1-x}As - GaAs - Al_xGa_{1-x}As$ type of structure where the band gap of the thin layer of GaAs is smaller than the surrounding AlGaAs leading to a GaAs quantum well. Electrically, the structure is a p-i-n structure where the cladding layers are doped p- and n-type, respectively. Hence the electrons and holes are confined in the thin GaAs quantum well layer. Optical confinement is built into active region (GaAs layer) as well, since the refractive indices of the AlGaAs cladding is lower than that of the active region (GaAs and AlGaAs are 3.65 and 3.3 at 850 nm when $x=0.5$, respectively). Therefore, both electrical and optical confinement help decrease the threshold current down to tens of milliamperes. The slight lattice mismatch between GaAs-AlGaAs, negligible strain induced defects which act as non-radiative recombination sources and other significant advantages make (Al)GaAs structures attractive. (The additional GaAs contact layer results in smaller contact resistance than AlGaAs with electrodes.) This type of laser diodes, namely **gain-guided lasers** have a disadvantage in terms of the spreading current. Although the current injected on stripe and the emission takes place in the middle of the active layer, some part of the current spreads laterally. This issue can be handled by the **index-guided lasers**, the sides of the middle part consists of the materials having bigger refractive index than the emission region.

Using a quantum well as active layer has more advantages in comparison with ordinary heterostructure laser diodes (the thickness of the active region changes between 50 and 300 nm). With a laser employing a quantum well, the undoped the active layer (GaAs) is ultra thin (5-20 nm) which decreases the threshold current and surrounded by doped barrier layers (AlGaAs). The density of states behave as a step-like function due to bound levels. The carriers are quickly captured by the quantum wells occupying selected energy levels as soon as the laser is injected, whereas the carriers in bulk semiconductors spread slowly in the conduction band diffusing and drifting into the states compared to quantum well. Put differently, density of states changes with the root of energy in bulk active layers, and carrier confinement ratio is around 10 to 70 percent, while it changes

with energy discreetly in quantum wells and carrier confinement rate is greater than 90 percent [15]. Advanced quantum well based laser diode designs employ (undoped) low refractive index undoped waveguide layers, surrounding the quantum well layer. This structure is embedded into yet another sandwich of doped cladding layers, typically with even lower index of refraction but doped to reduce the series resistance to obtain more efficient waveguide, namely, a separate confinement heterostructure (SCH). Quantum well with waveguide layers is called as ‘waveguide core’. Since the quantum well is very much thinner than the wavelength of the emitted radiation, and despite the fact that quantum well provides a good carrier confinement, it does not provide good optical confinement, and the optical mode is spread into the surrounding waveguide layers. The spread of the optical mode into the surrounding doped cladding layers is to be avoided as this will result in free carrier absorption of light.

For high power lasers, injection of current leads to increased optical output. Current commercial high power lasers operating between 800-1000 nm achieve output powers of 10-15 W with quantum efficiencies reaching 55 percent. Higher efficiencies and output powers are limited mainly by catastrophic optical damage at the mirrors of the cavity that take place at high currents. For a 100 μm wide optical waveguide with a 0.5 μm thick active layer, optical power density at the output mirror can easily exceed xxx W/cm^2 ($100 \times 10^{-4} \text{ cm} \times 0.5 \times 10^{-4} \text{ cm} = 0.5 \times 10^{-6} \text{ cm}^2$ gives $10 \text{ W}/(5 \times 10^{-7} \text{ cm}^2) = 20 \text{ MW}/\text{cm}^2$.) One possibility is to increase the cavity thickness, expanding the optical mode at the output mirror and reducing the optical density at the output mirror. Large optical cavities reaching 3.5-4.0 μm thickness are being employed for this purpose, Fig. 2.6.

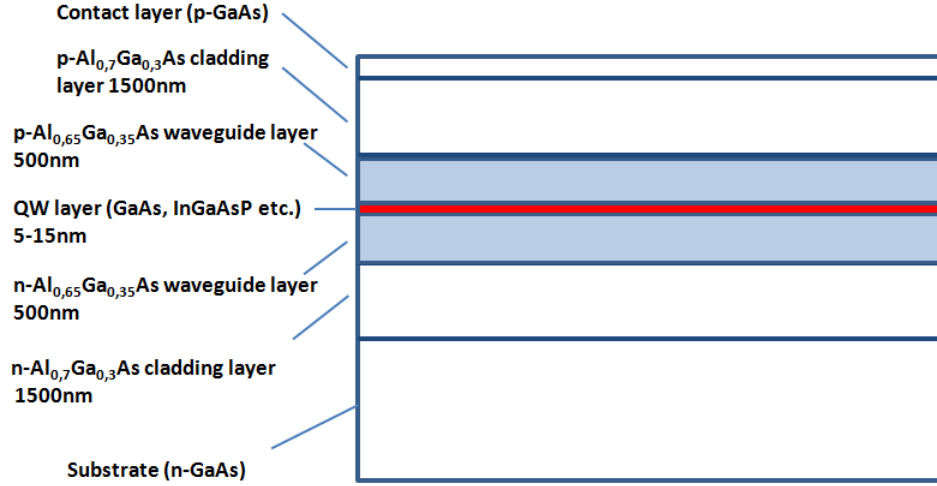


Figure 2.6: Schematics of a typical large optical cavity laser diode.

Further improvement into catastrophic optical damage is obtained by reducing optical absorption at the interface of the mirrors. In addition to avoiding electrical pumping of the active region close to the mirrors, it is possible to locally alter the band gap of the quantum well. Shifting this band gap of this region to the blue, the light emitted in the depths of the waveguide passes through the mirrors without absorption. These altered (passive) waveguide sections, adjacent to back and front facets of the resonators enhance the COMD threshold which is one of the main limitations in order to fabricate high-power laser diodes (HPLDs).

2.5 Summary

The progress in laser diode physics and technology has been spectacular. However, the demands of the market continues for higher efficiencies and optical powers. Quantum well structures are central to the high output powers obtained. The developments of both optical and electrical confinement created an opportunity to get high output power ($> 1W$). Using sophisticated designs, the threshold current is decreased down to tens of milliamperes (currently the value of output power demonstrated in laboratories is higher than 15 W) .

As the laser diode technology matured, its market or application fields increased as well, e.g. telecommunications, medical applications, materials processing etc. It seems the progress of laser diode technology continues relentlessly. Yet, there are many unsolved problems related to both design and fabrication issues. This study focuses on one of the problems of edge-emitting HPLDs: to develop the technology to increase the optical mirror damage threshold using IFVD QWI technique.

Chapter 3

Intermixing and Defect Theory of Semiconductors

3.1 Introduction

The reason semiconductors are so highly valuable with regards to device technology is that their physical properties can be changed by adding different types of impurities or defects. During fabrication of semiconductors or the growth of epitaxial layers, the required defects can be incorporated. On the other hand, it is also possible to encounter unintentional defects which can, in general, degrade or decrease the efficiency of the device.

There are many defects with different physical properties. These properties are not only electronic but also optical, stress related, thermal etc. that affect the eventual performance of the material in a given device. In this thesis, we concentrate on the electronic properties and the electronic structure of defects, as they are critical to the electrical and optical performance of laser diodes. Specifically, the role of point defects on $GaAs - Al_xGa_{1-x}As$ materials will be summarized. It will be shown that point defects play a major role in impurity free quantum well intermixing.

3.2 Defects in semiconductors

First, we distinguish between structural lattice defects and both intentional and unintentionally doped foreign atoms, and impurities: Defects involving intentionally introduced foreign atoms are referred to as **extrinsic defects** are also called as **impurities**.

Structural lattice defects can be divided by mainly two parts: point defects, which are due to misplaced atoms and line defects, which include rows of misplaced of atoms and can be considered as extended point defects. Well known among them are several types of dislocations. There are also planar defects, that comprises of misplaced planes of atoms [4]. In general, both point defects and line defects are detrimental to the performance of devices and in particular, to light emission. They may, however, be used to the advantage of device designer for example to introduce additional energy levels in the band gap to increase the speed of detection in some photodetectors as well as structurally reorder parts or all of a given heterostructure. Point defects can be classified as:

Vacancy defect, the vacant site formed by missing atom (X), and can be denoted by V_X .

Interstitial defect, atoms that occupy a interstitial sites in lattice where normally no atom is located, and can be denoted as I_X .

Substitutional impurity defect, a different atom Y substitute into the lattice site of a host atom X and is not a vacant site or interstitial atom, Y_X .

Antisite defect, occupation of a sublattice site by an atom of the alternative sublattice in an alloy or a compound.

Frenkel defect pair, of the complex of a vacancy and an interstitial defect, $V_X - I_X$.

Defects, in general, that are electrically active can be **donors** or **acceptors**, introducing free electrons or holes into crystal. P and B doped Si (P_{Si} , B_{Si}) are common examples to donors and acceptors as substitutional impurities one of

which has one more and the other one less valence electron than the host Si atom, respectively. On the other hand, substitutional impurities that have the same number of valence electrons as the host atom and are called as **isoelectronic(isovalent)** centers, e.g C is isoelectronic center for Si. Isoelectronic center can act as a donor, an acceptor or be electrically inactive.

3.3 Point defects in $GaAs - Al_xGa_{1-x}As$ materials

III-V compounds have six kinds of defects these defects are summarized in table 3.1 for GaAs. These defects are typically charged and charge level is determined by the Fermi level. Any physical process that affects the Fermi level will influence the charge state of the defect. Temperature, besides doping, is an added parameter that acts on the defects to alter their properties.

Table 3.1: The six point defects in GaAs

Donor defects	Acceptor defects
Column V vacancy-As	Column III vacancy-Ga
Column V antisite-As	Column III antisite-Ga
Column III interstitial-Ga	-
Column V interstitial-As	-

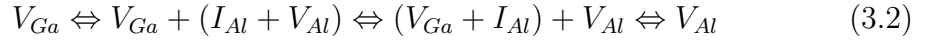
In GaAs related materials, defect formation during crystal growth can be controlled by As pressure. The types of defects formed in AlGaAs-GaAs system are different under high As-overpressure (As-rich concentration) growth conditions and low As-overpressure (As-poor concentration) growth conditions. The first one promotes Ga vacancies, As antisites, and As interstitials due to migration of Ga atoms, the latter promotes As vacancies, Ga antisites, and Ga interstitials.

Under equilibrium conditions, it is expected that Frenkel defects are formed dominantly in GaAs

$$I_{Ga} + V_{Ga} \Leftrightarrow 0 \quad (3.1)$$

since the vacancies and interstitials in group III diffuse in the fastest way. Thus diffusion of Ga atoms occurs via vacancies or interstitials and interdiffusion coefficient depends on As-overpressure during annealing [3].

High power laser diodes employ both GaAs and AlGaAs, so that other column III defects, V_{Al} and I_{Al} must also be considered. In the IFVD process, I_{Ga} atoms in the quantum well migrates to surface of the structure during annealing which is encapsulated by SiO_2 leaving V_{Ga} and then I_{Al} defects inside the barrier layers that form Frenkel pairs with V_{Ga} [5], inasmuch as interstitial defects diffuse more quickly than vacancy defects



The details in the IFVD process will be explained in the next Chapter.

3.4 Quantum well intermixing (QWI)

Using quantum wells in semiconductor lasers increases their efficiency, performance and robustness of the devices. However, varying the potential profile of quantum wells in a monolithic device is a problem. Altering the quantum well widths with selected area etch back and regrowth is expensive and cannot usually solve the problem. Although advances in regrowth techniques reduced the scattering and back-reflection losses at the regrowth interfaces, coupling efficiency is limited around 90 percent [6], because it includes several sensitive etch-regrow steps, Fig. 3.1a.

An alternative approach is to use QWI to selectively and locally modify the quantum well minimizing the monolithic integration problem. QWI can also be used inside the active region of band gap tunable laser, gain block of optical amplifier, electro-absorption modulators, detectors etc.

The passive waveguide, electrically not pumped, sections of a semiconductor laser cavity waveguide, adjacent to rear and front facets of the laser resonators, requires a larger effective quantum well band gap energy compared with photon energy of the light generated in active mid sections of the waveguide. Optical waveguides with variations in the effective band gaps of quantum well is necessary for many photonic integrated circuits (PICs) such as electro-absorption modulators(EAM) and optoelectronic integrated circuits (OEICs) such as distributed feedback lasers (DFBs). In the case of high power laser diodes, the passive waveguides adjacent to the mirrors are responsible for the optical output power of laser diodes, hence increasing the catastrophic optical mirror damage(COMD) threshold (Non-absorbing mirror, NAM technology), is critical for good performance.

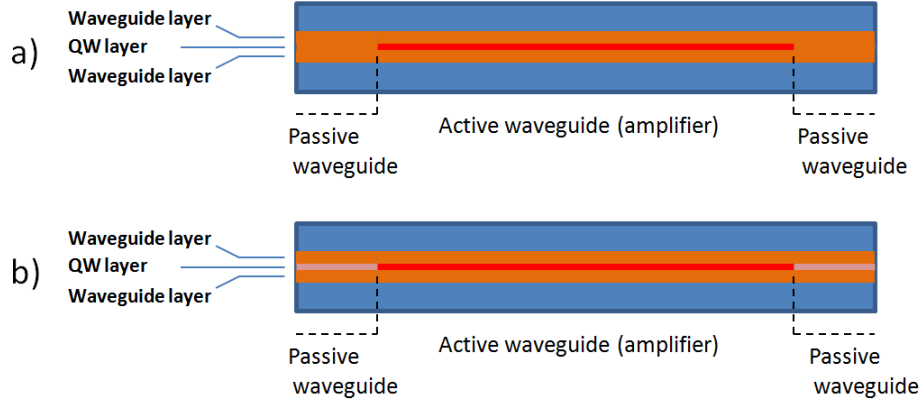


Figure 3.1: Active-passive waveguide formation by regrowth(a) and QWI(b) techniques.

Quantum well intermixing eliminates back-reflection and coupling problem with little disturbance for the index guided modes in single step, Fig. 3.1b. The idea of intermixing rests on the idea to change the quantum well-barrier structure after growth, usually increasing the band gap (Fig. 3.2), by several different but closely related techniques which are explained in the next section.

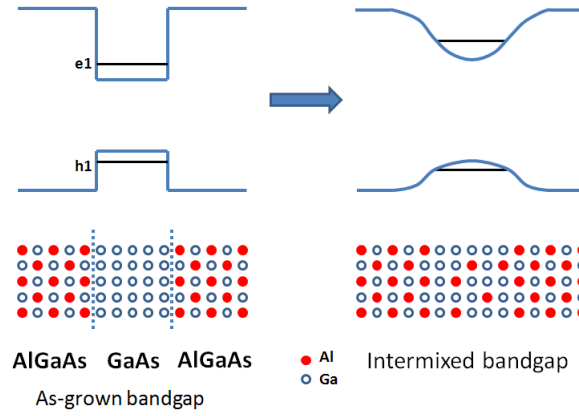


Figure 3.2: A schematic diagram of band gap change by (impurity-free) QWI for (Al)GaAs laser diode structure.

3.4.1 Quantum well intermixing techniques

It is important to note that there occurs three main changes in material properties upon applying intermixing: changes in the absorption coefficient, the material resistivity and the refractive index change. The changes in absorption coefficient can range from 1 dB/cm to 10 dB/cm while electrical resistances of the order of 100 kohms are necessary for electrical isolation. An index change as high as possible is sought because the index change is directly related with band gap energy [1].

Among a number of disordering techniques there are mainly three methods, impurity induced disordering (IID) , laser-induced disordering (LID), and impurity-free vacancy disordering (IFVD).

In **impurity induced disordering (IID)**, electrically active or neutral impurities are diffused during or after growth by external sources and then the material is annealed. It was first found, by N.Holonyak Jr. and his collaborators during Zn diffusion on AlAs-GaAs superlattice in 1981 [7]. The first intermixed lasers were fabricated using IID [8]. Since then, disordering studies quickly increased. IID can be performed in two ways surface dopant diffusion and ion-implantation. The impurities added are also classified into two types, electrically active (p- or

n- type, such as Zn and Si, respectively) impurities and neutral impurities such as F, B etc. Impurities trigger the disordering due to free carrier generation that enhance the formation of vacancies and interstitials during annealing: Zn diffusion, for instance, is carried about interstitially in Ga lattice and substitute with Ga atoms [1]. In the first technique, except in volume production, the sample and source (e.g. Zn doped silica or Zn_xAs_y alloys) of disordering is located in an evacuated quartz ampoule followed by annealing. However, free-carrier absorption losses of the intracavity laser beam are unavoidable because of IID which occurs under high impurity concentration which leads to high absorption losses. Moreover, electrically active impurities leads to poor electrical isolation due to leakage currents [1].

Implantation induced intermixing utilizes the damage which leads to formation of point defects by an energetic ion beam followed by an annealing step. Although, using neutral impurities results in low optical propagation losses, the residual damage and trap concentrations are almost inevitable which reduce the yield of devices[1]. On the other hand, in spite of implantation damage method performed successfully by Piva et al [9], and, Hashimoto [10] to obtain passive waveguide resonators, the deficiency of the lifetime and performance of devices was interpreted to be detrimental [1].

Laser induced disordering (LID) initially was performed on (Al)GaAs superlattice incorporating a Si encapsulant as a source of impurity by melting the sample [11], scanning with CW lasers or without an encapsulant by a nanosecond pulsed laser [12]. However, the first method, suffers from high free-carrier clusters and has limited spatial resolution. In the second one, although it is impurity free, high power pulsed beam can melt the structure and can create thermal shock damage which in turns out to be disastrous. Moreover, for both methods, melting the material may lead to complete and uncontrollable intermixing [1]. Alternatively, photo-absorption induced disordering was discovered by McLean et al [13], without melting the semiconductor, using CW laser beam. The energy of the beam between the band edge of active and cladding layers generated the heat only on active layer. This method is a promising technique, in particular, for GaInAs-GaInAsP and GaInAs/AlGaInAs structures since, these quantum well

structure have limited thermal stability [1].

IFVD is one of the most manageable techniques of QWI; it is a impurity-free process, in which diffusion of native defects leads to disordering after annealing without many of the problematic conditions in IID (Fig. 3.2 shows IFVD of (Al)GaAs high power laser diode structure). It retains crystal quality, no damage is observed after the process, and it is a convenient process for commercial production (Currently, high-power laser diodes are produced by this technique in *Intense company* - www.intenseco.com), etc. Although there are many successful demonstration of NAM technology for laser diodes and other applications, the physical mechanism is not understood completely [20]. Therefore, it is important to understand the interdiffusion mechanisms in order to digest the theory of IFVD.

3.4.2 Theory of interdiffusion in III-V materials

The self-diffusion in heterostructure semiconductors has been investigated since 1960: it has been an issue since heterostructure semiconductors were discovered. Establishing a theory on the atomic scale from experiments is a state-of-art challenge because the problems are not only about the sensitivities of characterization systems at such sizes and the systems' changing effects on samples but also the presence of huge variety of parameters that perturb the interdiffusion. Well investigated chronological summary of the deficiencies and improvements about interdiffusion mechanism for III-V materials can be found in [20].

The IFVD mechanism (in GaAs based structures) takes place in two stages but the time between two stages is very short. First, the generation of Ga vacancy defects (V_{Ga}) occurs followed by, the diffusion of them. The generation of V_{Ga} occurs during annealing, first in the GaAs cap layer by encapsulant (SiO_2) layer absorbing the interstitial Ga atoms. Then the atomic spaces created by V_{Ga} in cap layer is filled by other Ga atoms from below layers including quantum well (GaAs) layer. Once Ga atoms in the quantum well migrate upward, interstitial Al atoms (I_{Ga}) in AlGaAs waveguide layer surrounding the quantum well forms

Frenkel-pair with V_{Ga} s in the quantum well and self-diffusion happens between them.

As stated before, huge variety of experiments performed to understand how the mechanism of interdiffusion is measured may be divided in two wide classes; direct and indirect compositional determination. First one is much better since it can be directly fitted with a (Fickian) diffusion model, such as secondary ion mass spectroscopy (SIMS) [21], transmission electron microscopy (TEM) [22], Rutherford Backscattering Spectroscopy (RBS) [23]. Second class of methods measure interdiffusion composition indirectly, most widely used is PL [7-14] and X-ray diffraction techniques [33].

In QWI, it is assumed that the diffusion is Fickian and the error function solutions of the diffusion equation are used to obtain the composition profile, i.e.

$$\frac{dC}{dt} = D \frac{d^2C}{dz^2} \quad (3.3)$$

leads to

$$C(z) = C_{Al} + \left(\frac{C_{Ga} - C_{Al}}{2}\right) \left[\operatorname{erf}\left(\frac{a - z}{L_D}\right) + \operatorname{erf}\left(\frac{a + z}{L_D}\right) \right] \quad (3.4)$$

where C_{Al} is interpreted as the concentration of diffusing defects in barrier, whereas C_{Ga} is interpreted as the concentration of diffusing defects in quantum well, $2a$ is well width and z is the depth where $z = 0$ is the well center and $L_D = \sqrt{Dt}$ is diffusion length where D is diffusion coefficient and t is the annealing time. Therefore, the potential profile of quantum well is found by concentration equation with as-grown barrier height. Using envelope wave function in Schrödinger equation, intermixed band profile can be obtained numerically. It is known that the interdiffusion is conducted by group III vacancies (V_{Ga}) and interdiffusion coefficient, D_{int} , is given by,

$$D_{int} = fD_{vac}C_{Ga} \quad (3.5)$$

where D_{int} is the diffusivity of vacancies, C_{Ga} gives the concentration vacancies in group III and f is the correlation factor in the unity. D_{vac} and C_{Ga} are given by Arrhenius relationship which is used to get the relation of reaction rates with temperature variations,

$$D_{vac} = \alpha^2 \nu e^{\frac{-E_d}{kT}} \quad (3.6)$$

$$C_{Ga} = C e^{\frac{-E_f}{kT}} \quad (3.7)$$

where E_d and E_f are the activation energies of vacancy diffusion and the formation energy of the point defect, respectively. ν is the jump frequency and α is the jump distance, C is related with the entropy [20]. Thus, the interdiffusion coefficient is,

$$D_{int} = f\alpha^2 \nu C e^{-\frac{E_d+E_f}{kT}} \quad (3.8)$$

and diffusion prefactor is given by $D_0 = f\alpha^2 \nu C$ and we can conclude that C is directly related with the entropy since other terms in D_0 are constant. The main problem in getting a solid theory of interdiffusion mechanism for GaAs based materials is about D_0 due to the fact that its value varies by 21 orders in the literature. This unreasonable result is considered to be due to variations in experiment conditions [20]. However, the average of activation energies ($E_A = E_d + E_f$) and a histogram (from the experiments performed until 2000) was calculated by W.P. Gillin et al [20], and it was found to be between 0.32 - 6.3 eV and from the histogram, diffusion prefactor is found to be $0.2cm^2$ to $0.007cm^2$.

The Al concentration of interdiffused quantum well was calculated [24] and it was formularized as

$$x = x_0 \left\{ 1 + \frac{1}{2} \operatorname{erf} \left[\frac{z - L_z/2}{2\sqrt{Dt}} \right] - \frac{1}{2} \operatorname{erf} \left[\frac{z + L_z/2}{2\sqrt{Dt}} \right] \right\} \quad (3.9)$$

where x_0 is the Al fraction in the barriers.

Apart from the mathematics of the diffusion mechanism, the complete understanding of IFVD mechanism requires the consideration of stress; the evidence of stress dependence on (Al)GaAs quantum well structures was successfully demonstrated [25]. The generation of Ga vacancy defects is affected by the metallurgical reaction between encapsulant layer and cap layer, whereas their diffusion is affected by the stress. It was concluded that once the cap (GaAs) layer is under compressive stress, V_{Ga} s diffuse deeper into cap layer, while the GaAs layer is under tensile stress V_{Ga} s are trapped in the stressed region and almost no contribution to intermixing is observed [26]. That is why we use SiO_2 to enhance and SrF_2 for inhibit the intermixing: at annealing temperature $800 - 1000^\circ C$, former layer, is under compressive stress whereas the latter is under tensile stress.

3.4.3 Quantum well intermixing for high power laser diodes

Among practical solutions to fabricate semiconductor devices, the discovery that rearrangement of quantum wells in single step can be achieved, created many ways to enhance the yield of PICs and OEICs. Although this method is applied in a large number of fields such as photonic integrated circuits(PICs), optoelectronic integrated circuits(OEICs), biophotonics etc. we will focus on its application for high-power laser diodes. HPLDs are used as pump sources for solid state lasers (defense and aerospace systems), optical fiber lasers, YAG (yttrium aluminium garnet) lasers, direct (or fiber) coupled welding, soldering, micro machining processing, medical applications such as treatments for cancer (photo

dynamic therapy), digital printing, non-contact solution by laser coding etc. Using this method, on the one hand, the reliability, output power, brightness and yield of the laser diodes increases distinctly, on the other hand, packaging steps decreased and losses by fiber coupling are removed [14].

Between the stages of cleaving the wafers into laser bars and coating the facets for required reflectivities, there is a passivation of facets step where the COMD comes about. Ability to fabricate HPLDs with long device life time enormously depends on the mirror quality. Accumulation of photons(stimulated radiation) in the active waveguide region creates significant heat on facets before photons are emitted. Interface states or deep centers formed at semiconductor-insulator interface cause absorption at mirrors which arise due to oxidation of semiconductor material. Electron-hole pair generation resulted from the absorption at facets causes to bond breaking followed by facet oxidation and/or can result in non-radiative recombination which heats the facets. If the heat is high enough, it leads to COMD. Damage threshold of facets can be easily reached to $10\text{MW}/\text{cm}^2$. The heating can also oxidize the facet or decrease the band gap energy. Reduced band gap energy leads recursive to nonradiative recombination the process starts over owing to reabsorption of light [15].

QWI is the most common method for increasing the band gap of the NAM surfaces which also inhibits the current leakage into this area. Elaborating study of QWI for NAM regions by increasing the COMD level for (Al)GaAs structure can be found in [16].

In addition to QWI, there are other approaches increase COMD threshold. One of them is *reducing surface recombination velocity* which benefits from sulfur evaporation on facets which leads to decrease of nonradiative recombination velocity and increase of COMD threshold [17]. Another method is the *decreasing current crowding at the surface*, part of the biased current also increases the heat the surface. Reducing this type of nonradiative recombination can be achieved by avoiding the accumulation of carriers to accumulate to area close the facet [18]. Decreasing the light intensity can be managed by broadening the waveguide size as well which is namely large optical cavity (LOC) [19].

3.5 Summary

In conclusion of this chapter, the essence of the QWI technique, defect theory has been presented and specifically for (Al)GaAs structures. Advantages and application fields of QWI method with its all major aspects have presented. Finally, QWI for HPLDs, which is the most fascinating and popular application area of QWI, has explained by describing its increasing effects in terms of output power, mode confinement and COMD level. Alternative approaches to QWI have also been introduced briefly.

Chapter 4

Experimental

4.1 Introduction

IFVD is possibly the most reliable technique of QWI due to its advantages compared to other major method (IID) and its practicality in commercial applications and other specific benefits of IFVD makes it much more usable for monolithic integration.

IFVD is a post-growth technique used to increase the band gap energy of quantum well in desired areas, particularly for GaAs-AlGaAs structures: the self-diffusion of atoms in the well and the barrier (waveguide and cladding) results in the increase of the band gap energy. Before this happens, the semiconductor material (e.g AlGaAs-GaAs), in general, is sputtered by encapsulant material to deposit a layer to absorb the atoms (Ga atoms) from the quantum well during annealing ($800 - 1000^{\circ}C$) step which are followed by self diffusion of vacancy defects (V_{Ga}) in the well and interstitial defects (I_{Al}) in the barrier. As shown in Fig. 4.1, near the edges of cavities the encapsulant is deposited as SiO_2 to enhance the interdiffusion, whereas the remaining surface region (injected current area of the laser diode) of the sample is evaporated with SrF_2 to suppress the interdiffusion. Fig. 4.1 illustrates the idea of the fabrication of HPLDs with QWI,

with focused in this work, being enhancement and suppression during intermixing.

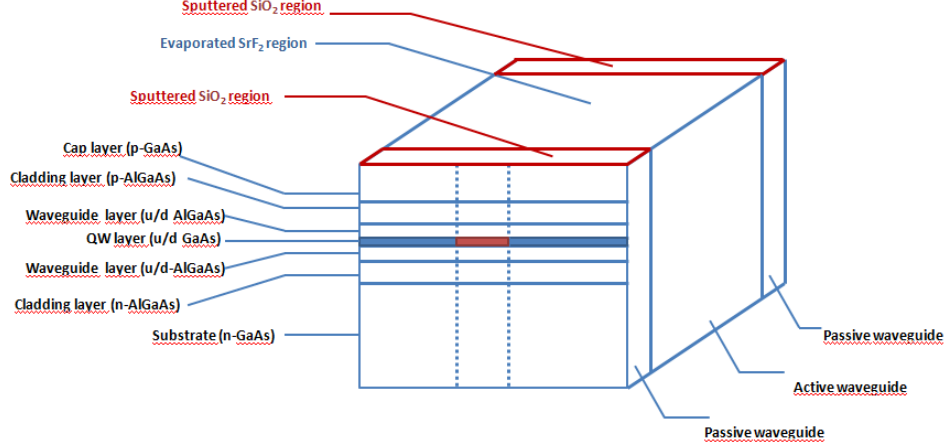


Figure 4.1: Schematics of intermixing regions on HPLD.

Although, there are many advantages of IFVD, the complete theory of impurity free diffusion or more specifically exact mechanism for the interdiffusion is still not well known [20]. Even though a large number of experiments and characterization techniques have been performed for about 25 years and this still goes on. In this thesis, 154 meV band gap energy change was achieved using IFVD on a GaAs/AlGaAs quantum well laser structures. As characterization method, photoluminescence(PL), depth profiling with X-ray photoelectron spectroscopy (XPS) were used to try to understand the details of interdiffusion mechanism.

In this chapter, laser structure used in this work, sample preparation techniques, experimental characterization methods and results of the experiments will be given.

4.2 High power laser structure

The experiments were performed on two different laser structures, No.1 and No.2, however, not equally. No.1 structure which was very limited, was used for the initial. No.2 structure was almost 2 inch in diameter and the remaining experiments were performed on this sample. Both were single quantum well $Al_xGa_{1-x}As - GaAs$ structures produced for laser diode processing were growth by MOCVD technique. Both structures use a cladding layer with high Al mole fraction ($x=0.70$ and $x=0.55$) and a waveguide layer with high Al mole fraction ($x=0.30$ and $x=0.37$). The transitions from AlGaAs layers to GaAs layers are graded. Table 4.1 and 4.2 shows the structure of lasers in detail.

Table 4.1: Epitaxial structure of the No.1 sample

Layer	Material	Mole fraction, x	Thickness, μm	Doping type
13	GaAs	-	0.1	P
12	Al(x)GaAs	$0 \rightarrow 0.7$	0.26	P
11	Al(x)GaAs	0.7	0.8	P
10	Al(x)GaAs	0.7	0.106	Undoped
9	Al(x)GaAs	$0.7 \rightarrow 0.3$	0.12	Undoped
8	Al(x)GaAs	0.3	0.055	Undoped
7	GaAs	-	0.005	Undoped
6	Al(x)GaAs	0.3	0.055	Undoped
5	Al(x)GaAs	$0.3 \rightarrow 0.7$	0.22	Undoped
4	Al(x)GaAs	0.7	0.1	Undoped
3	Al(x)GaAs	0.7	1.3125	N
2	Al(x)GaAs	$0.7 \rightarrow 0$	0.25	N
1	GaAs	-	0.2	N

Table 4.2: Epitaxial structure of the No.2 sample

Layer	Material	Mole fraction, x	Thickness, μm	Doping type
10	GaAs	-	0.5	P
9	Al(x)GaAs	0.55 $\rightarrow$ 0.05	0.05	P
8	Al(x)GaAs	0.55	1.5	P
7	Al(x)GaAs	0.55	0.1	Undoped
6	Al(x)GaAs	0.37	0.2	Undoped
5	GaAs	-	0.012	Undoped
4	Al(x)GaAs	0.37	0.2	Undoped
3	Al(x)GaAs	0.55	1.5	N
2	Al(x)GaAs	0.05 $\rightarrow$ 0.55	0.05	N
1	GaAs	-	0.4	N

The band gap structure of No.2 laser is given by Figure 4.2. It is a typical graded index separate confinement heterostructure (GRINSCH) of AlGaAs-GaAs laser diode structure.

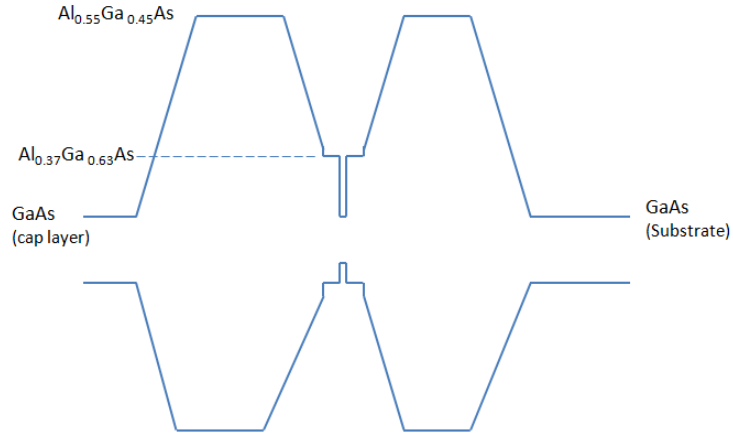


Figure 4.2: A schematic description of band gap structure of No.2 sample

4.3 Enhancement of intermixing by sputtering

SiO_2

Intermixing is achieved by encapsulating the top of the sample in order to provide layer that can absorb the atoms (Ga) from cap (GaAs) layer during annealing. Depletion of Ga atoms in the cap layer causes migration of other Ga atoms through the quantum well which is followed by interdiffusion of the atoms in the barrier (Al) and the atoms (Ga) in the quantum well which results in disordering of the quantum well and subsequent of the band gap. Among a number of techniques to promote the enhancement of intermixing spin-on silica layer encapsulating [27], SiO_2 encapsulating by PECVD (Plasma-enhanced chemical vapor deposition) [28] etc., sputtered SiO_2 encapsulating are the most reliable techniques. The enhancement is due to assisting of intermixing by bombardment in a plasma that generates point defects rather than only to provide a absorbing layer. Hence, we decided to use the sputter deposition technique for the encapsulating layer.

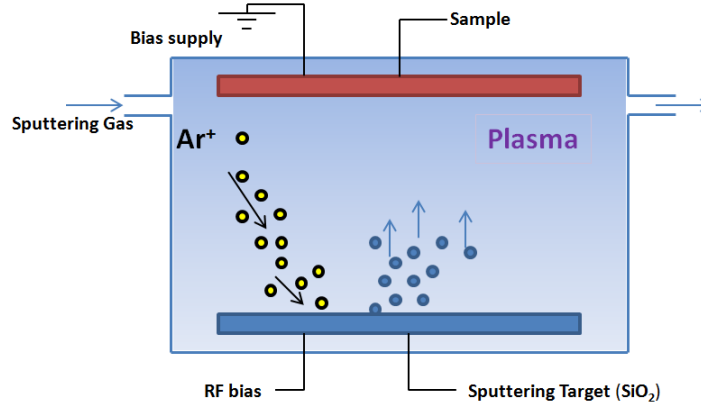


Figure 4.3: A schematic description of sputter deposition

Sputtering is a thin film deposition technique which is one of the physical vapor deposition techniques, Fig. 4.3. A sputtering system is composed of a target (SiO_2) material facing a substrate onto which SiO_2 will be deposited. Target atoms are bombarded, in a vacuum chamber, by ions of an inert gas (Ar)

onto the substrate by momentum exchange between charged atoms of sputtering gas and atoms of the target. Plasma environment created by the high electric field ensures that ions move rapidly onto negatively charged target.

Sputtering deposition techniques can be divided by three methods: DC, RF and magnetron sputtering. For conductive materials DC sputtering can be used, while RF sputtering is preferred for insulators. Magnetron sputtering technique can be used with either, it is preferred for higher ionization of inert gas in order to increase the sputtering rate and to obtain a narrower path. In our experiments we used RF sputtering system since our target was SiO_2 . Processes were performed under about $5 \times 10^{-6} mbar$, 200 sccm Ar gas flowing and 100 W applied to target.

Typically, free electrons in the environment are accelerated by negatively biased electrode (cathode) and ionizing Ar atoms to form, Ar^+ . Ionized atoms are strongly accelerated into the cathode which results in the creation of more free electrons maintaining the plasma. Once these free electrons interact with neutral gas atoms, the gas atoms emits photons due to energy conservation which is the reason of glowing of the plasma.

4.4 Suppression of intermixing by thermal evaporation of SrF_2

Suppressing of interdiffusion in (Al)GaAs laser structures can be accomplished by different deposition techniques and different encapsulant layers. After a large number of investigations to prevent disordering, thin films of SrF_2 was concluded as the best suppression layer [2]. In that work, to inhibit the interdiffusion, thermally evaporated SrF_2 operation was compared with other most common techniques, such as PECVD deposited SiO_2 and Si_3N_4 followed by 30 seconds RTP at $1000^\circ C$. The results show that SrF_2 is by far the best method to inhibit disordering. Hence, we decided to use SrF_2 to prevent the intermixing throughout the rest of this thesis. Though it is dangerous (poisonous) and extra care has to

be taken, we obtained good results to prevent intermixing using thin films of SrF_2 .

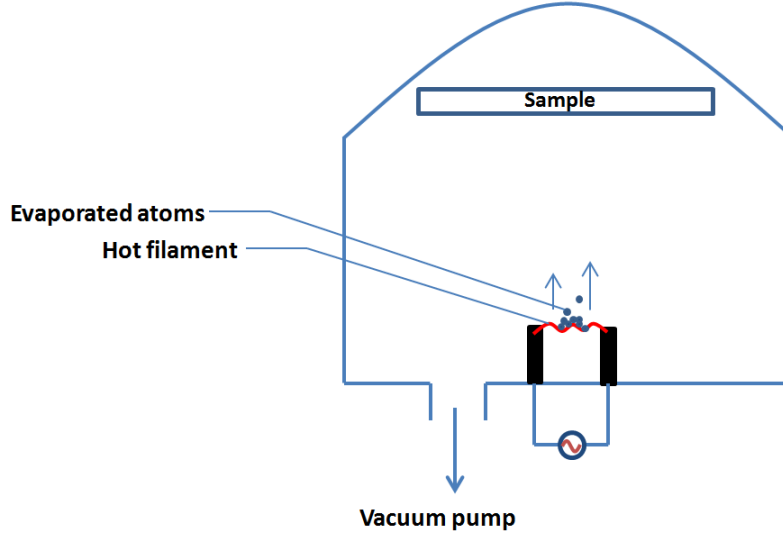


Figure 4.4: A schematic description of thermal evaporation deposition system

Thermal evaporation deposition of SrF_2 is also a physical deposition technique for thin-film technology. The goal is to use a source material (SrF_2 in our case) to coat a thin film on a sample. Deposition takes place by heating a filament like holder or boat (such as W, Mo or Ta which have high melting points and low vapor pressures) upon which the source material is placed. The material to be deposited either melts or sublimates that result in a vapor pressure to build up of the material to be deposited. Evaporation and subsequent adsorption leads to a condensed material that is coated on the substrate in the vacuum chamber, Fig.4.4.

The important parameter in this process is that the holder(boat) of the material should not react with the source material on it. For our process, phase diagrams shows that SrF_2 does not react with W (boat) which has a melting point of about $3422^{\circ}C$, whereas SrF_2 's sublimation point is around $1477^{\circ}C$.

4.5 Rapid thermal annealing (RTP)

RTP was first developed for ion implantation, however, being a transient heating process made it more useful than furnace processing, since the duration of annealing can be shortened from several hours to tens of seconds by RTP. Hence its application widened to thermal oxidation, silicide formation, and other applications in semiconductor device fabrication. More specifically, in one recipe, both heating and cooling take place rapidly in a wide range of temperatures, (i.e. 200-1250°C) and the problem of annealing duration limitation of semiconductor devices is dealt with desired ramp and steady rates eliminating the thermal shock problems either.

In RTP system, there are tungsten-halogen lamps that act as heat sources and placed, in general, upside and downside of the (Si) wafer on which the sample to be annealed is situated in order to obtain a good uniformity. To control the temperature, thermocouple or a pyrometer are used. The former is contacting device, while the latter is non-contacting device and measures thermal radiation of sample's surface, to determine the temperature.

QWI comes about at temperatures higher than the congruent evaporation temperature (T_c) which is a fundamental surface characteristic of semiconductors. It means that group V atoms (As) evaporate faster than group III atoms (Ga) in GaAs based structures. Therefore, in RTP, most of the time, samples are, in addition to SiO_2 encapsulating layer, sandwiched between fresh GaAs wafers in order to prevent overpressure of As which are called proximity caps.

4.6 Photoluminescence (PL) spectroscopy

Optical characterization of semiconductors can be performed by photoluminescence (PL) spectroscopy, phonon Raman scattering spectroscopy and infrared absorption spectroscopy. **PL**, is *particularly sensitive to impurity and defect induced properties of materials*, and **Raman scattering**, *can be used to determine lattice vibrations and stress, presence of impurities and free carriers*, can be monitored in the near UV, visible and near IR regions-over $0.4\text{-}1\mu\text{m}$, whereas absorption spectroscopy in the **IR**, *characterizes the thickness of layers, alloy composition of lattices, concentration of impurities and defects*, spans a large range: $1\text{-}5\mu\text{m}$ (near IR), $5\text{-}50\mu\text{m}$ (middle IR) and $50\text{-}1000\mu\text{m}$ (far IR). In our study, we used mainly PL spectroscopy due to the fact that changes in the band gap can be easily realized by detection of PL spectrum and, in particular, shift.

PL mechanism takes place as follows: Incident light from an (Ar^+) laser falls onto the surface of the semiconductor sample through the optical configuration as in the Figure 4.5. Photons with energies larger than the band gap of the sample are absorbed raising the electrons from valence band(VB) to conduction band(CB). It is important to note that the absorption of the incident light can occur in many different ways such as, by transferring electrons from a neutral donor to CB, from VB to a neutral acceptor, from VB to ionized donor and from ionized acceptor to the CB [29]. Once the excited electrons (in the CB) return to VB radiative emission is obtained.

In this study, PL spectra of as-grown with encapsulant (unprocessed) sample at 6K ws measured and observed emitted of light. In samples that were processed for intermixing, we observed increasing blue shifting of the PL peak emanating from the quantum well, indicating accompanied disordering and increasing band gap. In comparison with absorption spectroscopy, PL is a much better characterization technique, in particular for quantum well semiconductor structures, inasmuch as the discrete nature of energy levels in the quantum wells leads narrower peaks. Excitonic behaviour is also significant in PL spectroscopy, however, in our case, highly doped layers screen the Coulomb interaction between the carriers.

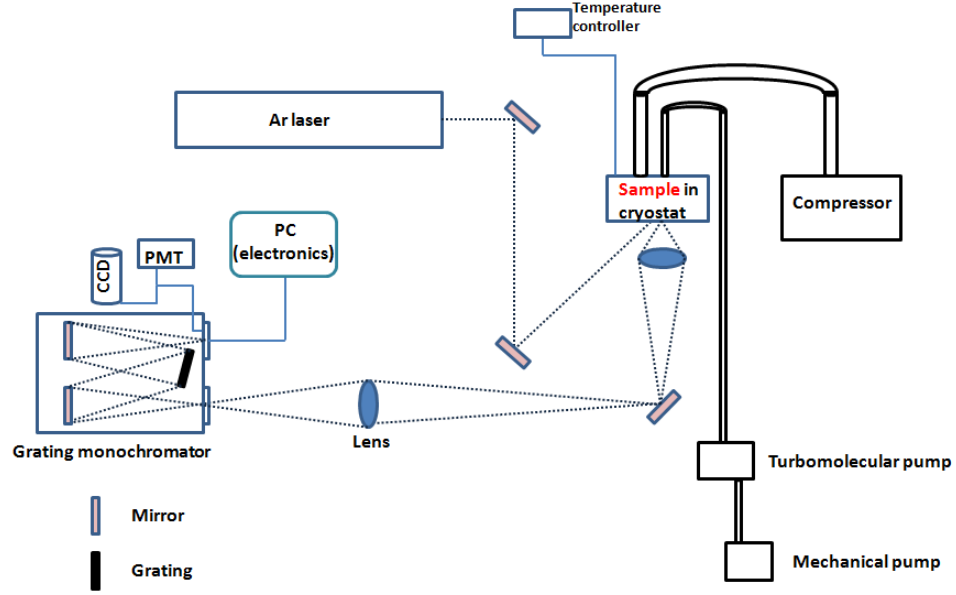


Figure 4.5: A schematic description of the Photoluminescence system

PL system used in our laboratory is illustrated in Fig.4.5. Laser source should have photon energy higher than the band gap of the sample in order to excite the electrons in the VB. Ar^+ gas laser, can typically operate at 457.9 nm, 488 nm and 514.5 nm. We used, in general, 514.5 nm line of the laser which correspond to a photon energy of about 2.41 eV which exceeds the bound energy levels of GaAs quantum well where the band gap energy of bulk GaAs is around 1.42 eV. The light is directed on to sample in the cryostat through the optical path shown in the Figure 4.5. Characterizing the semiconductor at low temperatures ensures a sharper and stronger luminescence peaks minimizing the thermal effects on the sample. For instance, at room temperature the thermal broadening is about 25 meV, whereas it may be reduced to <1 meV at liquid helium temperatures. The cryostat we used is cooled down to about 6 K. Vacuum level of the vacuum jacket in the order of 10^{-3} mbar is sufficient to cool down to the required temperature. Once the desired vacuum level is obtained, the compressor is activated and compressing the helium in the chamber, followed by the cooling.

Emitted light from the sample is transmitted to a double grating monochromator which selects a narrow range of wavelengths to transmit to input of the detector, which is either a charge-coupled device (CCD) or photomultiplier detector (PMT). In our system, as shown in the figure, Czerny-Turner grating configuration is used. Once we select a range of wavelengths, the monochromator scans the intended wavelength range and the peak as sharp and narrow. As in every (opto)electronic system, PL involves noise as well. The best signal-to-noise ratio is obtained by cooling the detector where we used liquid nitrogen to cool down the CCD detector, while the PMT is cooled down to $-20\text{ }^{\circ}\text{C}$.

4.7 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ECSA) is a surface analysis technique that is used to identify mainly the elemental composition in ultra high vacuum ambient (UHV, $<10^{-9}$ mbar). The technique is developed by Kai Manne Brje Siegbahn accompanied by Nobel Prize in physics (1981). XPS is based on **photoelectric effect** that uses X-rays as the radiation in order to eject the core electrons (photoelectrons) of the atoms of the surface material in the range of 1-10 nm (20 atomic layers). The spectrum is obtained recording the binding energy of the photoelectrons, Fig. 4.6.

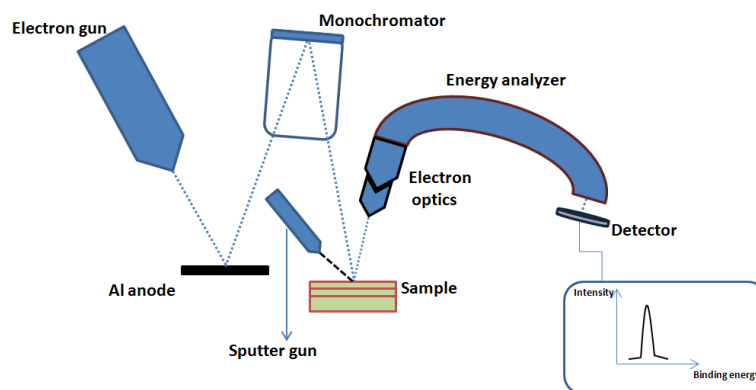


Figure 4.6: A schematic description of XPS setup.

Among a broad range of areas used for analysis of the XPS such as inorganic compounds, polymers, thin film semiconductors, catalysts, bio-materials etc. , we are interested in the elemental characterization of thin film semiconductors. Elemental composition of epitaxial layers below the top surface layer (depth profiling) in thin film structures is obtained combining the XPS with Ar^+ sputtering. Binding energy of the photoelectron from sputtered layers is obtained by the electron energy analyzer based on the conservation energy equation,

$$E_{binding} = E_{Xray} - (E_{KE} - \phi) \quad (4.1)$$

where $E_{binding}$ is the binding energy of photoelectron, E_{Xray} is the photon energy of Al K_α (~1487 eV) or Mg K_α (~1253 eV) X-rays, E_{KE} is the kinetic energy of the photoelectron and ϕ is the work function of the material. The binding energy of core electrons in the atomic orbitals produce peak intensities for each layer and the number of detected electrons are linearly related with the peak atoms in intensities. Besides elemental identification, amount of electrons detected gives the information about concentration of atoms. An important capability of XPS is the energy shift, called the chemical shift, of the photoelectron peaks due to formation of various bonds. This allows the determination of charge state of the atoms that are detected.

As in the figure, Al K_α x-ray photons produced by Al anode hitting electrons on it from the electron gun. Monochromator, employs only quartz material for X-ray monochromators due to its lattice spacing, is used to select certain energies of x-rays due to Bragg reflection, ~1487 eV, then these photons fall onto the sample. Photoelectrons ejected from sample are directed by electron lenses in order to slow and focus them. Decelerating helps to get better resolution. Electron energy analyzer is comprised of two hemispherical plates under applied voltage difference. After the photoelectrons reach to detector, the energy spectrum is derived measuring the electron current as a function of the potential difference applied to plates. Ar^+ sputtering at about 10^4 keV is used to etch the sample to get information from underlying layers.

4.8 Results and discussions

In these experiments, to enhance the interdiffusion samples were sputtered with SiO_2 , generally to a thickness of 200 nm, at 100 W, under 200 sccm flow of Ar^+ . Chamber base pressure was 5×10^{-6} mbar. The main reason to use sputtering to deposit SiO_2 , rather than using chemical deposition, is that bombardment of the surface with energetic ions is believed to create point defects on the surface. Suppressing the intermixing for active waveguide laser regions, on the other hand, was achieved by thermal evaporation of SrF_2 . In the literature, after a large number of investigations SrF_2 was observed to be the best material for suppressing the intermixing[2]. Then, the samples were annealed generally in an RTP system with forming gas flowing. During RTP, the samples were sandwiched between the GaAs wafers provide an overpressure of As. This inhibits the As diffusion and maximizing Ga diffusion into SiO_2 encapsulant. The demonstration of intermixing, i.e. increasing the effective band gap energy of quantum well where the light is emitted, is most commonly understood by photoluminescence spectroscopy: intermixed sample displays a blue shifted peak (at smaller wavelength) compared to as-grown (not processed) sample. Therefore, main characterization tool of our samples is luminescence spectroscopy. PL Characterizations were performed always under the same conditions, 514 nm Ar^+ laser line between 20-25 mW at 6.7 K. Apart from PL characterization, XPS technique was used to understand the detailed mechanism of IFVD which gave us a valuable outlook about movements of defects after sputtering and rapid thermal annealing.

4.8.1 Low temperature photoluminescence characterizations

A survey spectrum of the as-grown sample [GaAs(cap)/AlGaAs(clad)/AlGaAs(wg)/GaAs(QW)/AlGaAs(wg)/AlGaAs(clad)/GaAs(subs)] at 6.7 K is shown below. There are two main features. The blue shifted region of the spectrum above 600 nm is related to the $Al_{0.37}Ga_{0.63}As$ cladding layers. The band gap of the alloys of GaAs with Al at the point at 2 K are given by the following equation:

$$E_g = 1.5194 + 1.36x + 0.22x^2 \quad (4.2)$$

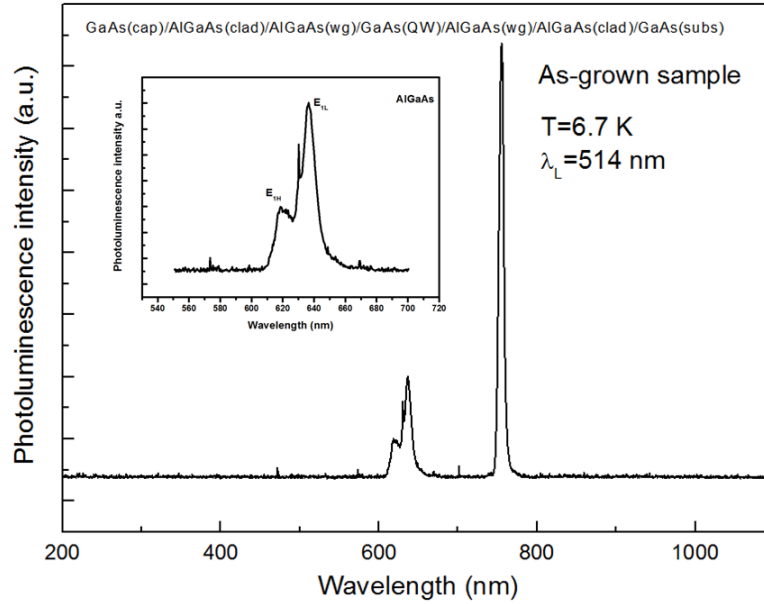


Figure 4.7: Spectrum of as-grown sample.

We identify the peaks at 620 nm and 632 nm as alloy transitions of AlGaAs cladding layer with $x=0.37$ as the AlGaAs layers with $x=0.55$ are expected to be silent due to the fact that AlGaAs become an indirect semiconductor when the Al mole fraction is ~ 0.45 , as shown in the below, Fig. 4.8a. The sharp peak in the spectrum is due to the GaAs quantum well. This quantum well forms with $Al_{0.37}Ga_{0.63}As$ waveguide barrier layers surrounding the GaAs quantum well. The

band offsets between GaAs and AlGaAs layers is shown below [34], Fig. 4.8b. The band offset for the valence band is about 0.20 eV for $x=0.37$ while it is 0.25 eV for the conduction band, from the analysis of the PL peak positions of the peak, we find that Al mole fraction is, $x=0.32$, i.e. smaller than design criteria of, $x=0.37$. The PL emission from the quantum well is located at 755 nm and the FWHM is 15 meV. While the width of the quantum well can be smaller, this is a reasonable value for MOCVD grown materials.

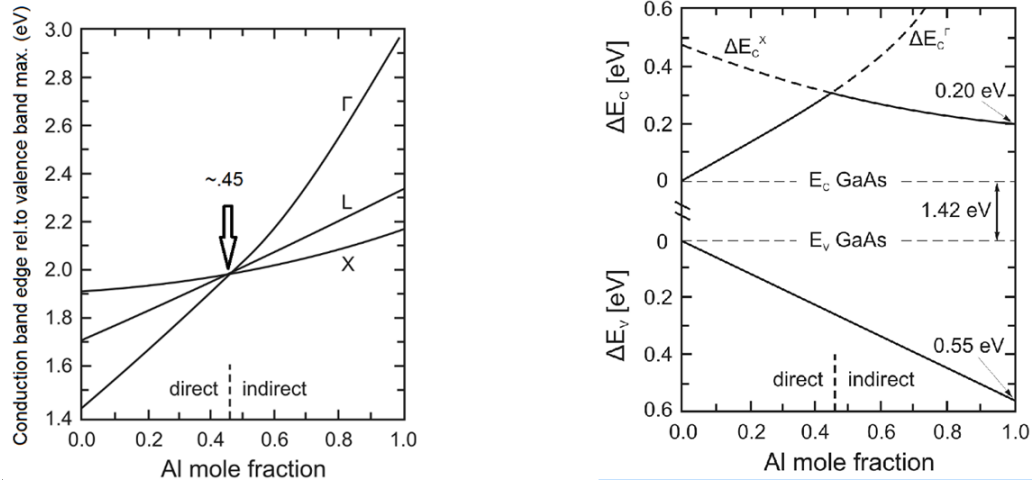


Figure 4.8: Spectrum of band offset due to mole fraction [34].

Our initial trials were conducted with a sample that had a quantum well luminescing at 772 nm. The results of annealing with RTP operating at 850°C , for this sample is given Table 4.1, Fig. 4.9. We observe a blue shift of the PL peak from the quantum well as a function of annealing time. This is to be expected since the annealing time is proportional to the diffusion length. The longer the diffusion time at high temperatures the larger is the diffusion length and the larger is the QWI. This reflects itself in terms of PL blue shift.

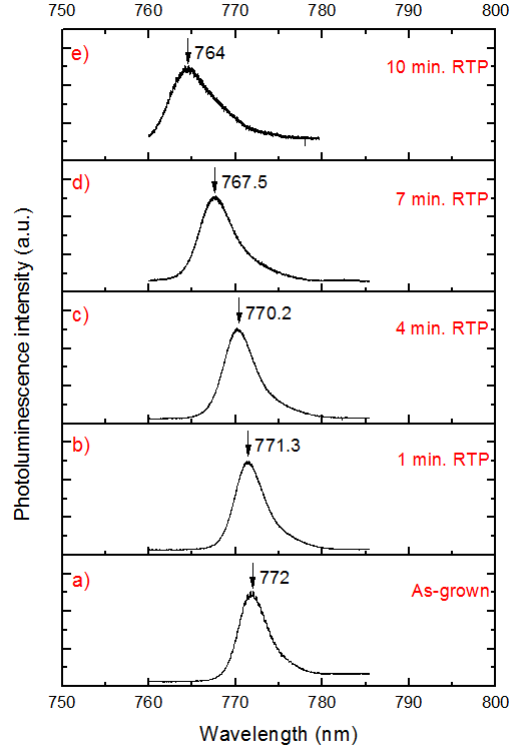


Figure 4.9: Photoluminescence spectra of IFVD samples. 200 nm SiO_2 sputtered on $Al_{0.7}Ga_{0.3}As - GaAs$ laser structure at $850^\circ C$ RTP with different times.

However, our RTP system could reach only up to $850^\circ C$. Therefore, our studies were limited to annealing conditions up to $850^\circ C$. The Figure 4.9 shows that under these circumstances QWI is quite limited. However, such small blue shifts can be observed in samples that were not coated with sputtered SiO_2 , as well. This meant that a small number of Ga vacancies can get absorbed by cap layer rather than encapsulating layer. In total 8 nm blue shift was observed which is not sufficient to conclude that QWI is achieved [1].

After an upgrade to the RTP system, we focused on IFVD at 850°C and higher temperatures. Intermixing the Ga vacancies in the quantum well and Al interstitials in the barrier layer was achieved by showing the temperature dependence of QWI on $\text{Al}_{0.55}\text{Ga}_{0.45}\text{As} - \text{GaAs}$ laser structure samples (all other experiments were performed on this structure). As in the Fig. 4.10, we obtained the best result at 950°C . Following the variations of annealing temperatures, we decided to obtain a better result by changing different parameters to obtain maximum blue shift.

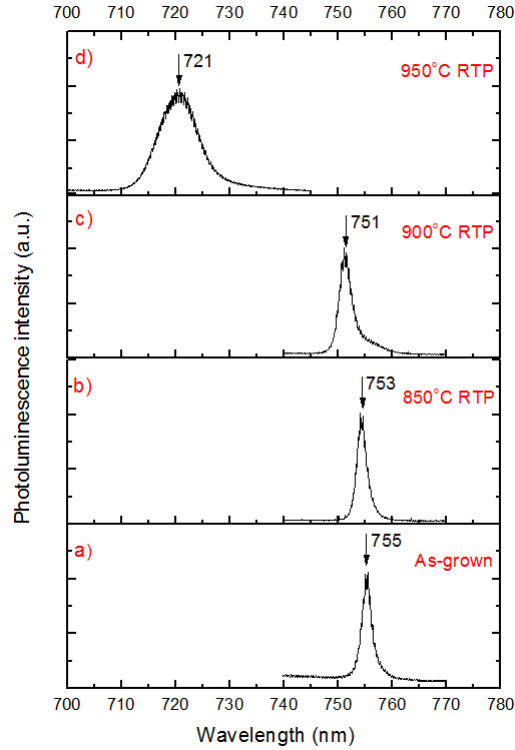


Figure 4.10: Photoluminescence spectra of IFVD samples. (200 nm SiO_2 sputtered on $\text{Al}_{0.55}\text{Ga}_{0.45}\text{As} - \text{GaAs}$ laser structure at different temperatures by 3 minutes RTP.)

According to Xin Wen et al [30], the degree of intermixing strongly depends on the thickness of the SiO_2 which we also studied in our work, Fig. 4.11 shows the intermixing linearly increases with the thickness of SiO_2 . We also studied the annealing time dependence on intermixing clearly because as in the Fig.4.9, the time dependence at $850^\circ C$ is somewhat uncertain as was discussed earlier. Hence, we decided to anneal the 400 nm SiO_2 sputtered sample in 1 minute intervals up to 3 minutes. Xin Wen et al showed that disordering degree increases with the thickness of SiO_2 and width of quantum well, while it decreases with increasing quantum well depth (distance between quantum well and surface of the sample). Although they proved that the interdiffusion rate increases with SiO_2 thickness, they could not reach the solubility limit: largest thicknesses they sputtered was $1.3\mu m$ and they obtained 90 meV of blue shift, whereas 130 meV of blue shift was obtained with 400 nm SiO_2 layer in our study. In general, an increase in FWHM of the PL peak arising from the quantum well with increase of SiO_2 thickness is observed. Similarly, an increase of FWHM of the PL peaks with annealing time is easily seen, from 2.4 nm (a) to 5.1 nm (d).

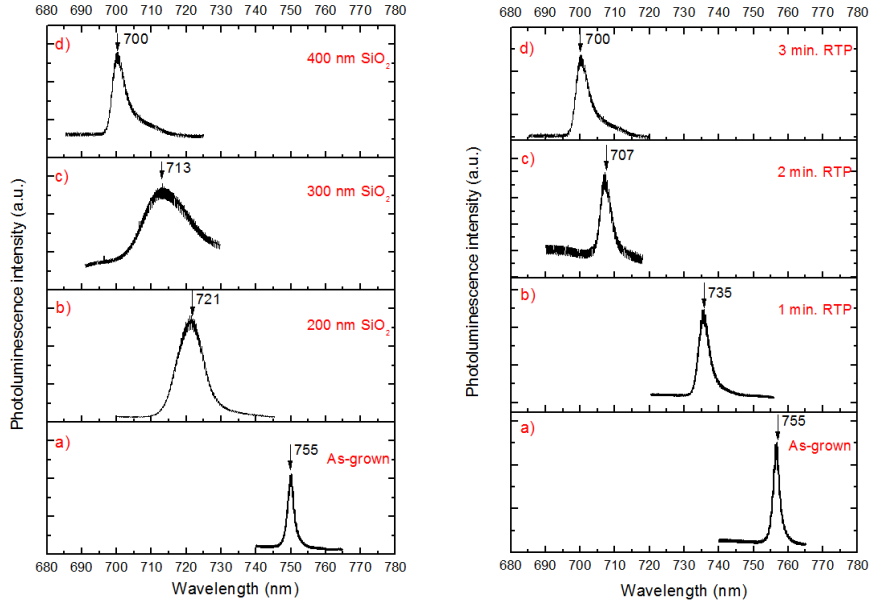


Figure 4.11: SiO_2 thickness dependence on intermixing at $950^\circ C$ 3 minutes RTP (left) and annealing time dependence for 400 nm SiO_2 sputtered at $950^\circ C$ (right).

One parameter that influence the degree of the intermixing, we believe, is the distance between quantum well and surface of the sample (quantum well depth). Observing such an effect is possible if the laser structure with lower thickness of cladding layer was available. However, we did not have access to such a sample. Therefore, we chemically (wet) etched the sample with thinner claddings by about $1.4\mu m$ using $H_2O - H_2O_2 - H_3PO_4$ (5 nm/s etching rate) leaving behind a sample with a $0.95\mu m$ thick cladding layers on the quantum well, whereas the original (in as-grown structure) thickness between quantum well and surface of the sample (without encapsulating SiO_2 layer) was $2.35\mu m$.

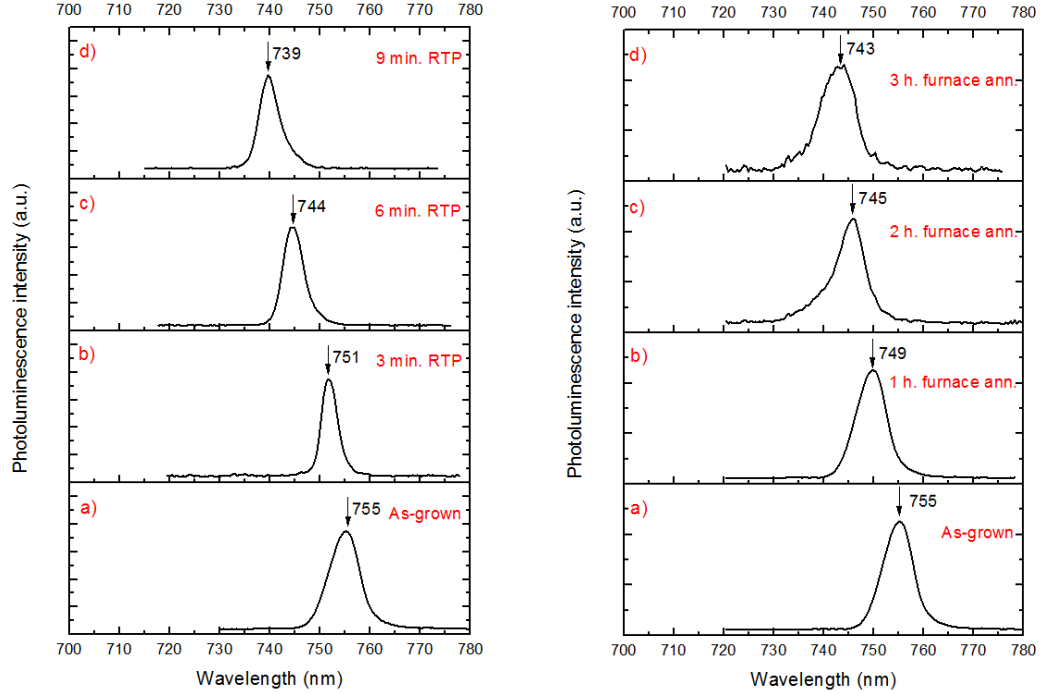


Figure 4.12: Photoluminescence spectra of $1.4\mu m$ etched, 200 nm SiO_2 sputtered sample at $900^\circ C$ for 9 minutes in total (left) and in furnace for 3 hours in total (right).

On this thinned down sample we first, performed the usual annealing process at $900^\circ C$ in both RTP and furnace, since we believed that at lower quantum well depth we could get sufficient blue shift compared to $950^\circ C$. Although both processes did not result in significant interdiffusion, RTP processing produced slightly better results compared with 3 hour furnace processing, Fig. 4.12. RTP reaches high temperatures using lamps whereas a standard high temperature

furnace works with blackbody radiation of high temperature ceramic tube. The difference between RTP and furnace annealing results is possibly due to different optical spectral distributions in RTP and furnace creating different carrier profiles that enhance migration. In any case, RTP is a preferred method due to lower thermal budget it offers to the sample as well as ease of operation and lower costs. Furthermore, there are many limitations in furnace processing as discussed in [31], e.g. the thermal degradation after long time furnace annealing.

A similar thinned down sample was annealed in RTP up to 9 minutes. Fig. 4.13 shows the largest blue shifted (154.7 meV) experiment in this thesis, in 9 minutes.

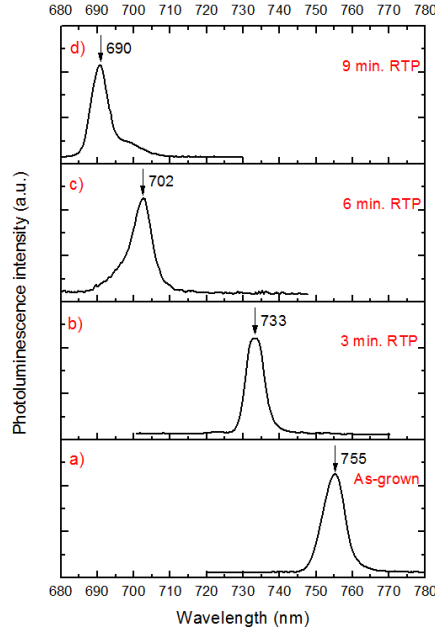
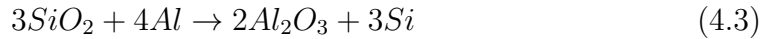


Figure 4.13: IFVD on $1.4\mu m$ etched, 200 nm SiO_2 sputtered sample at $950^\circ C$ for 9 minutes in total.

In the case of thinned down samples, under the same annealing conditions, the blue shift of the PL peak is smaller when compared with similar samples that were not etched. This result is in contrast with an earlier study [30] when the cladding layers were varied between different samples. In the study, $0.5\mu m$, $1\mu m$, and $2\mu m$ AlGaAs layer were used and the maximum blue shift was observed

in 0.5 μm layered sample. However, in our thinned down samples did not have a GaAs cap layer. This may lead to complications where oxidation of Al in the AlGaAs cladding layer prior to encapsulant deposition as well as oxidation with the encapsulant during annealing may take place with accompanying Si in-diffusion may take place. The interaction of SiO_2 with AlGaAs via



can take place, which can act as IID mechanism and shows the necessity of cap (GaAs) layer for IFVD disordering.

The importance of intermixing increases dramatically when it can be applied selectively on desired regions of the same sample. This means while intermixing is sought in selected regions, the rest of the sample needs to be protected from intermixing by suppressing possible intermixing processes. Suppressing of intermixing was achieved by SrF_2 thermal evaporation by Beauvais et al [2]. In their study, SrF_2 operation was compared with other most common techniques to inhibit the interdiffusion, plasma enhanced chemical vapor deposition (PECVD) of SiO_2 and Si_3N_4 followed by 30 seconds RTP at $1000^\circ C$. For 20 nm thick cladding layers the degree of disordering ΔE observed was 260, 286 and 7 meV for SiO_2 , Si_3N_4 and SrF_2 depositions, respectively. The results show that SrF_2 is by far the best method to suppressing the disordering. On the other hand, for 1000 nm thick cladding layers the shift, ΔE , observed was 17 meV by SrF_2 deposition which points to increasing the thickness of cladding layers makes it difficult to suppress the disordering. They also varied the SrF_2 thickness between 105 and 185 nm and observed almost no difference between samples with different SrF_2 thicknesses. Our study gives better results in terms of the duration of annealing and also about two times longer distance of quantum well to surface layer. After 3 minutes annealing, rather than 30 seconds, only 20 meV (9 nm blue shift) disordering was observed, while the FWHM changed from 2.4 nm (a) to 10 nm (d), (Fig. 4.14).

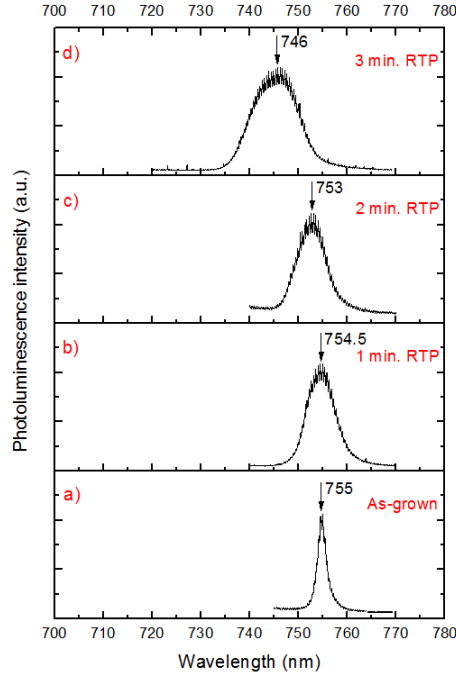


Figure 4.14: Suppression of the intermixing by thermally evaporated 100 nm SrF_2 for 3 minutes at $950^\circ C$.

4.8.2 XPS characterization

XPS analysis was used to understand the diffusion of various elements in the samples under IFVD mechanism in detail by comparing an as-grown sample and sample that had 55 nm (130 meV) blue shift (400 nm SiO_2 sputtered sample annealed at $950^\circ C$ for 3 minutes). The analysed elements were Ga, As, Al, Si, O and C (surface contamination). Both samples were Ar^+ sputtered along with XPS spectra collection to obtain depth information in about 35 cycles which corresponds to 70 minutes. In this section, first, the XPS spectra of as-grown (unprocessed, SiO_2 encapsulated but not annealed) sample and then intermixed sample will be examined. Next, concentration depth profiles of main elements (Ga, Al, As and Si) will be compared in an effort to identify the diffusion of said species. Binding energy values were compared with both the literature and mainly with a comprehensive handbook about XPS spectra of elements [32].

4.8.2.1 XPS analysis of unprocessed sample

Figure 4.15 illustrates the initial surface peak and all peaks through out all cycles for C(1s). Almost every sample is exposed to the atmosphere is subject to small amount of carbon contamination. The main chemical states of C(1s) for contamination are C-C, C-O-C and O-C=C and two of them (C-C and C-O-C) were observed in the spectrum of both as-grown and intermixed samples. The binding energies are 284.0 eV and 286.0 eV, respectively.

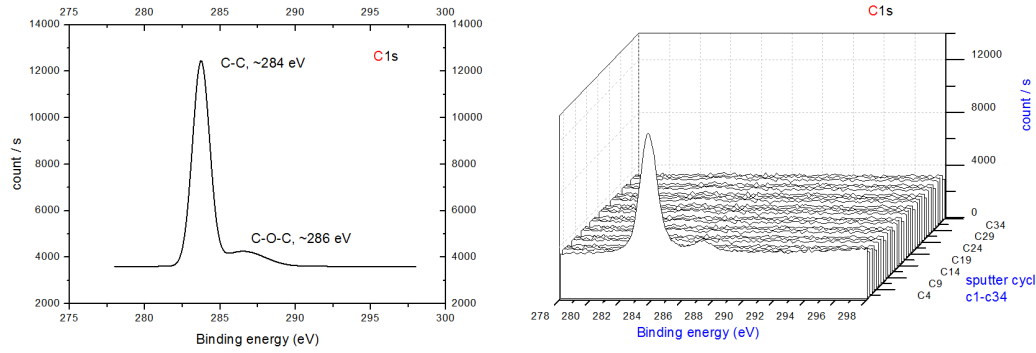


Figure 4.15: First C(1s) peak (left) and all analyzed C(1s) peaks of unprocessed sample.

As in case of oxygen, shown in Fig. 4.16, the binding energy of O(1s) is about 530.0 eV.

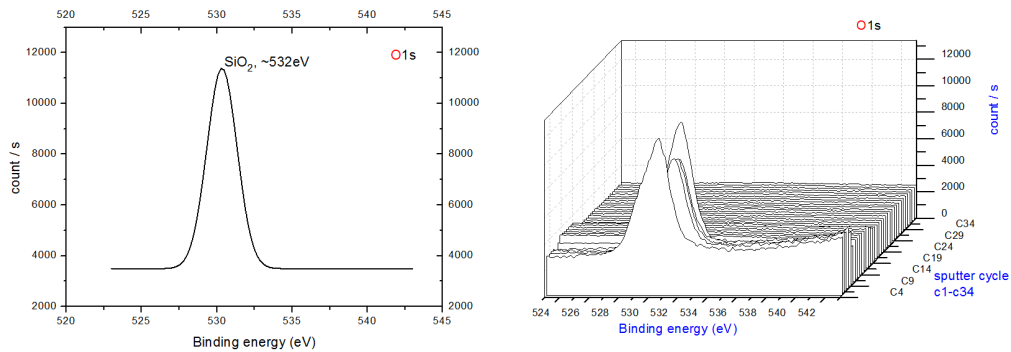


Figure 4.16: First O(1s) peak (left) and all analyzed O(1s) peaks of unprocessed sample.

Common chemical states of O(1s) are metal oxides (529-530 eV), metal carbonates (531.5-532.0 eV), Al_2O_3 (531.1 eV), SiO_2 (532.9 eV), organic C-O (531.5-532.0

eV), organic C=O (533.0 eV) and $O - F_x$ (535.0 eV) [32]. The peak observed in this analysis is matched with the chemical state of SiO_2 which is the only expected state for this sample, 0.9 meV difference can result from strain of SiO_2 layer on GaAs cap layer.

XPS peak for arsenic is acquired for As(3d) photoelectrons and GaAs, As_2O_3 , As^{3+} (GaAs native oxide) and As^{5+} (GaAs native oxide) are the common chemical states that can be found in XPS analysis of these samples. The binding energies are 40.8 eV, 44.1 eV, 44.8 eV and 45.6 eV, respectively [32]. The value of the peak in our XPS spectrum is the state of GaAs as expected and it is seen in the 7th cycle (Fig. 4.17), because 500 nm GaAs cap layer is placed below the surface layer of 400 nm SiO_2 , (Table 4.2).

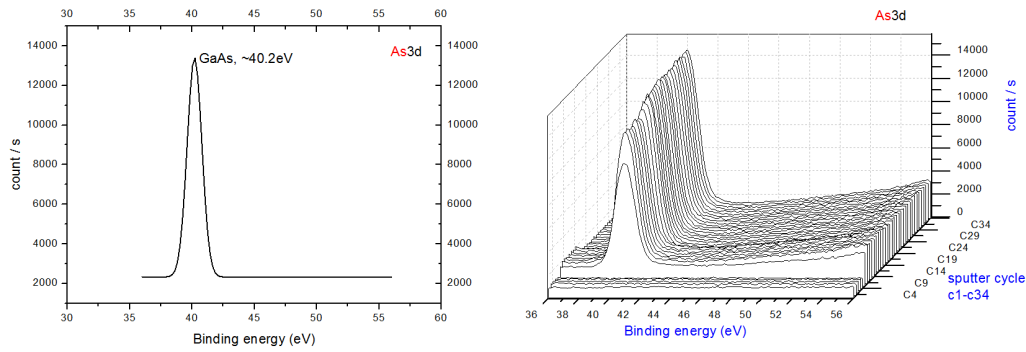


Figure 4.17: First As(3d) peak at 7th cycle (left) and all analyzed As(3d) peaks of unprocessed sample.

Figure 4.18 illustrates the primary XPS peak of aluminum Al(2p). Most common chemical states of Al(2p) are Al metal (72.6 eV), aluminosilicate (74.4 eV), Al-oxide (74.6 eV) and Al-foil (75.6 eV). It is clear that the peak in the figure corresponds to the state of Al metal. The first peak is observed at 15th cycle in the AlGaAs cladding layer below the GaAs cap layer.

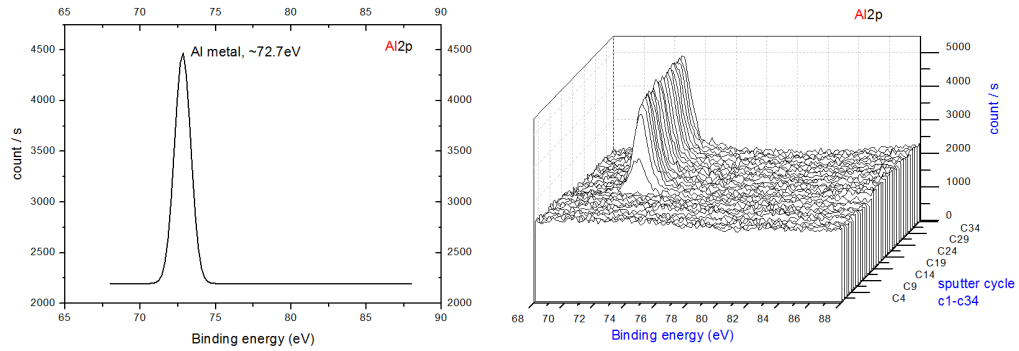


Figure 4.18: First Al(2p) peak at 15th cycle (left) and all analyzed Al(2p) peaks of unprocessed sample.

The most significant element in order to make a comprehensive conclusion in this study is Ga, it being the principal migrating element during annealing. Ga is typically monitored using Ga(2p) both as $Ga2p_{1/2}$ as well as $Ga2p_{3/2}$. In Fig. 4.19, we present the spectra for both Ga(2p) peaks. We also display the depth distribution of these peaks.

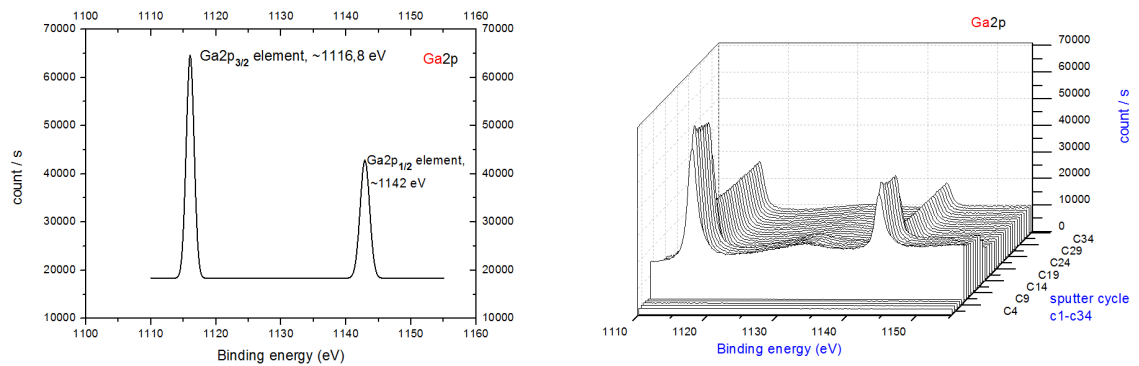


Figure 4.19: First $Ga2p_{3/2}$ and $Ga2p_{1/2}$ peaks at 7th cycle (left) and all analyzed $Ga2p_{3/2}$ and $Ga2p_{1/2}$ peaks of unprocessed sample.

$Ga2p_{1/2}$ is found around the 1140-1145 eV as native oxide or elemental Ga. In

conclusion, the peaks recognized in our spectrum shows that Ga(2p) peaks as the state of GaAs since As(3d) peaks also begin with the 7th sputter cycle.

To monitor Si, Si(2p) signal was used in the XPS measurements. However, one has to be careful as Ga($3p_{3/2}$) significantly overlaps with Si(2p). Although the Ga is monitored by the Ga($3p_{1/2}$) and Ga($3p_{3/2}$) signal observed at 1116.8 and 1142.0 eV, this might become critical when the $SiO_2/GaAs$ interface is monitored, Figure 4.20. During depth profiling with XPS, this may lead to misleading interpretation of Si diffusion into the GaAs material. A comparison of Ga($3p_{3/2}$) peak with Si(2p) peak as well as that of O(1s) allows one to unambiguously identify the $SiO_2/GaAs$ interface.[33].

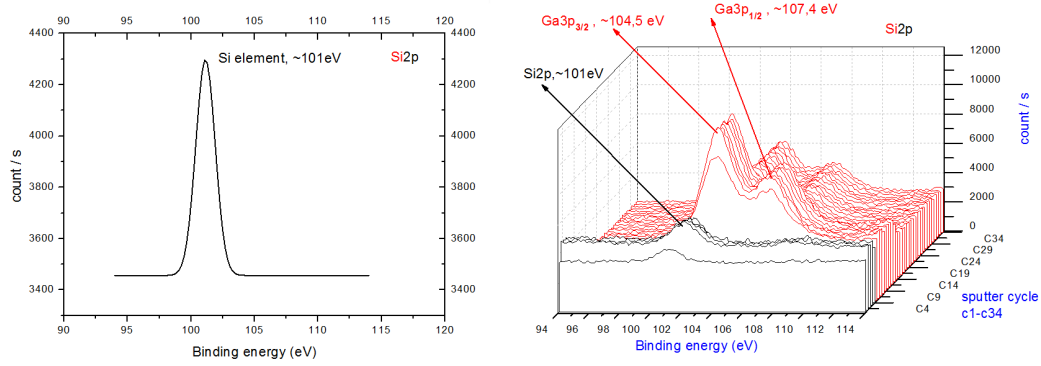


Figure 4.20: First Si(2p) (left) and all analyzed Si(2p) peaks within overlapped Ga($3p_{1/2}$) and Ga($3p_{3/2}$) peaks of unprocessed sample .

As indicated in [37], the diffusion coefficient of Ga is larger than Al , thus the larger migration of Ga defects are expected rather than Al defects, from QW through the surface. Ultimately, vacancy defects of Ga atoms in QW and the interstitials of Al are combined (intermixed) as Frenkel pairs which results in the increase of the quantum well band gap.

XPS depth profile of the samples was carried out by sputtering the surface which etches the sample in order to understand the etch depth after the XPS measurement. Depth profile measurements were performed on the samples by using Bruker Dektak profilometer. Also 3D map scan was also performed to realize encapsulating layer, cap layer and cladding layer, Fig. 4.21. From the surface profile it was found that the sample had a sputtered crater depth of about $1.82\text{ }\mu\text{m}$, which indicates that XPS analysis for unprocessed sample was obtained down to middle of the upper AlGaAs cladding layer.

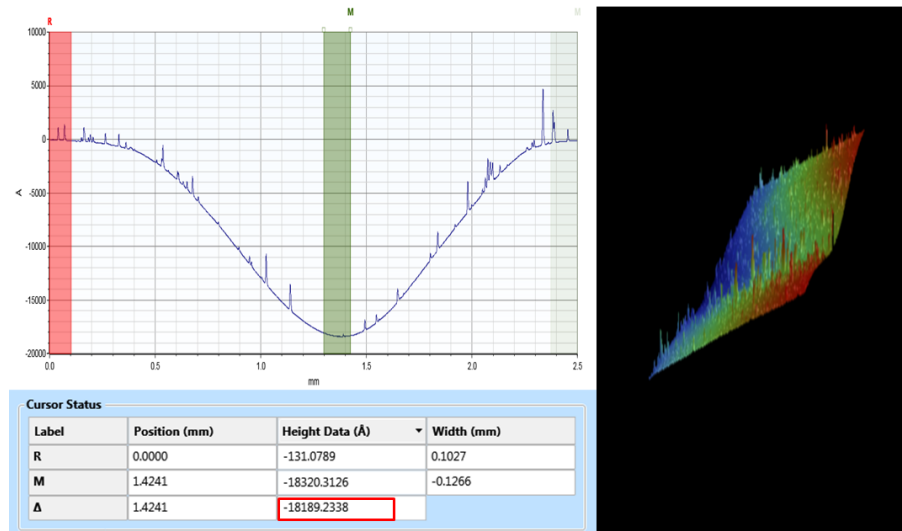


Figure 4.21: Etched profile of unprocessed (as-grown) sample, during XPS analysis by sputtering

Figure 4.22 illustrates the XPS concentration depth profile of an as-grown (unprocessed) sample for the chemical states of C(1s), O(1s), Ga(2p), Si(2p), As(3d) and Al(2p). The evolution of both Si and O signals indicate the presence of the sputtered SiO_2 layer ending around sputter time of 10 min. The decreasing strength of these at the very surface is due to carbon contamination. It is found that both Si and O seem to diffuse into the GaAs cap layer. As oxygen contamination such extent can not be present during epitaxial growth, this is surprising. This may be due to contamination/redeposition during sputtering process or an artifact of nonuniform sputtering. As we do not observe shifts of Al, Ga or As throughout this region, we conclude that this is an artifact of the measurement.

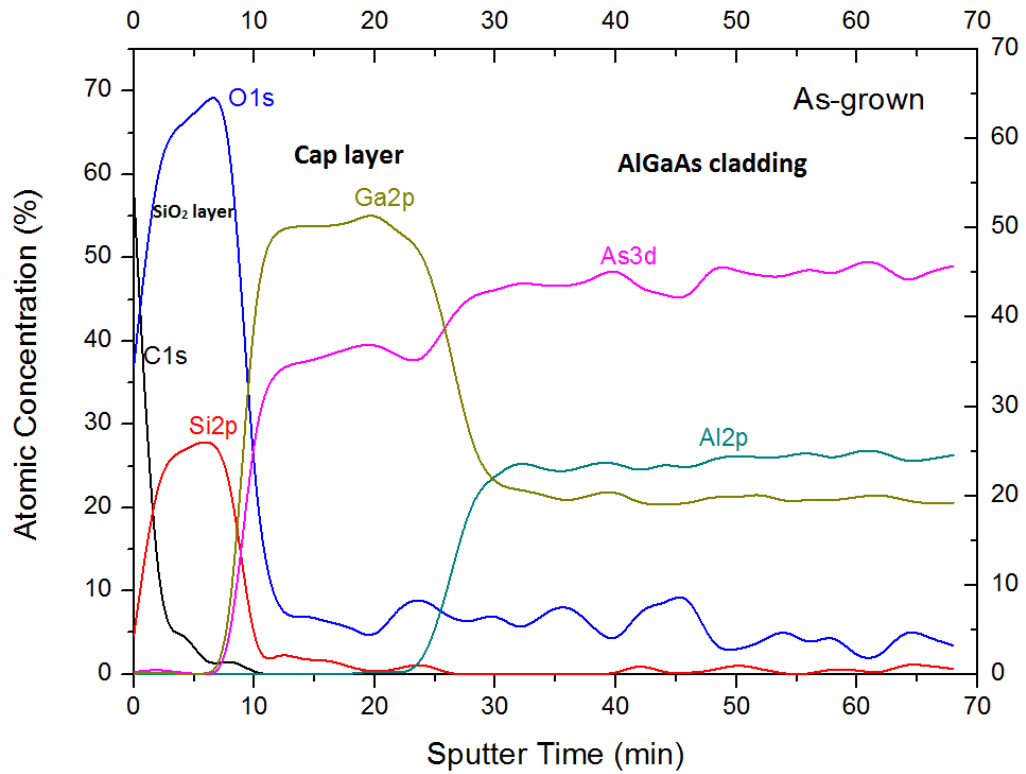


Figure 4.22: XPS depth profile of as-grown AlGaAs/GaAs high power laser diode structure (unprocessed, SiO_2 encapsuated but not annealed).

Furthermore, at least several examples of such data in the literature [33] suggests that this is a common occurrence. Lowered than expected As concentration in the cap layer may be due to preferential sputtering effects, well known in the literature [36]. Deeper into the sample, it is seen that As and Al signal concentration increases and Ga concentration decreases which is expected due to transition from GaAs cap layer to AlGaAs cladding layer. The similar magnitudes of Al and Ga signals are proof that Al mole fraction in the AlGaAs cladding layers is compatible with specification of $x=0.55$.

4.8.2.2 XPS analysis of processed (intermixed) sample

As indicated before, carbon contamination is possible for the samples subjected to atmosphere. Detectable but small quantity of C contamination is observed on the surface of the sample. It is seen in only first sputter cycle with binding energy about 283.1 eV which corresponds to C-C binding, Fig. 4.23. In the following, we present and compare the results of XPS analysis of intermixed sample with as-grown sample.

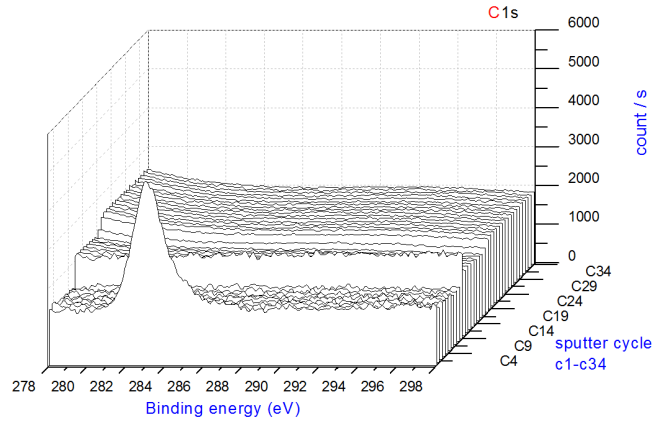


Figure 4.23: C(1s) peaks of 130 meV intermixed sample, 400 nm SiO_2 sputtered following 3 minutes rapid thermal annealing at $950^\circ C$ for 3 minutes.

Figure 4.24 illustrates the O(1s) peaks through the first 10 sputter cycles with the binding energy of 531.4 eV which matches with the chemical state of SiO_2 [32].

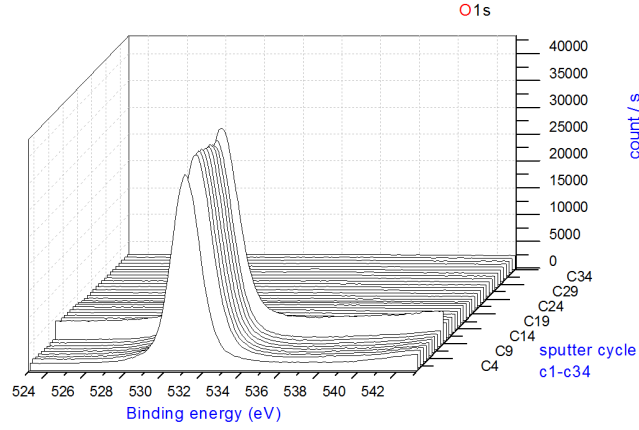


Figure 4.24: O(1s) peaks of 130 meV intermixed sample, 400 nm SiO_2 sputtered following 3 minutes rapid thermal annealing at $950^{\circ}C$ for 3 minutes.

As(3d) spectrum of intermixed sample begins at close to 10th sputter cycle where O(1s) and Si(2p) peaks end up, Fig. 4.25. The binding energy of As(3d) is observed as 40.8 eV corresponding to the chemical state of GaAs.

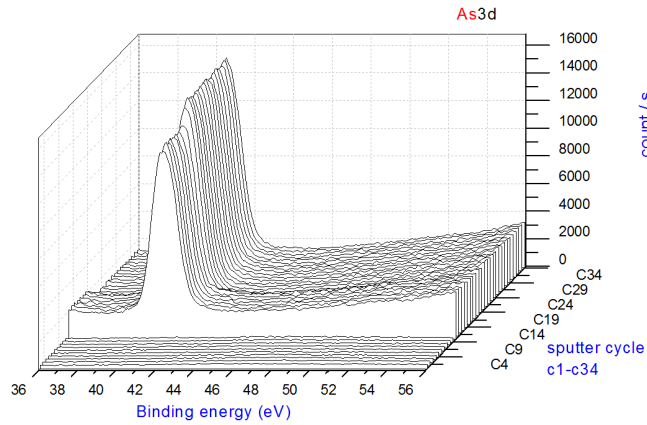


Figure 4.25: As3d peaks of intermixed sample with 130 meV PL shift, 400 nm SiO_2 sputtered following 3 minutes rapid thermal annealing at $950^{\circ}C$ for 3 minutes.

Figure 4.26 shows the Al(2p) spectrum of intermixed sample starting with 18th sputter cycle where AlGaAs cladding layer is placed. Observed peak in the figure is about 73.3 eV, corresponds to the state of Al metal.

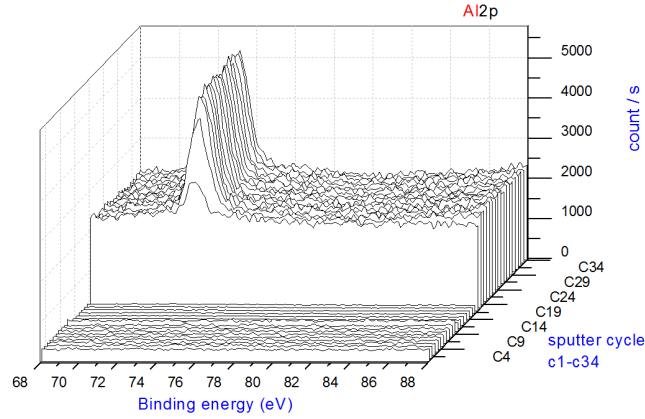


Figure 4.26: Al(2p) peaks of intermixed sample with 130 meV PL shift, 400 nm SiO_2 sputtered following 3 minutes rapid thermal annealing at $950^\circ C$ for 3 minutes.

Ga(2p) peaks start at close to 10th cycle with the binding energies of 1116.8 eV and 1143.6 eV which are related of $Ga2p_{3/2}$ and $Ga2p_{1/2}$, respectively, Fig. 4.27. Ga spectrum begins just before As spectrum.

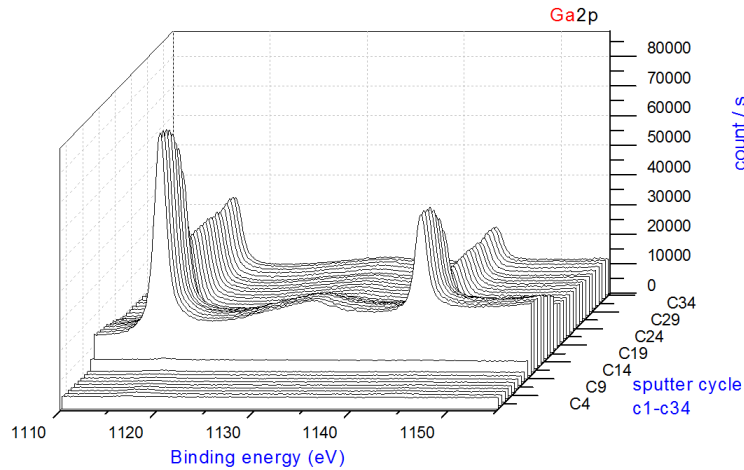


Figure 4.27: Ga(2p) peaks of intermixed sample with 130 meV PL shift, 400 nm SiO_2 sputtered following 3 minutes rapid thermal annealing at $950^\circ C$ for 3 minutes.

Figure 4.28 illustrates the Si(2p) XPS spectrum with Ga(3p) signal. Binding energy value of Si(2p) is seen at energy of 101.0 eV, and Ga(3p) at 104.5 and 107.4 eV. As discussed earlier, the overlapping can be demonstrated as the peaks of Si(2p) must finish as O(1s) sputter cycles which are placed between about 1-10th cycles.

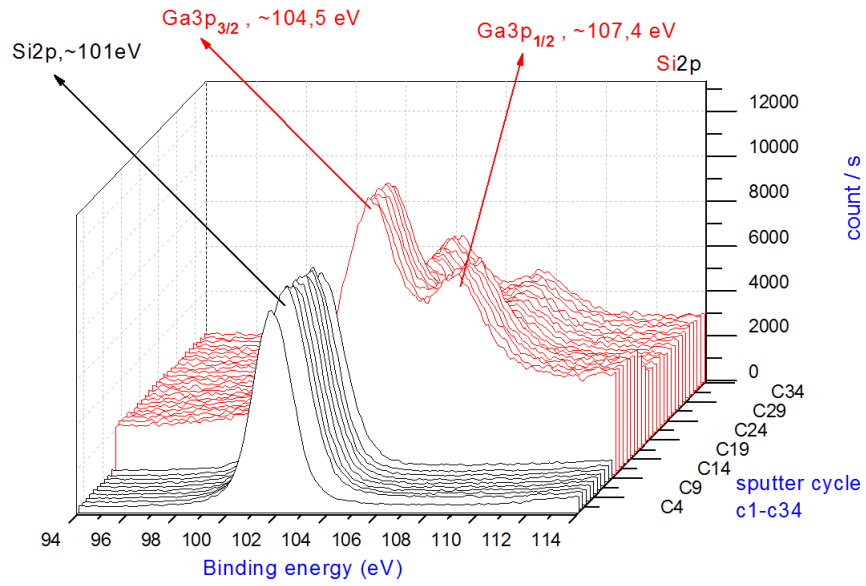


Figure 4.28: Si(2p) peaks of intermixed sample with 130 meV PL shift, 400 nm SiO_2 sputtered following 3 minutes rapid thermal annealing at 950°C for three minutes.

Figure 4.29 shows the profile of etched sample (intermixed) during XPS by sputtering. It was etched about $1.83\ \mu\text{m}$ which indicates that XPS analysis for intermixed sample was obtained down to middle of the AlGaAs cladding layer.

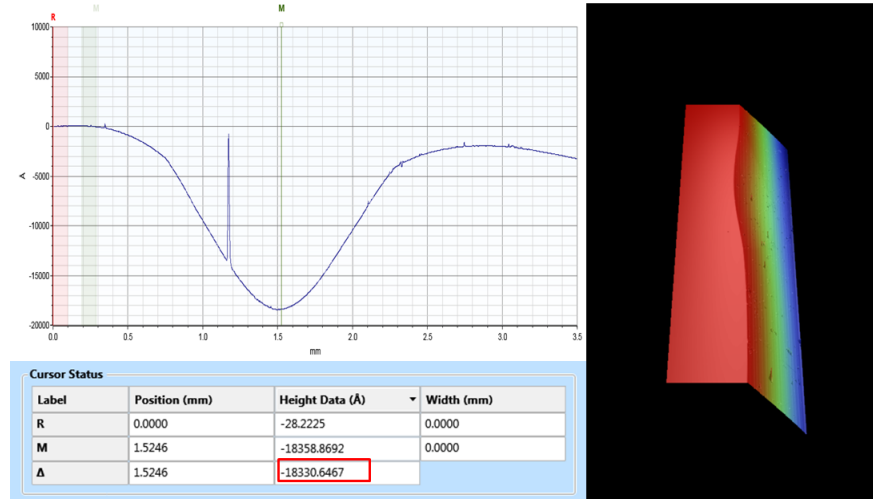


Figure 4.29: Etched profile of intermixed sample, during XPS analysis by sputtering.

Fig. 4.30. gives the XPS depth profile of intermixed sample ($400\ \text{nm}\ \text{SiO}_2$ sputtered followed by 3 minutes annealing at 950°C). Calculated Ga/As concentration difference between unprocessed and processed sample is noticed that Ga concentration is much larger than As comparison with data of unprocessed sample in Fig. 4.22. It is also recognized that after intermixing, some part of Al atoms migrated towards the surface of the sample. Furthermore, this analysis gives us an opportunity to calculate the concentration ratio of elements for intermixed and unprocessed sample, at the beginning of 3rd region. Detailed comparison of the XPS depth profiles of both unprocessed and intermixed sample is given in the next section.

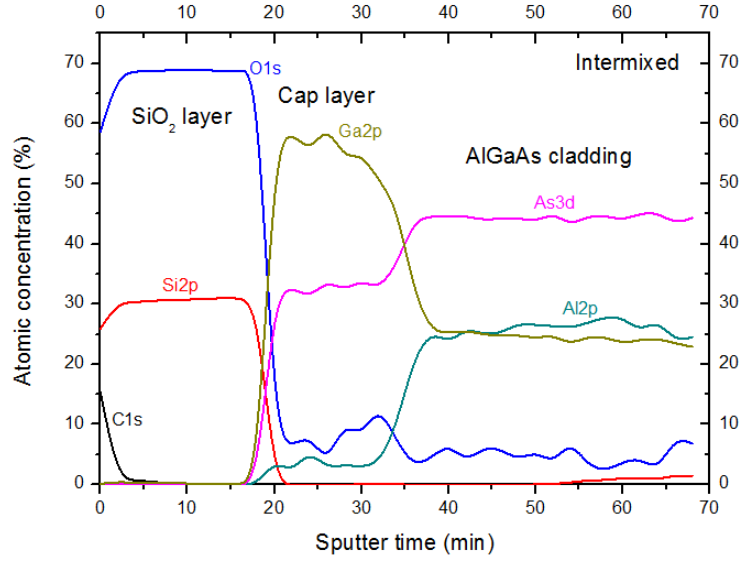


Figure 4.30: XPS depth profile of intermixed AlGaAs/GaAs high power laser diode structure (400 nm SiO_2 sputtered followed by 3 minutes annealing at $950^\circ C$)

4.8.3 Discussions

The first goal of this thesis is to study IFVD on LOC AlGaAs/GaAs laser diode structures with GaAs quantum wells in order to increase the band gap of the quantum well. Changes in the electronic structure of the quantum well reflects as a shift of the photoluminescence from the quantum well. During our experiments it was found that the maximum blue shift of the intermixed quantum well emission is 130 meV corresponding to 55 nm. The maximum intermixing was achieved by varying the parameters during QWI: annealing temperature, duration of annealing and thickness of encapsulating SiO_2 layer.

Figure 4.31 illustrates the relation of annealing temperature and the degree of intermixing. It is observed that the PL shift increases considerably after annealing at $900^\circ C$, Table 4.2. PL shift data shows an exponential-like dependence on the annealing temperature as indicated in Figure 4.31. This exponential-like behavior is in parallel with to the exponential dependence of the diffusion coefficients on temperature. Increasing temperatures lead to dramatic increase in diffusion coefficients which then increases the diffusion length of the species under consideration.

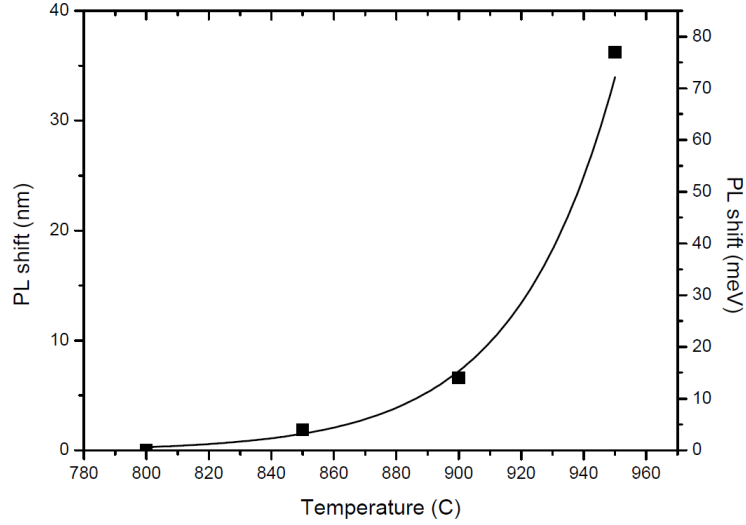


Figure 4.31: The degree of intermixing with annealing temperature (for maximum 3 minutes with 200 nm SiO_2 sputtered sample).

Once the QWI is integrated with laser diode structure, the duration of annealing will influence the other parts of the laser structure. The thermal degradation might seriously affect the reliability and life time of the laser diode after annealing for 2-3 minutes. As the annealing temperature is increased the duration of annealing should be decreased in order to obscure the operation of the laser diode. Therefore, demonstration of the relation of the degree of interdiffusion and annealing time is limited up to 3 minutes, as shown in Fig. 4.32. It is observed that this relation is almost linear as can be expected. In a very simplistic picture, the bound state energies are proportional to the quantum well width, L which can be expected to effectively change of the order of diffusion length that is proportional to the square root of time.

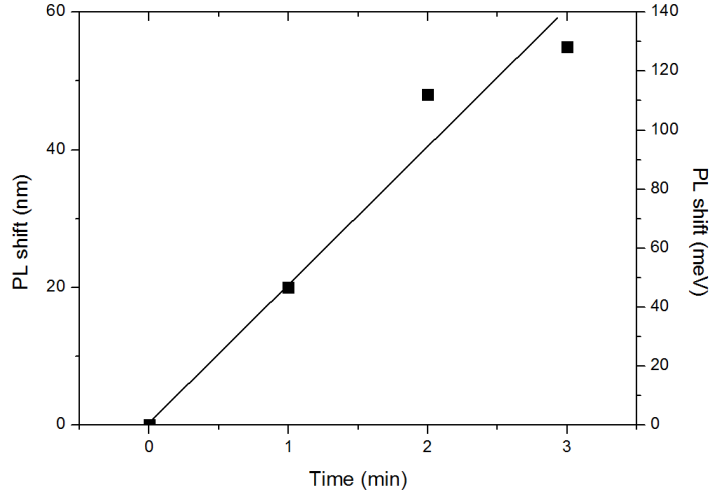


Figure 4.32: The degree of intermixing with duration of annealing (400 nm SiO_2 sputtered sample annealed at $950^\circ C$).

The role of oxide thickness in absorbing migrating Ga atoms has also been discussed previously, in the literature [30]. It is suggested that thicker oxide layers may enhance migration due to their capacity to absorb more Ga atoms. In the literature, SiO_2 layers up to 1300 nm have been used and shown to have the ability to absorb Ga atoms [30]. Hence, we also decided to study the relation of the degree of intermixing with SiO_2 thickness of up to 400 nm, Fig. 4.33.

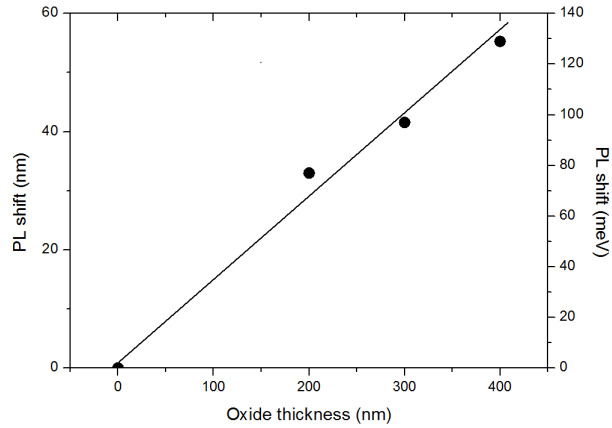


Figure 4.33: The degree of intermixing as a function of thickness of the encapsulating SiO_2 layer, which is annealed at $950^\circ C$ for three minutes.

In the Fig. 4.34, full width at half maximum (FWHM) of the shifted PL peak is presented. It is found that as the annealing time increases the FWHM also increases which suggests that disorder in the quantum well next to cavity NAM increases. As is seen in the Fig. 4.32, in 3 minutes PL shift change as 55 nm and corresponding FWHM change is about 5.5 nm. As the non-absorbing regions are not electrically pumped, this does not present a problem for the cavity.

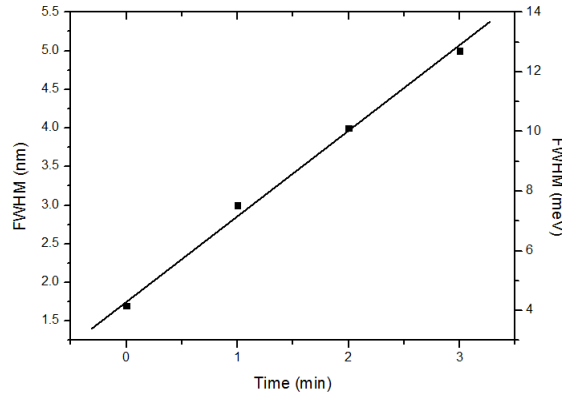


Figure 4.34: Photoluminescence line-width as a function of annealing duration (400 nm SiO_2 sputtered sample annealed at 950°C).

The comparative and detailed Figure of 4.35 demonstrates the diffusion of Ga atoms (defects) towards surface which results in interdiffusion of Ga vacancies in the quantum well with Al interstitials in the neighbourhood barrier layer. After XPS analysis, the intermixed sample depth was checked by measuring the depth profile using Dektak surface profilometer. According to this data, the plot can be divided into three region; First region is the 400 nm encapsulated SiO_2 layer, second region is the 500 nm GaAs cap layer and the third part is approximately 900 nm of AlGaAs cladding layer. Figures 4.21 and 4.29 illustrates depth profiles (etched by sputtering during XPS in order to obtain depth profile of atoms) of the as-grown and intermixed samples, respectively, obtained from Dektak surface profilometer. In Fig. 4.35, as-grown Si(2p) line is seen less than intermixed Si(2p) line, it is probably related with inhomogeneous encapsulating layer deposition which can explain the difference of depth profiles between as-grown and intermixed samples.

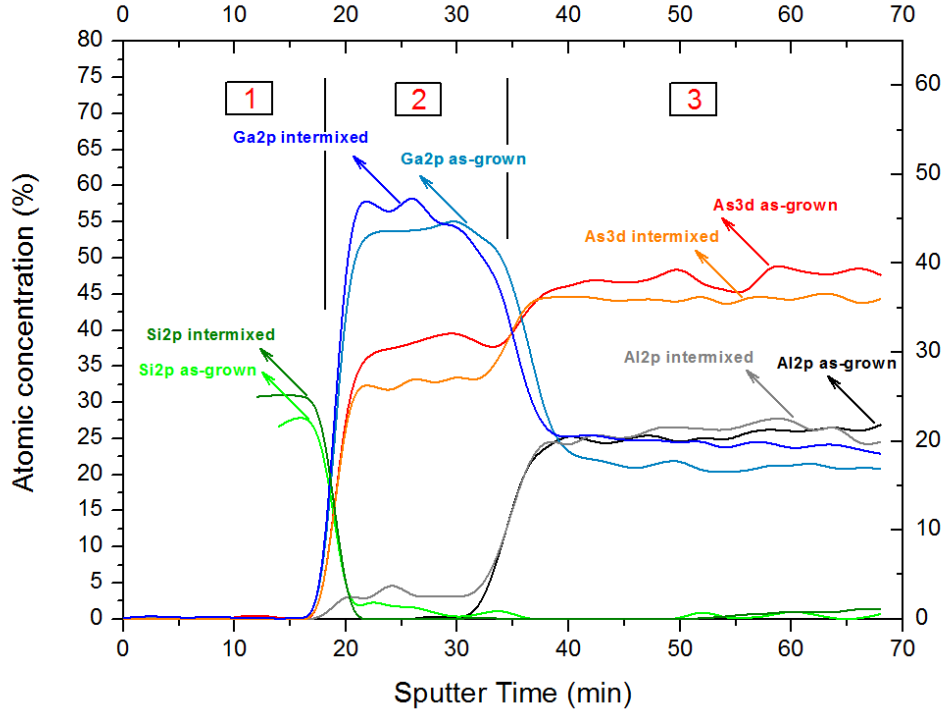


Figure 4.35: XPS depth profile of intermixed (400 nm SiO_2 sputtered followed by annealing at $950^\circ C$ for 3 minutes) and unprocessed (400 nm SiO_2 sputtered but not annealed) sample.

The demonstration of intermixing is described by comparing the unprocessed sample with the intermixed sample. In Fig. 4.35, in 2nd and 3rd region, we observe that in the intermixed sample Ga concentration is higher than the as-grown (unprocessed) sample which shows the migration of Ga atoms from quantum well and AlGaAs cladding layer: Ga(2p) concentration ratio of intermixed/unprocessed samples is 1.24. A similar behaviour holds also for Al concentration profile. Diffusion of Al from AlGaAs cladding layer into the GaAs cap layer is clearly observed. Another evidence for QWI might be given as the behaviour of As atoms since the figure illustrates that the number of As atoms in the intermixed sample is lower than the as-grown sample. We also note the shifting Ga profile for the intermixed sample towards the surface at the AlGaAs/GaAs interface, a clear indication of Ga migration towards the surface.

However, expected observation of Ga atoms in the encapsulant layer (SiO_2) has not been realized. There might be several reasons for this, first, as reported in [33], the small Ga amount of the SiO_2 layer can only be recognized with the intense Ga-Auger line, which we did not utilize. Second, in such large optical cavity laser diode structures for short periods of annealing (Table 4.2), Ga atoms may not have reached to SiO_2 layer. Instead, they may occupy point defects in the cap layer where encapsulated SiO_2 layer may have only acted to provide As-overpressure.

Chapter 5

Conclusions and Future Work

The first goal of this research was to achieve the impurity-free quantum well intermixing (QWI) on high power, large optical cavity GaAs-AlGaAs laser structures. In the absence of such data for high power laser diodes with thick layers, this study provides data important to understand the intermixing processing high power laser diodes. For proper application to high power laser diodes, apart from enhancement of intermixing, suppression of intermixing is required as well, for active laser diode waveguide region, hence suppression of disordering was also studied. High-power semiconductor laser fabrication suffers performance limitations during emitting such as catastrophic optical mirror damage (COMD), spatial mode instability, propagation losses and overheating. Among a number of effects considered that influence the degree of intermixing, annealing temperature, duration of annealing, distance between quantum well and surface, and thickness of encapsulating layer were varied in order to obtain maximum disordering and hence maximum PL peak shift. Second aim of this thesis was to investigate the impurity-free vacancy disordering (IFVD) phenomenon in detail by XPS analysis. Although this phenomenon is reliable and has been studied over decades, the exact mechanism is still unknown [20]. XPS analysis of intermixed structures was expected to present information about concentration and location of intermixed atoms that might shed light into the nature of diffusion and diffusing species.

Intermixing was achieved by demonstrating temperature dependence of QWI between 850-950 °C on 200 nm SiO_2 sputtered sample. The maximum blue shift was observed to be up to 34 nm blue shift at 950 °C. Dependence of the degree of disordering on the thickness of SiO_2 encapsulating layer was also studied by varying the thickness of the encapsulant between 200 and 400 nm and annealing at 950 °C for 3 minutes. We find that disordering, and therefore the blue shift is larger for 400 nm thick layers when compared with thinner layers. There are also some reports that even at 1250-1300 nm SiO_2 layer, degree of intermixing increases[30]. Dependence of QWI on the duration of annealing was also studied on 400 nm SiO_2 sputtered samples annealed at 950 °C between 1-3 minutes and it was found that degree of QWI varies linearly with the duration of annealing. Another parameter that affects the degree of the intermixing is believed to be the distance between QW and surface (QW depth) of the sample. Having only one laser structure, we tried shorten the QW depth by chemical etching. A blue shift of 65 nm for samples annealed for 9 min at 950 °C was observed which let us conclude that intermixing changes with QW depth inversely. However, etched samples removes the GaAs cap layer and oxidation of the exposed Al as well as possible Si in-diffusion from the sputtered SiO_2 may have been occurred which can lead to impurity induced disordering rather than impurity free disordering. Finally we found that 100 nm of SrF_2 layer is sufficient to suppress QWI under condition where QWI is enhanced with SiO_2 with blueshift of 55 nm.

XPS analysis of as-grown and intermixed samples was made. XPS characterization gave us information about the variations in the atomic concentration profiles of various elements thought to be active in the intermixing process. In (Al)GaAs laser structures, impurity-free vacancy disordering takes place by migration of Ga atoms from QW to surface of the sample followed by interdiffusion of Ga vacancy atoms with interstitial Al atoms in barrier layers adjacent to the QW layer. Comparison of as-grown and intermixed samples using XPS analysis successfully showed the remarkable increase of Ga concentration above the QW layer. However, Ga atoms were not observed in SiO_2 layer which is believed to absorb Ga atoms during annealing. This may be due to lack of sensitivity of the XPS analysis used in this work. A better approach would have been to use

Ga-Auger line, which is believed to be more sensitive to low concentrations of Ga.

The critical experimental parameter in fully understanding intermixing is the value of the diffusion coefficient of the species under study. These differ a lot in the literature. For GaAs/AlGaAs interdiffusion, the measured diffusion prefactors differ by 21 orders of magnitude and while the corresponding activation energy varies between 0.32 eV and 6.2 eV in literature. Despite Arrhenius plot and histogram studies, by W.P. Gillin, all of the data for diffusion coefficient in the literature converges into two distinct values.

Future investigations could focus on QW depth relation, stress effect and optimizing SiO_2 layer thickness. The degree of diffusion depends on the diffusion coefficient which, in turn, manifests itself as diffusion length. Under equivalent preparation conditions, using several samples with different distances between the QW and surface, interdiffusion experiments could be performed. This study may give reliable diffusion coefficient calculations. Furthermore, for IFVD, there are limited experiments about effects of stress effect in the literature. However, there is no consensus on the exact nature of the effects of stress in enhancement or suppression of disordering. Stress effect related experiments could be performed with encapsulating layers which have different thermal expansion coefficients, for instance, Ga_2O_3 , GaO_2 or As_2O_3 can be deposited on surface of the as-grown sample, or between as-grown sample and SiO_2 layer. Solubility limit of encapsulated SiO_2 layer is still unknown. It could be investigated with even thicker encapsulant layer than $1.3 \mu m$.

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